EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.5: Fischer-Tropsch Product Upgrading

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Abstract

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are Texaco Energy Systems LLC or TES (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR) in addition to the U.S. Department of Energy (DOE). TES is providing gasification technology and Fischer-Tropsch (F-T) technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology, and KBR is providing engineering.

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was developed to mitigate the identified risks (Phase II RD&T Plan, October 2000). The potential technical and economic risks to the EECP from Task 2.5 can be mitigated by demonstrating that the end-use products derived from the upgrading of the F-T synthesis total liquid product can meet or exceed current specifications for the manufacture of ethylene and propylene chemicals from F-T naphtha, for the generation of hydrogen from F-T naphtha to power fuel cells, for direct blending of F-T diesels into transportation fuels, for the conversion of F-T heavy product wax to transportation fuels, and the conversion of F-T Heavy product wax to a valuable high melting point food-grade specialty wax product. Product evaluations conducted under Task 2.5 of Phase II successfully mitigated the above technical and economic risks to the EECP with the development of product yields and product qualities for the production of chemicals, transportation fuels, and specialty food-grade waxes from the F-T synthesis products.

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Executive Summary

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

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Background

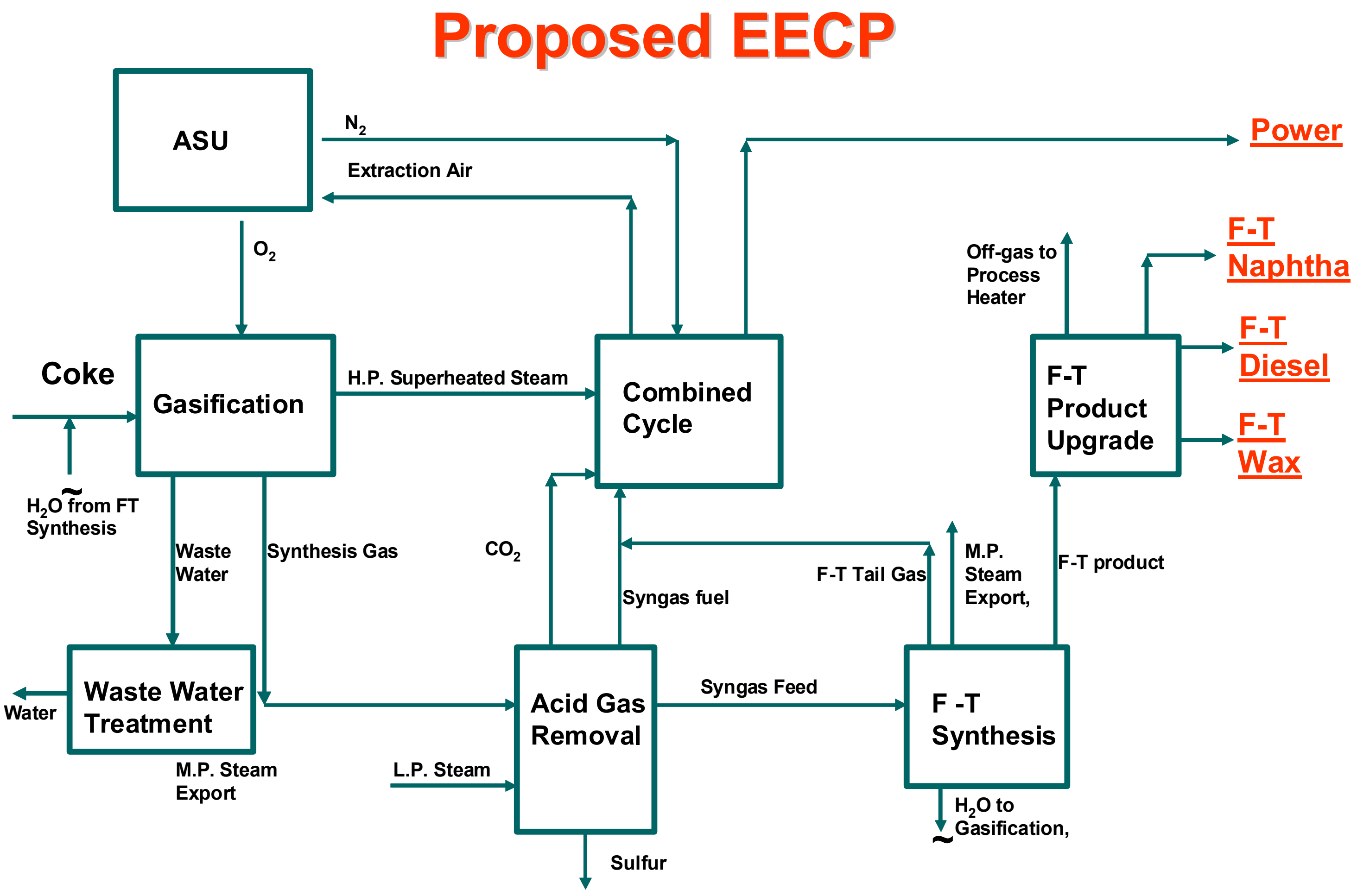
The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and will consume approximately 1,235 short tons per day of petroleum coke. The EECP Concept is illustrated in **Schematic 1,** which follows. **Schematic 1** identifies the various Subsystems (Applications of Technology) to be integrated into the EECP.

EECP Concept

As shown is **Schematic 1**, petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen (H_2), carbon monoxide (CO), water vapor, and carbon dioxide (CO_2) with small amounts of hydrogen sulfide (H_2S), methane, argon, nitrogen (N_2), and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. One portion of the stream is treated in the AGR to remove CO_2 and and H_2S then forwarded to the F-T Synthesis Unit. The other portion is treated in the AGR to remove the bulk of H_2S with minimal CO_2 removal and then forwarded as fuel to the General Electric frame 6FA gas turbine. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO_2. The resulting CO_2 and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides (NOx) emissions. The bulk of the nitrogen is also sent to the gas turbine as a separate stream, where its mass flow also helps increase the power production and reduces NOx emissions.

Overall, approximately 75% of the sweetened syngas is sent to the gas turbine as fuel. The remaining 25% is first passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur and then forwarded to the Fischer-Tropsch Synthesis Unit. In the F-T reactor, CO



Schematic 1 - EECP Concept

and H_2 react, aided by an iron-based catalyst, to form mainly heavy straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid, and light F-T liquid are sent to the F-T Product Upgrading Unit (F-TPU) while F-T water, a reaction byproduct, is returned to the Gasification Unit and injected into the gasifier. The F-T tail gas and AGR off gas are sent to the gas turbine as fuel to increase electrical power production by 11%.

In the F-TPU, the three F-T liquids are combined and processed as a single feed. In the presence of a hydrotreating catalyst, hydrogen reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracker light ends. The resulting four liquid product streams are naphtha, diesel, low-melt wax, and high-melt wax and leave the EECP facility via tank truck. Hydrotreating of the neat F-T naphtha and F-T diesel products reduces reactive acids, olefins, and oxygenates levels and alleviates corrosion and product instability concerns.

Future coproduction plants can maximize valuable diesel transportation fuel by conversion of the F-T synthesis wax product by hydrocracking. The upgraded neat F-T diesel or hydrotreater neat F-T diesel product along with hydrocracker F-T diesel product could be final blending components in transportation diesel. Both the hydrotreater neat F-T naphtha and the hydrocracker naphtha by-product could be suitable feedstock components to either a chemical plant steam cracker or to a fuel cell reformer.

The power block consists of a GE PG6101 (6FA) 60 Hz heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas as start-up and backup fuel, and a mixture of syngas from the gasifier, off gas from the AGR Unit, and tail gas from the F-T Synthesis Unit as the primary fuel. Nitrogen gas for injection is supplied by the ASU for NOx abatement, power augmentation, and the fuel purge system.

The Praxair ASU is designed as a single train elevated pressure unit. Its primary duty is to provide oxygen to the gasifier and Sulfur Recovery Unit (SRU), and all of the EECP's requirements for nitrogen and instrument and compressed air. ASU nitrogen product applications within the EECP include its use as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NOx emissions, and as an inert gas for purging and inerting. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor, hence oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums as they enter the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS off gas, oxygen, and air to a burner. In the thermal reactor, the H_2S, a portion of which has been combusted to sulfur dioxide (SO_2), starts to recombine with the SO_2 to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser where all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H_2S and SO_2 are converted to sulfur. The sulfur is removed in the second pass of the primary sulfur condenser, and the gas goes through a reheat, catalytic reaction, and condensing stage two more times before leaving the SRU as a tail gas. The molten sulfur from all four condensing stages is sent to the sulfur pit, from which sulfur product is transported off site by tank truck.

The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO_2 back to H_2S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along with the condensate from the SRU knockout drums to the SWS. H_2S is removed from the quenched tail gas in an absorber by using lean methyldiethanolamine (MDEA) solvent from the AGR Unit. The tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

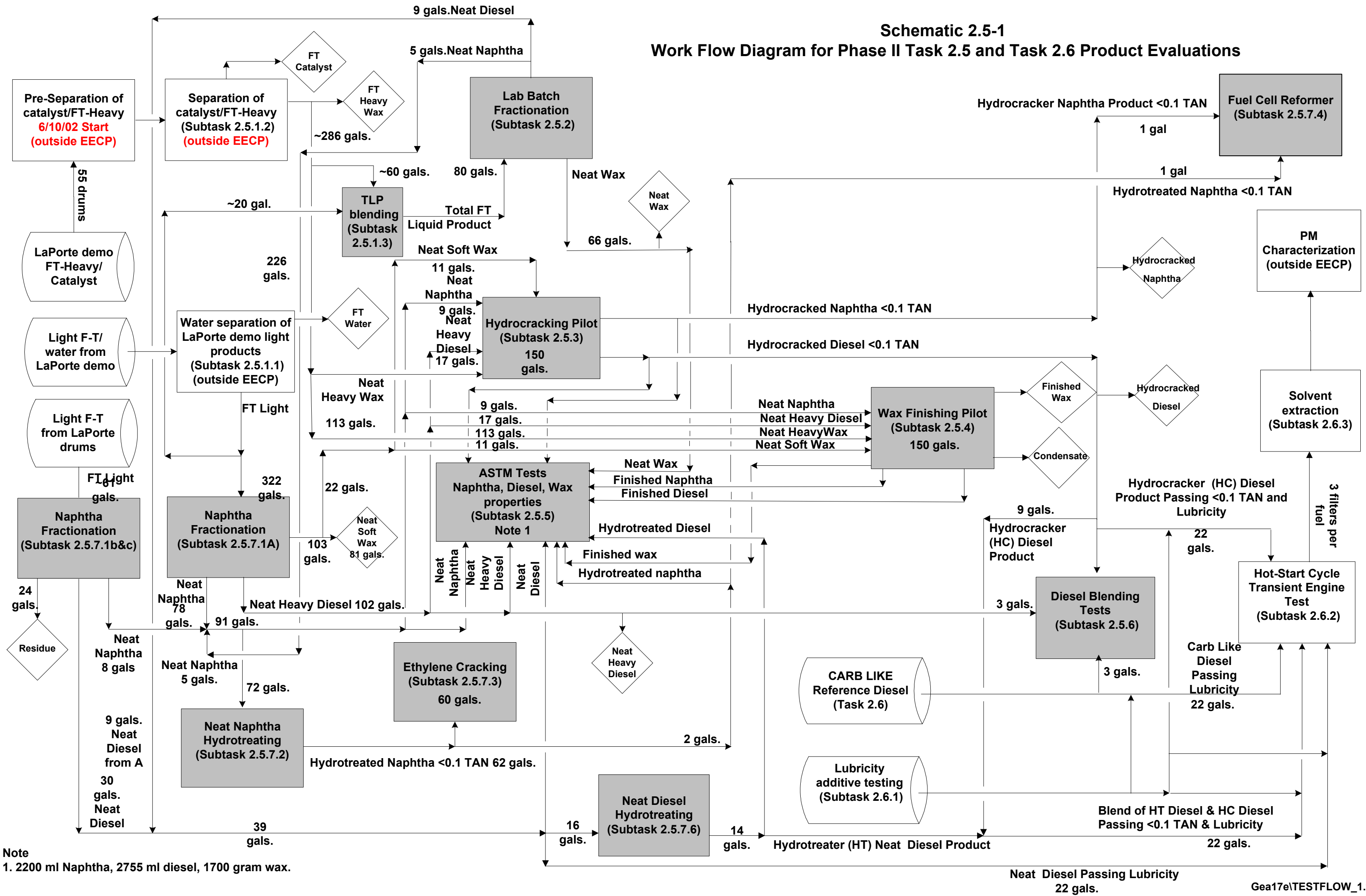
Subtask Product Evaluations Performed for Task 2.5 Outside DOE Funding

Each of the EECP subsystems (applications of technology to be integrated in the EECP) was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The intent of the work carried out under Phase II Task 2.5 entitled “F-T Product Upgrading” and Task 2.6 entitled “Fuel/Engine Performance and Emissions” is to mitigate technical and economic risks. The risks to the EECP from Task 2.5 and Task 2.6 can be mitigated by demonstrating that the products derived from the upgrading of the F-T synthesis total liquid product can meet or exceed current specifications associated with producing an acceptable naphtha feedstock component for a chemical plant thermal or ethylene cracker to produce ethylene and propylene or as a naphtha feedstock component for hydrogen fuel generation from a fuel cell reformer, finished diesel transportation fuels, and specialty food-grade wax products.

Testing conducted during Phase II Task 2.5 entitled “F-T Product Upgrading” determined the actual conversion and product quality using the licensor processes. The chronological flow of work from left to right is illustrated in **Schematic 2.5-1** showing the individual Subtask performance evaluations performed for both Task 2.5 and Task 2.6.

Preparation of the F-T Light and Heavy Product streams the LaPorte Alternative Fuels Development Unit (AFDU) for upgrading was completed and documented under Subtasks 2.5.1.1 and 2.5.1.2 entitled “Preparation of LaPorte AFDU Products.” Subtasks 2.5.1.1 and 2.5.1.2 lead to the generation of end products for Task 2.5 and Task 2.6. Subtasks 2.5.1.1 and 2.5.1.2 were conducted and documented outside the DOE funding for Phase II.

Schematic 2.5-1
Work Flow Diagram for Phase II Task 2.5 and Task 2.6 Product Evaluations



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Subtask 2.5.1 Preparation of LaPorte AFDU Products

The F-T synthesis total liquid product used in all Phase II Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emissions" product evaluations was produced at the LaPorte AFDU.

Experimental

Subtasks 2.5.1.1 and 2.5.1.2 are illustrated in **Schematic 2.5.1-1** as the shaded blocks and a summary of the results are presented herein. Subtasks 2.5.1.1 and 2.5.1.2 were conducted and documented outside the DOE funding for Phase II. No Subtask Reports were prepared for these activities for the DOE and therefore no Subtasks Reports are appended to this Phase II Topical Report.

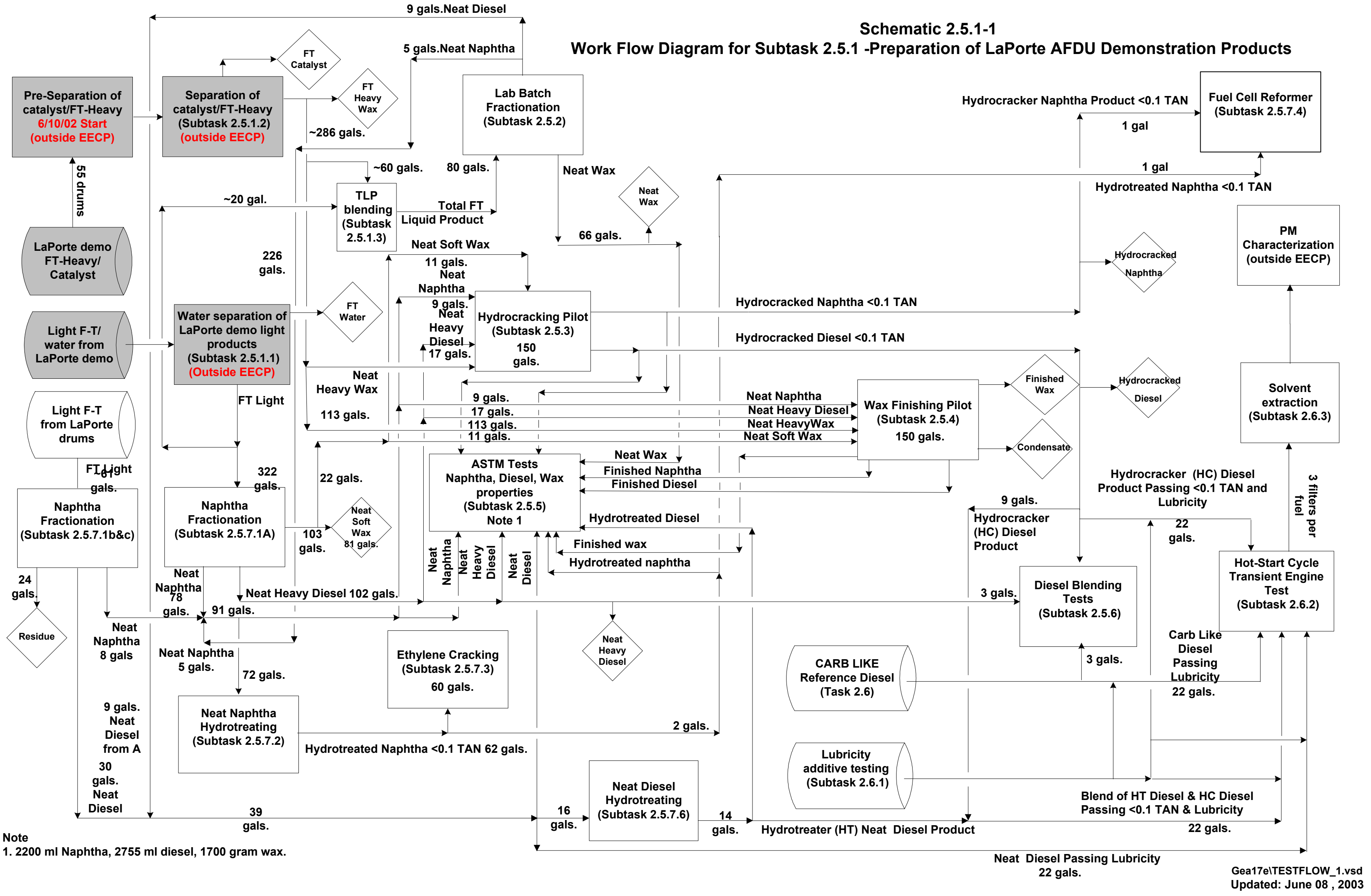
Results and Discussion

Subtask 2.5.1.1 Water Separation from F-T Light Product

The LaPorte AFDU design did not allow for the separation of water from the F-T Light products. To ensure accurate product upgrading results, free water must be separated from the F-T Light product. Southwest Research Institute (SwRI) separated the free water and light F-T products at their facility in San Antonio, Texas. The presence of free water in the LaPorte AFDU F-T Light product stream can cause foaming and poor separation problems during distillation. Two distillation tasks, Subtask 2.5.2 entitled "Lab Batch Fractionation" and Phase II Subtask 2.5.7.1 entitled "Naphtha Fractionation", are being conducted to generate end-use products meeting naphtha, diesel, and wax boiling range quality specifications for production of chemicals, transportation fuels, or specialty wax products.

The presence of water in the neat F-T naphtha overhead distillation products produced in Subtask 2.5.7.1.b and c is a high risk because the neat F-T naphtha is a feedstock blending component to Subtask 2.5.3 entitled "Hydrocracking Pilot" which generated the hydrocracker F-T diesel product for use in the Task 2.6 product evaluations. Water in the feed can result in damage and deactivation to the hydrocracking catalyst. Damage caused by water to the hydrocracking catalyst can result in the soft and hard wax feedstock blend components not being selectively hydrocracked into a diesel and naphtha product. The economic and technical risks identified for Subtask 2.5.3 end-use products for Task 2.6 product evaluations would not be mitigated.

Separation of the free water and F-T Light product was accomplished outside the DOE funding for Phase II.



Schematic 2.5.1-1
Work Flow Diagram for Subtask 2.5.1 -Preparation of LaPorte AFDU Demonstration Products

Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Subtask 2.5.1.2 Catalyst Separation from F-T Heavy Product

The F-T synthesis technology for the EECP uses an iron catalyst to produce a broad range of paraffin and olefin hydrocarbons with minor amounts of oxygenates and acids. The LaPorte AFDU used the primary filtration system developed by Rentech and Texaco. The F-T heavy product (wax) from this filter system contained more than the 10 ppmw of the F-T synthesis iron catalyst that the product upgrading pilot plants are designed to handle.

Separation of the catalyst from the F-T heavy product was accomplished outside the DOE funding for Phase II. This work was completed and documented under Subtask 2.5.1.2 entitled "Catalyst/Wax Separation to 10 ppmw" Therefore, no Subtask 2.5.1.2 Report was prepared for the DOE and no Subtask 2.5.1.2 Report is appended to the Phase II Task 2.5 Topical Report.

The presence of catalyst greater than 10 ppmw in the F-T heavy product is a high technical risk. The F-T heavy product (Hard wax) is a feedstock blend component that is common to the feed slates for Phase II Subtask 2.5.3 entitled "Hydrocracking Pilot" and the Phase II Subtask 2.5.4 entitled "Wax Finishing Pilot". The presence of greater than 10 ppmw catalyst in the feed slates to these pilot plants can cause termination of these pilot plant operations due to pressure drop problems, flow distribution problems in the catalyst bed, and poor catalyst performance from lack of efficient contacting of the catalyst and feed in the product upgrading pilot plant reactors. In the Phase II Subtask 2.5.4 entitled "Wax Finishing Pilot", catalyst carry over from feed into the finished wax product could result in failure of the food-grade wax to meet the Saybolt color specification.

From an economic perspective, trace catalyst from F-T synthesis, which can be trapped using commercially available filter materials loaded in to a guard-bed reactor, may be present in the product upgrading feed. Guard-bed reactors located ahead of the main catalyst bed reactor(s) of the product upgrader can easily be sized for up to a one year of operation at the ten ppmw F-T catalyst concentration level in the feed. Spikes in F-T catalyst concentration in the feed will significantly reduce the on stream operating cycle time for the guard-bed reactor which results in a medium technical risk to the EECP. Replacing the filter materials of the guard bed reactor more than once a year will increase the operating expenses of the proposed EECP which means economic risk to the EECP is high. Breakthrough of F-T catalyst to the product upgrader main catalyst bed reactor will likely cause increased pressure drop problems, flow maldistribution problems, and poor catalyst performance from inefficient catalyst contacting with the feed. High pressure drops and poor performance will cause catalyst in the product upgrader main catalyst bed reactor to be changed on a more frequent cycle as well. The EECP team predicts that the EECP catalyst/wax filtration system will be able to reduce the F-T catalyst in the upgrader feed to less than 10 ppmw.

Subtask 2.5.1.1 entitled "Water Separation of LaPorte Commingled Water and F-T Light Product Streams" successfully removed free water from the LaPorte AFDU F-T light product. The removal of free water mitigated the risks to the distillation of the F-T Light Product performed by Subtask 2.5.7.1.a entitled "Naphtha Fractionation" which recovered neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products as end-use products for Task 2.5 product evaluations. Subtask 2.5.1.2 entitled "Catalyst/Wax Separation to 10 ppmw" successfully removed F-T catalyst particles to the 10 ppmw concentration specification in the LaPorte AFDU F-T heavy product. The removal of F-T catalyst particles mitigated the risks to the Task 2.5 product evaluations where the F-T heavy product was a feed component.

Fischer-Tropsch Product Upgrading (Task 2.5)

Each of the EECP subsystems (Applications of Technology to be integrated in the EECP) was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The intent of the Phase II RD&T work carried out under Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emissions" was to mitigate those technical and economic risks identified with these Tasks. The risks to the EECP from Task 2.5 and Task 2.6 can be mitigated by demonstrating that the products derived from the upgrading of the F-T synthesis total liquid product can meet or exceed current specifications.

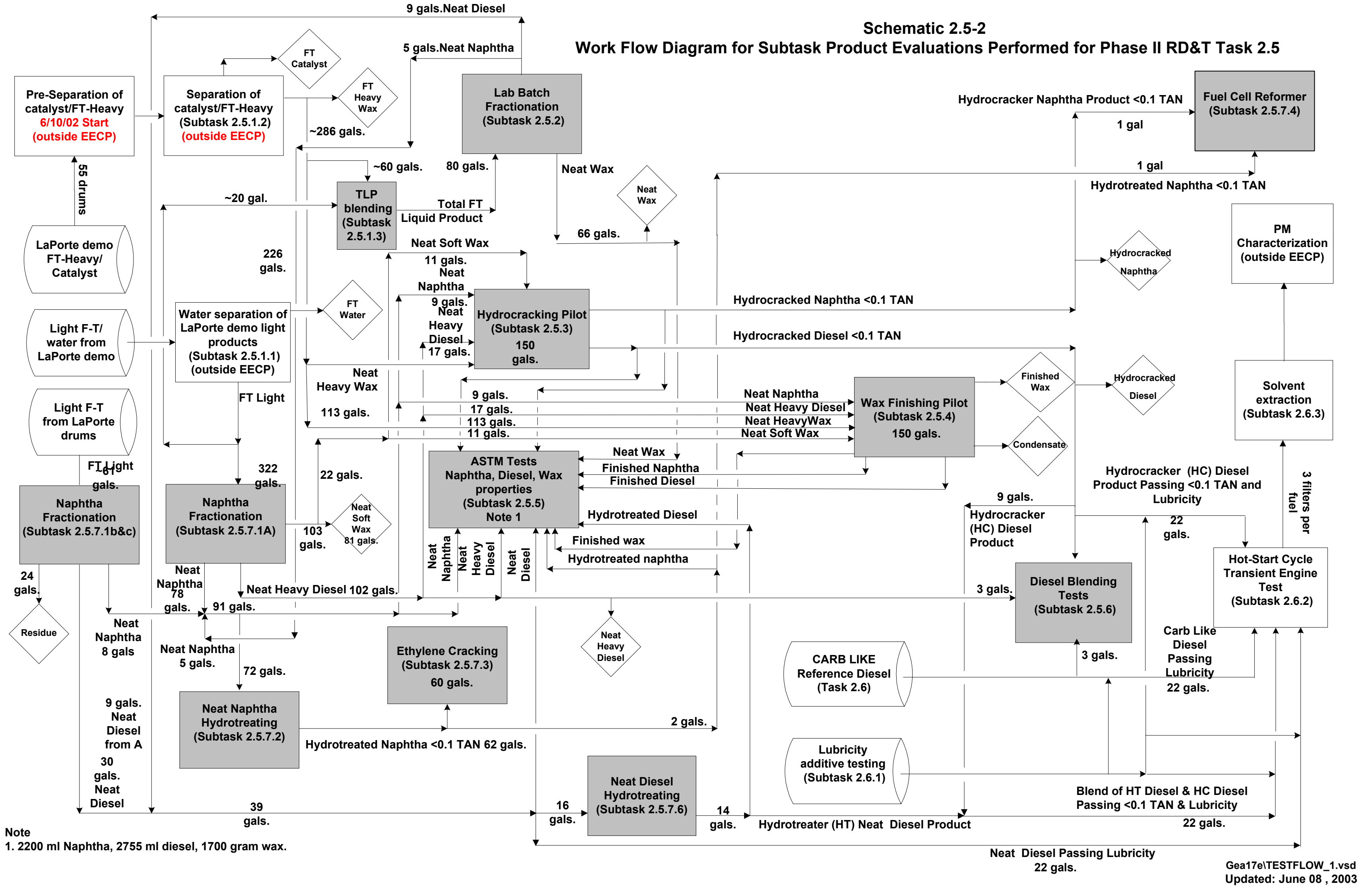
While some product upgrading licensor technologies have not been applied to the F-T product liquids, previous information indicates that these licensor technologies are adaptable. Therefore, the technical risks associated with F-T product upgrading based on available knowledge of feed properties is considered to be low, making the overall risks to the EECP low. Yields and physical properties of the upgraded F-T products have been estimated based on the component analysis of the feed properties. Since these estimates are based on empirical correlations, the economic risk is considered medium.

Testing conducted during Phase II Task 2.5 entitled "F-T Product Upgrading" was used to determine the actual conversions and product qualities from the licensor processes. The chronological flow of work from left to right is illustrated in **Schematic 2.5-1**, which show the individual subtask performance evaluations performed for both Task 2.5 and Task 2.6. The individual subtask product evaluations performed for the Phase II Task 2.5 are illustrated in **Schematic 2.5-2** as the shaded blocks. A summary of the results obtained on each subtask will be presented in this report. Reports for each subtask funded by the DOE were prepared and are appended to this Task 2.5 Topical Report.

These subtask reports include the following: Appendix A: Subtask 2.5.2 Report entitled "Lab Batch Fractionation;" Appendix B: Subtask 2.5.3 Report entitled " Hydrocracking Pilot;" Appendix C: Subtask 2.5.4 Report entitled "Wax Finishing Pilot;" Appendix D: Subtask 2.5.5.b Report entitled "Oxygen Test Method Development;" Appendix E: Subtask 2.5.6 Report entitled " Diesel Blending Tests;" Appendix F: Subtask 2.5.7.1

Report entitled “Naphtha Fractionation;” Appendix G: Subtask 2.5.7.2 Report entitled “Neat Naphtha Hydrotreating;” Appendix H: Subtask 2.5.7.3 Report entitled “Ethylene Cracking;” Appendix I: Subtask 2.5.7.4 Report entitled “Fuel Cell Reformer;” and Appendix J: Subtask 2.5.7.6 Report entitled “Neat Diesel Hydrotreating.”

Schematic 2.5-2
Work Flow Diagram for Subtask Product Evaluations Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Subtask 2.5.2 Lab Batch Fractionation

Experimental

The F-T liquid products from the LaPorte AFDU must be distilled to the required fuel or specialty wax product boiling range specifications. There are technical and economic risks to the EECP if the F-T products undergo degradation or liquid yield losses to light ends during the distillation process. There are technical risks to the Subtasks of Task 2.5 regarding the degree of laboratory fractionation efficiency, recovery of products and possible contamination of distilled products for end-use product evaluations. These technical and economic risks to the EECP are mitigated if the distilled products achieve the desired yield recoveries and qualities meeting chemical, transportation fuel, or specialty wax product boiling range specifications in order to satisfy the end-use evaluation needs of the Subtasks illustrated in **Schematic 2.5-1**.

The Phase II Subtask 2.5.2 Report entitled "Lab Batch Fractionation" is presented as Appendix A to this Task 2.5 Topical Report. As illustrated in the flow of work in **Schematic 2.5-1,** the water free F-T Light Product from Subtask 2.5.1.1 entitled **"**Water Separation of LaPorte Commingled Water and F-T Light Product Streams" was blended in a ratio-of-production blend with the F-T heavy product from Subtask 2.5.1.2 entitled "Catalyst/Wax Separation to 10 ppmw." The F-T blend is then fractionated in Subtask 2.5.2 entitled "Lab Batch Fractionation" to maximize the recoveries of a initial boiling point (IBP)-466K (380°F) neat F-T naphtha product, a 466K (380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T wax product.

Results and Discussion

Table 2.5.2-1 presents the results for the distillation product yields from the Subtask 2.5.2 mass balance closure. The technical risks to the EECP identified with the distillation to the required fuel or specialty wax product boiling range and quality specifications were mitigated with the successful completion of Subtask 2.5.2. The recoveries of neat F-T naphtha, neat F-T diesel, and neat F-T wax from Subtask 2.5.2 were maximized. **Table 2.5.2-2** presents the results from the inspection testing conducted on the IBP-466K (380°F) neat F-T naphtha distillation product from Subtask 2.5.2. The IBP-380°F (466K) neat F-T naphtha product met quality specifications for end-product use in Task 2.5. **Table 2.5.2-3** presents the results from the inspection testing conducted on the 466K (380°F) to 644K (700°F) neat F-T diesel distillation product from Subtask 2.5.2. The 466K (380°F) to 644K (700°F) neat F-T diesel product met quality specifications for end-product use in Task 2.5. **Table 2.5.2-4** presents the results from the inspection testing conducted on the 644K (700°F) plus neat F-T wax distillation product from Subtask 2.5.2. The 644K (700°F) plus neat F-T wax product met quality specifications for end-product use in Task 2.5. In order to maximize the recovery of neat F-T naphtha, neat F-T diesel, and neat F-T wax products for Task 2.5 product evaluations, the Subtask 2.5.2 neat F-T naphtha product, neat F-T diesel product, and neat F-T wax product for Task 2.5 were tested and approved prior to being considered for blending with the neat F-T naphtha, diesel, and wax products from Subtask 2.5.7.1.b and c entitled “Naphtha Fractionation.”

Table 2.5.2-1 - Subtask 2.5.2					
Mass Balance Closure Around Subtask 2.5.2 Lab Batch Fractionation					
Feed Analyses	**F-T Heavy Product**	**F-T Light Product**			
Weight, kg (lbs)	**214.5 (472)**	**59.5 (131)**			
Wt%	**78.3**	**21.7**			
Product Analyses	**Neat F-T Naphtha IBP-380F IBP-466K**	**Neat F-T Diesel 380F-700F 466K-644K**	**Neat F-T Wax 700F+ 644K+**	**Losses**	**Recovery**
Weight, kg (lbs)	**11.5(23.5)**	**27.7(61)**	**231.7 (509.7)**	**3.2 (7)**	
Wt%	**4.2**	**10.1**	**84.5**	**1.2**	**98.8**

The distillation of a ratio-of-production blend representing the LaPorte AFDU F-T light product and F-T heavy product streams was successfully completed in Subtask 2.5.2 and resulted in the maximum recovery of neat F-T naphtha product, neat F-T diesel, and neat F-T wax products. Subtask 2.5.2 distillation products met the necessary fuel and specialty wax product boiling ranges and quality specifications with the minimal introduction of background contaminants from equipment and handling.

Table 2.5.2-2 - Subtask 2.5.2

Neat F-T Naphtha Product Properties
From Subtask 2.5.2 Lab Batch Fractionation

(Blend Component with Subtask 2.5.7.1.b and c Neat F-T Naphtha)

ILT ID No.		**2066772**	
Gravity, °API		**57.1**	
Specific Gravity		**0.7503**	
Nitrogen	**ppmw**	**2.5**	
Sulfur	**ppmw**	**<6**	
		Temperature, (K)	**(°F)**
Simulated Distillation, V%			
	1%	**334**	**141**
	5%	**360**	**188**
	10%	**369**	**204**
	30%	**422**	**300**
	50%	**432**	**319**
	70%	**447**	**345**
	90%	**466**	**379**
	95%	**468**	**383**
	99%	**470**	**387**

Table 2.5.2-3 - Subtask 2.5.2

Neat F-T Diesel Product Properties
From Subtask 2.5.2 Lab Batch Fractionation

(Blend Component with Subtask 2.5.7.1.b and c Neat F-T Diesel)

ILT ID No.		**2066770**	
Gravity, ºAPI		**43.5**	
Specific Gravity		**0.8086**	
Nitrogen	**ppmw**	**11**	
Sulfur	**ppmw**	**<6**	
		Temperature, (K)	**(ºF)**
Simulated Distillation, V%			
	1%	**439**	**331**
	5%	**467**	**382**
	10%	**486**	**416**
	30%	**526**	**487**
	50%	**572**	**570**
	70%	**605**	**630**
	90%	**636**	**686**
	95%	**643**	**698**
	99%	**653**	**716**

Table 2.5.2-4 - Subtask 2.5.2			
Neat F-T Wax Product Properties From Subtask 2.5.2 Lab Batch Fractionation Wax Testing Limited To Material Balance Closure on Subtask 2.5.2 (Wax Intended As End-use Product for Subtask 2.5.8 Wax Fractionation - Work Did Not Proceed on Subtask 2.5.8)			
ILT ID No.		**2066769**	
Gravity, °API			
Specific Gravity			
		Temperature, (K)	**(°F)**
Simulated Distillation, V% (Difficult to dissolve wax in Carbon Disulfide Solvent)			
	1%	**679**	**763**
	5%	**689**	**781**
	10%	**693**	**788**
	30%	**773**	**932**
	50%	**962**	**1273**
	53%	**>1008**	**>1355**
	90%		
	95%		
	99%		

Subtask 2.5.3 Hydrocracking Pilot

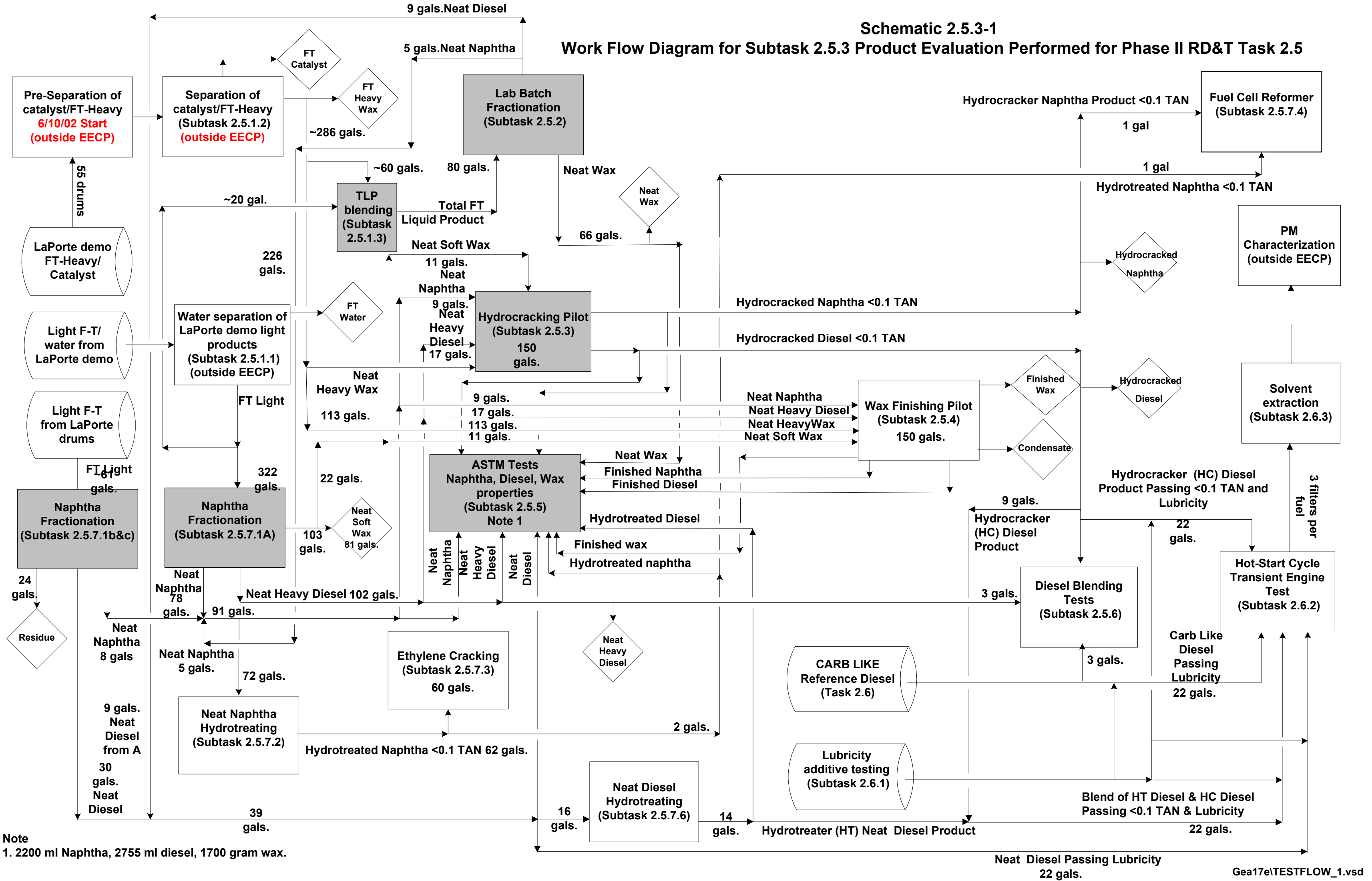
Experimental

A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.3 entitled "Hydrocracking Pilot." Documentation of the work and detailed discussions are to be found in the Subtask 2.5.3 Report attached as Appendix B to this topical report. The flow of work for Subtask 2.5.3 is illustrated in **Schematic 2.5.3-1**.

One objective of the DOE EECP is to produce transportation fuel such as diesel. There are a number of barriers to producing transportation fuel from the F-T light product and heavy product streams. One economic barrier is the desired result that the EECP have a favorable economic return on investment. In order to achieve favorable economics, the finished products from the EECP need to receive premium values. The neat F-T naphtha and neat F-T diesel products have premium qualities such as low sulfur content, low aromatic content, and high hydrogen content. The neat F-T diesel product has a high cetane number that may justify higher prices in the market place. The quantity of distillate transportation fuels from the EECP will be small when compared to typical fuel amounts produced by even small refineries. Therefore, it will be difficult to achieve a premium value or a large market share for the transportation fuels produced from the EECP.

Future coproduction plants will likely need to maximize the conversion of the primary F-T product, a highly paraffinic wax represented by the LaPorte AFDU F-T heavy product stream, into a high cetane quality transportation diesel to mitigate economic risks. The diesel product from hydrocracking of the F-T heavy product wax is expected to be a stable and a desirable high cetane blending component in transportation diesel. The hydrocracker F-T naphtha product was expected to be a desired feed component for chemical plant thermal or ethylene crackers for the production of ethylene and propylene and potentially a feed for hydrogen fuel generation from a fuel cell reformer. The technical and economic risks to the EECP to be mitigated for the conversion of the F-T heavy product wax into distillates is adapting existing hydrocracking technology to achieve high yields of high quality diesel transportation fuel. Processing technology to maximize hydrocracking of paraffinic heavy gas oil to diesel product is known and practiced for gas oil feeds from conventional crude sources but is not commercially practiced for synthetic waxes such as the F-T heavy product wax. Although hydrocracking technology has not been commercially applied to F-T heavy product wax, the concept of processing paraffinic gas oil feeds considered similar in composition is commercially proven. Future design solutions can be formulated from the data base developed during the research phase. Performance estimates on product yield structures, appropriate selection of hydrocracking catalyst, reactor bed configuration, and operating conditions can be prepared for future economic case evaluations The Subtask 2.5.3 entitled "Hydrocracking Pilot" product evaluation is structured in such a way to mitigate these risks.

Schematic 2.5.3-1
Work Flow Diagram for Subtask 2.5.3 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Updated: June 08 , 2003

Producing a high yield of diesel product by the hydrocracking processing route is a technical challenge based on the hydrocracker's primary feed blend component the F-T heavy product wax from the LaPorte AFDU which exhibits an extended heavy carbon number distribution. ChevronTexaco ISOCRACKING® technology was utilized in the Subtask 2.5.3 product evaluation. Mitigating technical and economic risks to the EECP would require the Subtask 2.5.3 product evaluation to confirm a product yield distribution along with product sampling, testing of the hydrocracker diesel product against transportation fuel quality specifications, and testing the hydrocracker naphtha by-product for determination of its final product market disposition.

Equipment

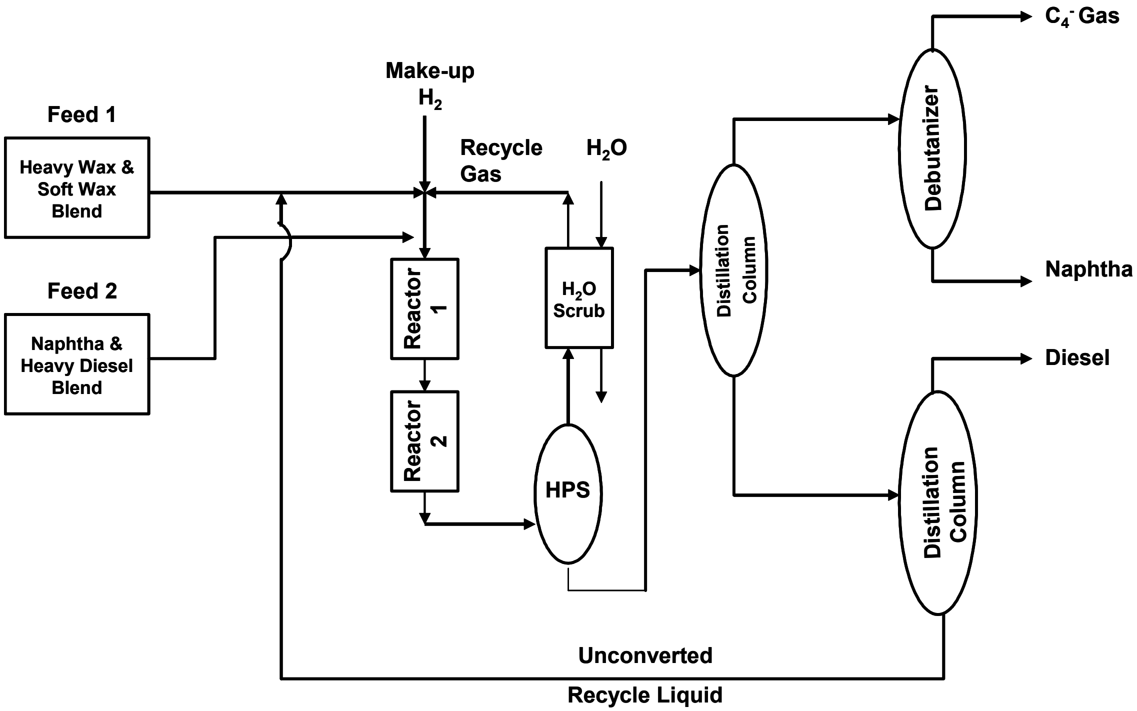
Chevrontexaco Technology Marketing (TEMA) performed Pilot Plant Run 81-143 for the hydrocracking test of the Fischer-Tropsch product. **Figure 2.5.3-1** shows the block flow diagram of the pilot plant setup for the hydrocracking test. This is the standard configuration for a hydrocracking pilot plant. Feed 1 containing the heavy wax and soft wax blend is mixed with the unconverted recycle liquid. Then it combines with the make-up hydrogen and recycle gas before mixing with the naphtha and heavy diesel blend (Feed 2). The combined feeds enter the hydrocracking reactors. There are two reactors in series. The reactors contain commercially-proven, middle-distillate-selective ISOCRACKING® catalyst. The reactor effluent then goes to a high pressure separator (HPS) where the liquid is separated from the vapor. The liquid is sent to distillation where it is separated into butane and lighter gases, naphtha (C5 to 466K, C5 to 380^{o}F), diesel (466K to 644K, 380^{o}F to 700°F) and unconverted liquid to be recycled to the feed. The vapor from the HPS, composed mainly of hydrogen, is scrubbed with water to remove the trace amount of NH_3 formed from the nitrogen in the feed. It is then recycled back to the reactors

Feed Composition

The hydrocracker pilot plant feed for Subtask 2.5.3 represented a ratio-of-production blend of the LaPorte AFDU F-T Light Product from Subtask 2.5.1.1 and the F-T heavy product from Subtask 2.5.1.2. The hydrocracker pilot plant was equipped with a dual feed delivery system. It was necessary to split the hydrocracker feed into two feed blend components to carry out the Subtask 2.5.3 hydrocracker pilot plant evaluation. One hydrocracker feed blend component was a IBP-644K (700°F) combined stream of neat F-T naphtha and neat F-T diesel. The IBP-644K (700^{o}F) blend component was charged to the pilot plant in its ratio-of-production from an enclosed cold feed receiver that was externally cooled to avoid the loss of feed vapors. The remaining hydrocracker feed blend component was the 644K (700°F) plus combined stream of neat F-T soft and neat F-T hard waxes charged in its ratio-of-production from an enclosed, externally heated feed receiver. The neat F-T hard wax feed component to the hydrocracker required elevated temperatures to melt the wax to permit it to flow into the reactor.

The 644K (700^{o}F) plus F-T wax was distributed between the LaPorte AFDU F-T light product and F-T heavy product stream. It was necessary to carry out the distillation

Figure 2.5.3-1
Hydrocracking Pilot Plant Block Flow Diagram



of the F-T light product stream in Subtask 2.5.7.1.a entitled “Naphtha Fractionation.” This distillation was necessary to obtain a neat F-T naphtha product, a neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax product to allow for segregation of these product cuts between the two hydrocracker pilot plant feed systems. A summary of the results for the Subtask 2.5.7.1.a distillation is included as part of the Subtask 2.5.7.1. Test Report in Appendix F.

As previously discussed, the hydrocracker pilot plant has two feed systems and two blends were made for the pilot plant test—the diesel and naphtha blend (Feed 2) and the heavy wax and soft wax blend (Feed 1). The Subtask 2.5.7.1.a distillation of the F-T light product stream from the LaPorte AFDU provided the diesel and naphtha components for the Subtask 2.5.3 hydrocracker pilot plant feed blend (Feed 2). The F-T heavy product wax from the LaPorte AFDU was filtered to less than 10 ppmw solids by Subtask 2.5.1.2 and blended with the Subtask 2.5.7.1.a neat F-T soft wax distillation product to prepare the Subtask 2.5.3 hydrocracker pilot plant heavy and soft wax feed blend (Feed 1). **Table 2.5.3-1** gives the total volume and proportions of the hydrocracker pilot plant feed blends. The ratio of each feed component in the blend in the hydrocracker feed was made to reflect a ratio-of production blend of the F-T light product and F-T heavy product streams from the LaPorte AFDU. Properties of these two hydrocracker feed blends are given in **Table 2.5.3-2**.

Results and Discussion

The composition and type of hydrocracking catalyst used and the specific operating parameters employed in the Subtask 2.5.3 product evaluation are proprietary technology licensor information and are not disclosed herein. The boiling range target for the hydrocracked diesel product was 466K to 644K (380F to 700°F). The following lists the expected hydrocracked F-T diesel product quality based on the target boiling range:

- Cloud Point/Cold Flow Plugging Point <283K (10°C/50°F)
- Flash Point >323K (50°C/122°F)
- Cetane Number/Cetane Index >70
- Viscosity @ 313K (40°C/104°F) >2.0 cSt
- TAN <0.05 mg KOH/g

Hydrocracker F-T diesel product properties were taken during the hydrocracker pilot plant yield periods during the pilot plant production run period. **Table 2.5.3-3** documents the yields relative to feed as well as the product properties from the hydrocracker pilot plant test program. Acceptable mass balance closures were obtained during the course of the production run. Hydrocracking of the ratio-of-production feed blend representing the LaPorte AFDU F-T light product and F-T heavy hroduct streams to 644K (700°F) minus distillate products resulted in the consumption of 951 standard cubic feet of hydrogen per barrel (SCFB) of hydrocracker feed or 169 standard cubic meters (m^3) of hydrogen per cubic meter of hydrocracker feed (m^3/m^3). The cloud point of the hydrocracker F-T diesel product was 257K (3°F). The average specific gravity of the hydrocracker F-T diesel product was approximately 0.784 (49°API) and the cetane indices were in the high 70’s.

Table 2.5.3-1 Hydrocracker Feed Blends

	Feed Component	**Volume, m^3**	**Volume, Gallons**	**Volume % of Blend**	**% of Feed to Reactor**	**ID**
Feed 2	Heavy Diesel	0.0594	15.7	66	15.9	WOW9258
	Neat Naphtha	0.0307	8.1	34		
Feed 1	Heavy Wax	0.437	115.5	91.5	84.1	WOW9257
	Soft Wax	0.0405	10.7	8.5		

Table 2.5.3-2

Feed Properties for Hydrocracking Pilot Plant

	Description		Heavy Wax / Soft Wax Blend		Diesel/Naphtha Blend	
	Sample ID		WOW9257		WOW9258	
	Gravity, °API		33.8		45.3	
	Specific Gravity		0.86		0.80	
	Nitrogen	wt, ppm	6.3		9.1	
	Sulfur	wt, ppm	3.2		2.2	
PONA	Aromatic	Vol %			pending	
	Olefin	Vol %			42.8	
	Paraffin/Naphthene	Vol%			37.2	
	Total N-paraffins	wt %	32.4			
	Oxygen by NAA	wt %	0.74		3.33	
	ASTM Color				0.3	
	Pour Point	K (°C)			257 (-16)	
	Cloud Point	K (°C)			302 (29)	
	Karl Fischer Water	ppm			0.25	
Simulated Distillation, LV%			Temperature, K	°F	Temperature, K	°F
		IBP			330	134
		0.5%			337	147
		5%			390	243
		10%			410	279
		30%			465	378
		50%			554	538
		70%			596	613
		90%			632	678
		95%			644	699
		99%			660	729
		EP			665	738
Simulated Distillation, WT%		IBP (1 %)	616	650		
		5%	681	767		
		10%	692	786		
		30%	754	898		
		50%	900	1160		
		61%	998	1338		
		EP (61.4%	1008	1355		

Table 2.5.3-3

Yields Relative to Feed and Product Properties

Run Number	81-143	
Run Hours	1214-1238	
Prod. Yields	WT. %	VOL. %
Total C4-	4.6	
C5-466 K (380°F)	35.6	43.1
466-644K (380°F-700°F)	59.9	64.6
Total C5+	95.5	107.7
H2 Consumption	sm^3/m^3	SCF/B
	169	951
Material Balance Closure, wt%	99	
Diesel Product Properties		
Specific Gravity	0.78	
Gravity, °API	49.1	
Cloud Pt, K (°C)	257 (-16)	
Flash Pt, K (°C)	342 (69)	
Cetane Index	78	
Simdist (D2887)		
Volume Percent	Temperature, K	°F
St	399	258
5	462	372
10	480	405
30	524	484
50	561	551
70	596	613
90	630	675
95	639	690
99.5	647	705

Diesel Production and Blended Product Qualities

A total of 0.151 cubic meters (m^3) (40 gallons) of on-specification hydrocracked F-T diesel was produced during the hydrocracking operations. The first 0.123 m^3 (32.5 gallons) collected were labeled as WOW9298. A total of 0.083 m^3 (22 gallons) of WOW9298 were sent to Southwest Research Institute (SwRI) for Lubricity Additive Testing (Subtask 2.6.1), Hot-Start Cycle Transient Engine Testing (Subtask 2.6.2), and Solvent Extraction (Subtask 2.6.3). A total of 0.0038 m^3 (1 gallon) was retained for analysis. The remaining 0.036 m^3 (9.5 gallons) of WOW9298 along with 0.011 more cubic meters (3 gallons) of pilot plant diesel product produced late in the pilot plant run were blended with 0.0397 m^3 (10.5 gallons) of the hydrotreated diesel and labeled as WOW9306. The hydrocracked-hydrotreated diesel blend was made because there was not enough hydrotreated diesel (See Subtasks 2.5.7.1.a and Subtask 2.5.7.6) for the product evaluations of Subtask 2.6.1 entitled "Lubricity Additive Testing," Subtask 2.6.2 entitled "Hot-Start Cycle Transient Engine Test," and Subtask 2.6.3 entitled "Solvent Extraction." Again, 0.0038 cubic meters (one gallon) of the hydrotreated-hydrocracked diesel blend was retained for analysis and 0.0833 m^3 (22 gallons) were sent to SWRI for Task 2.6.2 and Task 2.6.3. The final 0.015 m^3 (four gallons) of pilot plant diesel produced at the end of the run were labeled as WOW9311. A total of 0.0038 cubic meters (one gallon) was retained for analysis and the other 0.011 m^3 (three gallons) were sent to SwRI for Subtask 2.5.6 entitled "Diesel Blending Tests." The following **Table 2.5.3-4** summarizes the hydrocracker F-T diesel blends and its purpose. **Table 2.5.3-5** gives the product properties for the various diesel blends. The hydrocracker F-T naphtha products from the pilot plant run were all blended together and labeled as PGQ1145. The hydrocracker F-T naphtha was used in Subtask 2.5.7.4 entitled "Fuel Cell Reformer" product evaluation. The hydrocracker F-T naphtha product qualities are given in **Table 2.5.3-5**. The hydrocracker F-T naphtha product had a Total Acid Number (TAN) of less than 0.05 milligram potassium hydroxide (KOH) per gram. The Research Octane was low (as expected)—less than 40.

The hydrocracked F-T diesel blend (WOW9298) met all of the product quality targets as listed below.

	Expected Product Spec's	**Actual (WOW9298)**
Cold Flow Plugging Point	< 263 K (14°F)	257 K (3°F)
Flash Point	> 323 K (122°F)	349 K (169°F)
Cetane Number/ Cetane Index	>70	73.6/74.9
Viscosity @ 40°C	> 2.0 cSt	3.0 cSt
TAN	<0.05 mg KOH/g	<0.05 mg KOH/g

The hydrocracked F-T diesel had a cloud point of 257K (3ºF). The hydrotreated diesel had a cloud point of 280K (44ºF). The blend of hydrocracked and hydrotreated diesel resulted in a cloud point of 272K (30ºF).

Subtask 2.5.3 product evaluation entitled "Hydrocracking Pilot" was successful in maximizing the conversion of the 644K (700°F) plus F-T wax feed component into a high cetane quality transportation diesel. The desired quantity of hydrocracker F-T diesel product was generated for end-use product in Task 2.5 and Task 2.6 product evaluations.

Table 2.5.3-4 Hydrocracked Diesel Blends for Testing

ID	Description	Purpose
WOW9298	0.123 m^3 (32.5 gallons) produced Shipped 0.0833 m^3 (22 gallons); 0.0038 cubic meters (1 gallon) retained for analysis	Task 2.6.2 Hot Transit Engine Testing & Task 2.6.3 Solvent Extraction for hydrocracked diesel
WOW9306	0.036 m^3 (9.5 gal) WOW9298 + 0.011m^3 (3 gal) HCR Diesel 0.0397m^3 (10.5 gal) HDT Diesel Shipped 0.0833 m^3 (22 gallons); 0.0038 cubic meters (1 gallon) retained for analysis	Task 2.6.2 Hot Transit Engine Testing & Task 2.6.3 Solvent Extraction for hydrotreated diesel
WOW9311	0.011 m^3 (3 gallon) produced at the end of the run	Task 2.5.6 Diesel Blending

Table 2.5.3-5
Hydrocracked Product Properties

Description		Naphtha		Diesel		Diesel Blend		Diesel	
						55% HCR'd Diesel		End of Test	
ID		PGQ1145		WOW9298		WOW 9306		WOW9311	
Specific Gravity		0.71		0.78		0.79		0.79	
Gravity, °API		67.1		48.9		48.6		48.7	
Nitrogen	wt ppm	< 0.1		< 0.1		< 0.15			
Sulfur	wt ppm	2.1		< 1		< 1			
AED Analyses									
Oxygen	wt %	not available							
Alcohol	wt %	not available							
Olefins	wt %	not available							
ASTM Color				0.0		0			
Pour Point	K (°C)			245 (-28)		263 (-10)			
Cloud Point	K (°C)			257 (-16)		272 (-1)			
Cold Filter Plugging Point	K (°C)			258 (-16)		270 (-3)			
Karl Fischer Water	ppm	< 10							
Aromatics	wt %			pending		pending			
Ramsbottom Carbon	wt %			0.05		0.05			
TAN	mg KOH / g	< 0.05		< 0.05		< 0.05			
Viscosity at 40 °C	cSt			3.0		3.0			
Flash Pt	K (°C)			349 (76)		354 (81)			
Ash Oxide, D482	wt %			< 0.005		< 0.005			
Research Octane		<40							
Cetane Number				73.6					
Cetane Index				74.9					
		Temperature							
		K	°F	K	°F	K	°F	K	°F
Simulated Distillation, LV%	IBP	294	70	360	188	360	189	340	152
	0.5%	296	74	390	242	397	256	370	207
	5%	329	132	462	373	467	382	457	363
	10%	333	140	481	407	487	417	482	409
	30%	369	204	525	486	526	487	535	503
	50%	397	256	560	549	560	549	567	562
	70%	424	303	594	609	595	612	599	618
	90%	454	358	627	669	629	672	629	673
	95%	461	370	635	683	637	688	636	686
	99%	471	388	642	697	647	706	644	699
	99.5%	474	394	645	701	651	713	645	702
D86 Distillation, LV%	IBP			439	330	444	340		
	5%			474	394	479	402		
	10%			495	431	497	435		
	30%			534	502	534	501		
	50%			570	566	567	562		
	70%			601	623	601	622		
	90%			631	676	630	674		
	95%			639	691	638	689		
	EP			640	692	645	701		

The hydrocracker F-T diesel performed well in Subtask 2.5.6 entitled “Diesel Blending Tests” product evaluations as a direct blending component in transportation diesel. The hydrocracker F-T diesel performed well as a test fuel and as a blend component in a test fuel prepared with hydrotreater F-T diesel in the product evaluations of Subtask 2.6.1 entitled “Lubricity Additive Testing,” Subtask 2.6.2 entitled “Hot-Start Cycle Transient Engine Emission Test,” and Subtask 2.6.3 entitled “Solvent Extraction.” The hydrocracker F-T diesel test fuel and the test fuel blend composed of hydrocracker and hydrotreater F-T diesel products passed lubricity standards with additive addition and reduced the engine emissions of NO_x, Total Particulate Matter (PM), Hydrocarbons (HC), CO, and the Soluble Organic Fraction (SOF) by 12% to 13%, 16% to 17%, 38% to 63%, 17% to 21%, and 21% to 39%, respectively, compared to a Tier II California Air Resources Board (CARB)-Like diesel reference fuel. The hydrocracker F-T naphtha product did not perform to expectations in Subtask 2.5.7.4 as a fuel cell reformer feed for the generation of hydrogen fuel.

Subtask 2.5.4 Wax Finishing Pilot

A summary is presented below of the important findings which mitigated potential risks to the EECP as result of the work conducted in Subtask 2.5. 4 entitled “Wax Finishing Pilot.” The flow of work for Subtask 2.5.4 is illustrated in **Schematic 2.5.4-1**. Documentation of the work and detailed discussions are included in Appendix C of this report. Subtask 2.5.4 entitled “Wax Finishing Pilot” will mitigate the technical and economic risks identified with the production of a low- and a high-melting point, food-grade wax product from the 644K (700°F) plus neat F-T wax product.

The LaPorte AFDU F-T heavy product wax contains mostly normal paraffins with minor amounts of olefins, oxygenates, and acids. The value of the wax, with appropriate upgrading to maximize finished high-melting point, food-grade wax product, is expected to benefit the economics of the EECP. The expected finished food-grade wax production from the EECP is inline with capacities of current wax manufacturers and as such should not depress the wax market price from an over supply of new product.

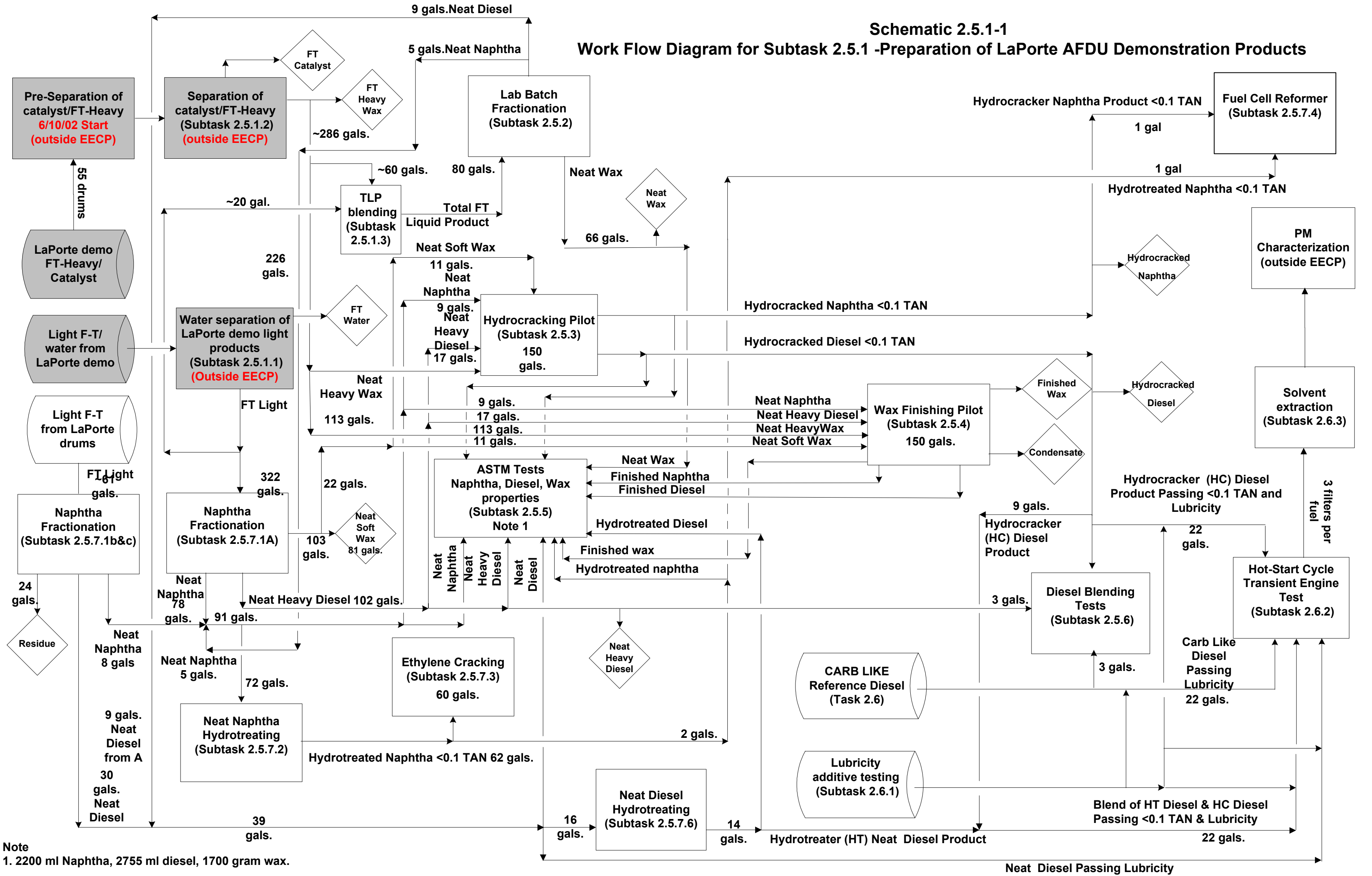
Specialty Low- and Medium-Melting Point Waxes

The refined EECP Fischer-Tropsch synthetic paraffinic low- and medium-melting point wax products obtained after wax finishing are expected to be ideal candidates for several product applications. **Table 2.5.4-1** presents some of the product properties desired. The low-melting point wax product may be used in the manufacturing of matchstick coatings, MDF board, particle board, wax emulsions, and textile sizing. The medium-melting point wax product may be used for hot-melt adhesives, coatings, plastics processing, candle-blend component, packaging-blend component, and rubber compounding and as a component for many wax blends. The low- and medium-melting point wax products obtained after wax finishing will target US Food and Drug Administration (FDA) regulations for food-grade applications.

Specialty High Melting Point Waxes

The refined EECP Fischer-Tropsch synthetic paraffinic high-melt wax product obtained after wax finishing is expected to be similar to petroleum-based paraffin wax in chemical composition, but exhibiting a higher melting point and hardness as a result of its anticipated higher molecular weight. **Table 2.5.4-2** presents some of the product properties desired. It is expected that these physical properties would make the refined EECP F-T synthetic paraffinic hard-wax product an ideal candidate for several applications such as hot melt adhesives, coatings, hardening additives, potting and cable compounds, graphic arts applications, printing inks, plastics lubrication, color concentrates, and as a component for many wax blends. The high-melt wax product obtained from wax finishing will also target FDA regulations for food-grade applications.

Schematic 2.5.1-1
Work Flow Diagram for Subtask 2.5.1 -Preparation of LaPorte AFDU Demonstration Products



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Updated: June 08 , 2003

Table 2.5.4-1

Desired Low- and Medium-Melting Point Wax Product Properties

Typical Properties	Low Melt	Medium Melt	Analytical Method
Congealing Point, K (°F)	325 to 329 (125 to 133)	338 to 345 (149 to 161)	ASTM D 938
Drop Melting Point, K (°F)	325 (125)	346 (163)	ASTM D 127
Cloud Point, Degree K (°F)	327 (129)	<358 (185)	ASTM D 2500
Saybolt Color	+30	+30	ASTM D 156
Odor	<1	<1	ASTM D 1833
Oil Content at 241K (-26^{o}F), %m	<0.5	<0.5	ASTM D 721
Penetration at 298K (77^{o}F), 0.1 mm	40	11	IP 376
Penetration at 316K(109^{o}F), 0.1 mm		26	IP 376
Kinematic Viscosity at 373K (212^{o}F), mm^2/s	2.9	5 to 8	ASTM D 445
Ultraviolet (UV) Absorptivity	<0.01	<0.01	ASTM D 2008

Table 2.5.4-2

Desired High-Melting Point Wax Product Properties

Typical Properties	High Melt	Analytical Method
Congealing Point, K (°F)	371 (208)	ASTM D 938
Drop Melting Point, K (°F)	381 (226)	ASTM D 127
Cloud Point, K (°F)	379 (223)	ASTM D 2500
Saybolt Color	+30	ASTM D 156
Odor	<1	ASTM D 1833
Oil Content at 241K (-26^{o}F), %m	<0.5	ASTM D 721
Penetration at 298K (77^{o}F), 0.1 mm	1	IP 376
Penetration at 316K (109^{o}F), 0.1 mm	3	IP 376
Penetration at 338K (149^{o}F), 0.1 mm	12	IP 376
Kinematic Viscosity at 373K (212^{o}F), mm^2/s	12.8	ASTM D 445
UV Absorptivity	<0.01	ASTM D 2008

The technical and economic risks to the EECP to be mitigated for upgrading the F-T heavy product wax is adapting existing processing technology to achieve high-value finished high-melting point, food-grade wax quality. Another technical and economic risk to the EECP is the application of separation technology to achieve narrow boiling point or viscosity ranges to separate melting point wax grades from the finished wax product obtained from Subtask 2.5.4 entitled "Wax Finishing Pilot'' without product degradation. Processing technology to achieve high-value, finished, food-grade wax quality is known and practiced for waxes from conventional crude oil but is not known for synthetic waxes such as the F-T heavy product wax. Typically, wax finishing employs hydrotreating to achieve the strict food-grade wax product specifications of Plus 30 Saybolt color, 0.5 wt% maximum oil content, and passing the FDA approval for wax by Code Federal Regulations (CFR) 21CFR 172.886 which stringently controls the polynuclear aromatic hydrocarbon content of food-grade waxes for direct use in foods or indirect contact with foods in packaging materials.

The Subtask 2.5.4 product evaluation will be carried out with the Bechtel Corporation Wax Hy-Finishing^{SM} technology. Bechtel Wax Hy-Finishing^{SM} technology has not yet been applied to the hydrogenation of F-T Heavy product wax. All previous applications of the technology have been associated with petroleum derived feeds producing food and medicinal grade waxes with nominal boiling points of 644K (700°F) and higher. Although Bechtel Wax Hy-Finishing^{SM} technology has not been applied to F-T heavy product wax, the concept of processing feeds considered similar in composition is commercially proven. Mitigating the risks to the EECP would require Subtask 2.5.4 to confirm a design basis with a product yield distribution along with product sampling, testing of finished wax physical properties for quality assurance, and examination of evidence of thermal degradation during the separation of finished high melting point and low melting point food grade waxes. In addition to the food grade wax products, the highly paraffinic finished diesel product is expected to be a desired transportation diesel. The highly paraffinic finished naphtha product is expected to be a desired feed component for a petrochemical plant thermal or ethylene cracker for the production of ethylene and propylene or as a feed component to a fuel cell reformer to generate hydrogen fuel.

Experimental

The wax finishing pilot plant feed for Subtask 2.5.4 represented a ratio-of-production blend of the LaPorte AFDU F-T light product from Subtask 2.5.1.1 and the F-T heavy product from Subtask 2.5.1.2. The Subtask 2.5.4 wax finishing pilot plant was equipped with a dual feed delivery system. It was necessary to split the wax finishing feed into two feed blend components to carry out the pilot plant evaluation. One wax finishing feed blend component was a IBP-644K (700°F) combined stream of neat F-T naphtha and neat F-T diesel. The blend was charged to the pilot plant in its ratio-of-production from an enclosed cold feed receiver that was externally cooled to avoid the lost of feed vapors. The remaining wax finishing feed blend component was the 644K (700°F) plus combined stream of neat F-T soft and neat F-T hard waxes. The blend was charged in its ratio-of-production from an enclosed hot feed receiver that was externally heated. The neat F-T hard wax feed component to the hydrocracker requires elevated heating temperatures to melt the wax to aid in its flow to the receiver.

The 644K (700°F) plus F-T wax was distributed between the LaPorte AFDU F-T light product and F-T heavy product stream. It was necessary to carry out the distillation of the F-T light product stream in Subtask 2.5.7.1.a entitled "Naphtha Fractionation" to obtain a neat F-T naphtha product, a neat F-T diesel product, and a 644K (700^{o}F) plus neat F-T soft wax product. This distillation permits the segregation of these product cuts between the two wax finishing pilot plant feed systems. A summary of the results for the Subtask 2.5.7.1.a distillation is included in Appendix F in the Subtask 2.5.7.1 Test Report

As previously discussed, the wax finishing pilot plant has two feed systems and two blends were made for the pilot plant test—the diesel and naphtha blend (Feed 2) and the heavy wax and soft wax blend (Feed 1). The Subtask 2.5.7.1.a distillation of the F-T light product stream from the LaPorte AFDU provided the diesel and naphtha components for the Subtask 2.5.4 wax finishing pilot plant feed blend (Feed 2). The F-T heavy product wax from the LaPorte AFDU was filtered to less than 10 ppmw solids by Subtask 2.5.1.2 and blended with the Subtask 2.5.7.1.a neat F-T soft wax distillation product to prepare the Subtask 2.5.4 wax finishing pilot plant heavy and soft wax feed blend (Feed 1). **Table 2.5.4-3** gives the total weights and proportions of the wax finishing pilot plant feed blends. The ratio of each feed component in the blend in the wax finishing feed was made to reflect a ratio-of production blend of the F-T light product and F-T heavy product streams from the LaPorte AFDU. Properties of these two wax finishing feed blends are given in **Table 2.5.4-3**.

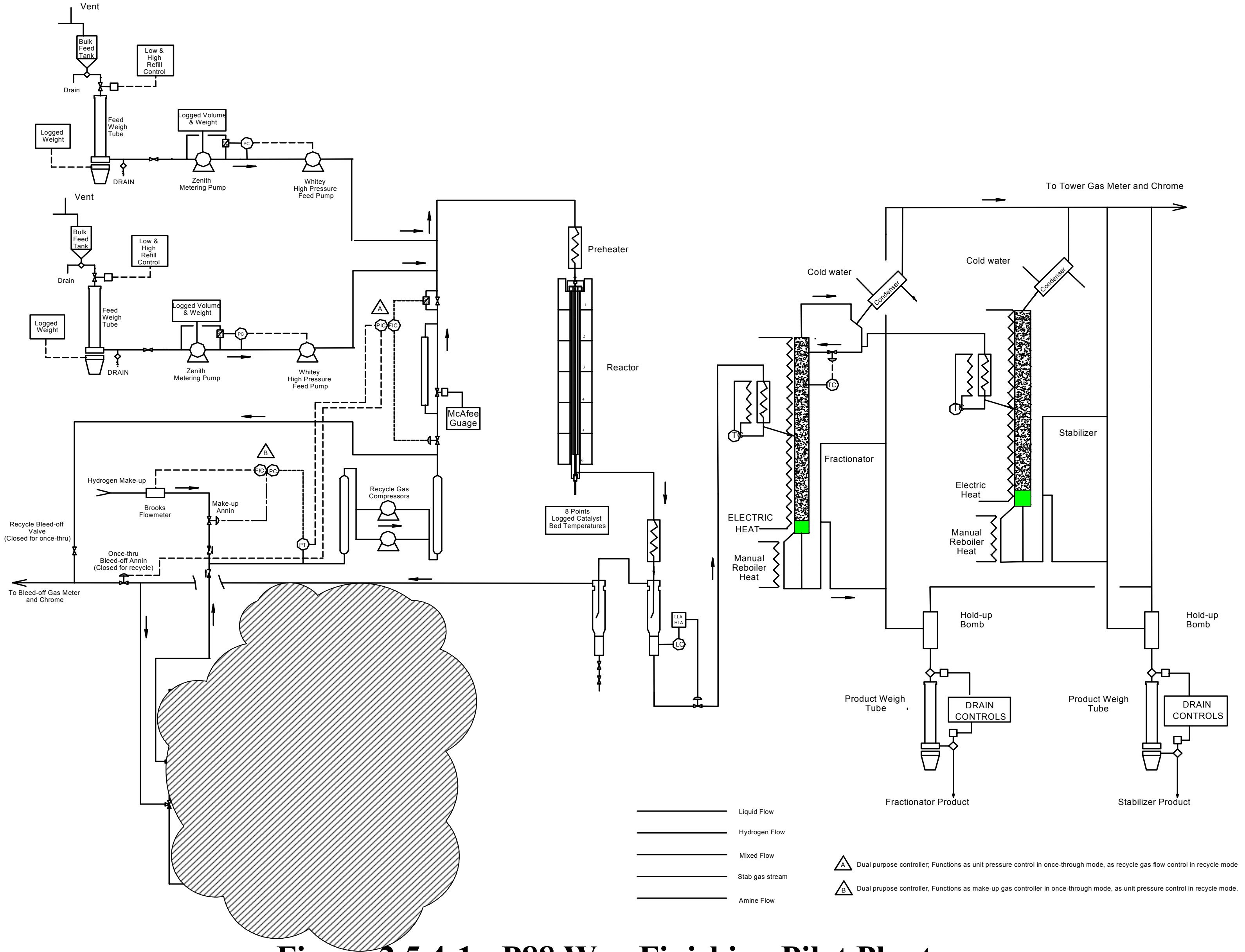
Equipment

Figure 2.5.4-1 presents a simplified process flow diagram of the P88 wax finishing pilot plant. The naphtha/diesel feed (2) and the wax feed (1) are separately charged into bulk feed tanks, then routed to a feed weigh tube. The weight is logged. The feeds are pumped into the preheater using a metering pump, followed by a high pressure booster pump. The wax feed (1) is heated to 422K (300°F), while the naphtha/diesel feed (2) is at ambient temperature.

During the catalyst screening task, once-though hydrogen is used. The amount of makeup gas is controlled by a flow meter in the hydrogen make-up line. The gas is compressed to the required pressure by a recycle gas compressor and combined with the liquid feeds. The combined gas/liquid mixture is heated in the preheater to the required reactor temperature. The reactor is an isothermal fixed-bed reactor with 6 heater blocks and 8 thermocouples to log catalyst bed temperatures. The maximum single reactor catalyst bed capacity is 434 cubic centimeters (cc). The maximum feed rate is 800 cubic centimeters per hour. The maximum temperature is 811K (1000 °F). A 260 cubic centimeter catalyst bed was used and the feed rate was varied from 130 to 260 cubic centimeters per hour (0.5-1 Liquid Hourly Space Velocity (LHSV)). The reactor bottoms are cooled and routed to a separator, where the reactor product gas is removed from the liquid. The bleed–off gas flow is measured and analyzed. The liquid reactor product continues to the fractionator. The fractionator is an atmospheric tower where the finished naphtha/diesel product is separated from the finished wax product. The fractionator bottoms are collected in a holdup bomb and the amount of product is weighed. The fractionator overhead flows to the stabilizer tower, where the liquid product is collected and measured in a holdup bomb and the amount of product is weighted. The off-gas from the fractionator and stabilizer are combined, the flow rate is measured and the gas is analyzed.

Table 2.5.4-3 - Feedstock Inspection Testing			
Analytical Tests	**Test Method**	**F-T Naphtha & F-T Diesel**	**F-T 664K (700 °F)+ Soft & Hard Waxes**
F-T Naphtha	Blend Component , wt%	4.84	
F-T Diesel	Blend Component, wt%	10.12	
F-T 664K (700°F)+ Soft Wax	Blend Component, wt%		7.04
F-T 664K (700°F)+ Heavy Wax	Blend Component, wt%		78
Durasyn Content, wt.%	(ASTM D-5442 Modified)		
Gravity, API	(ASTM D-1298)	46.0	32.5
Gravity, Specific	(Calculated)	0.7972	0.8628
Distillation by GC		ASTM D-2887, K (°F)	ASTM D-2887 Modified High Temp, K (°F)
	IBP	356 (181)	
	5%	397 (255)	
	10%	423 (301)	
	20%	449 (349)	
	30%	489 (420)	
	40%	532 (498)	
	50%	560 (548)	
	60%	585 (594)	
	70%	604 (628)	
	80%	624 (663)	
	90%	643 (697)	
	95%	654 (718)	
	FBP	690 (783)	
Acid Number, mg KOH/g	(ASTM D-664)	4.79	0.86
Hydrogen Content, wt%	(ASTM D-4808)		14.3
Flash Point, K (°F)	(ASTM D-92)		522 (480)
	(ASTM D-93)	302 (29)	
Viscosity, cSt	(ASTM D-445)		
@ 313 K (104°F)		1.979	
@ 373 K (212°F)		0.924	Not determined
@ 394 K (250°F)			23.48
Pour Point, K (ºF)	(ASTM D-97)	283 (50)	
Melting Point, K (ºF)	(ASTM D-87)		379 (223)
Congealing Point, K (ºF)	(ASTM D-938)		371 (208)
Oil Content, Wt% (<15% Oil)	(ASTM D-721)		Not determined
Solvent Extractable,	(ASTM D-3235)		not determined

Table 2.5.4-3 - Feedstock Inspection Testing			
Analytical Tests	**Test Method**	**F-T Naphtha & F-T Diesel**	**F-T 664K (700 °F)+ Soft & Hard Waxes**
Wt% (>15% Oil)			
FDA UV Absorbance	(21CFR 172.886)		
	Part One		
	280-289 nm		1.106 (fail)
	290-299 nm		0.921 (fail)
	300-359 nm		0.741 (fail)
	360-400 nm		0.262 (fail)
	Part Two		
	280-289 nm		0.236 (fail)
	290-299 nm		0.183 (fail)
	300-359 nm		0.134 (fail)
	360-400 nm		0.024 (fail)
Color, ASTM	(ASTM D-1500)	0.5	7.5
Color, Saybolt	(ASTM D-156)		Out of range
Sulfur, ppmw	(ASTM D-2622 if >30 ppmw)	N/A	N/A
	(ASTM D-5453 if <30 ppmw)	2.9	<3.0
Nitrogen, ppmw	(ASTM D-4629)	11.7	<3.0
Aromatics, % Aromatics, %	(ASTM D-1319) ChevronTexaco ILT Lab	19.1 (high) none	
Olefins, %	(ASTM D-1319)	56.7	
Oxygen by NAA, wt. %	ChevronTexaco ILT Lab	3.33	0.74
Water and Sediment, vol%	(ASTM D-1796)	<0.05	
Metals, Iron, ppmw	ChevronTexaco ILT Lab	0.6	60.1
Conradson Carbon Residue, 10% Bottoms, wt. %	(ASTM D-524)		0.142
Ash, wt%	(ASTM D-482)		0.017



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A Dual purpose controller; Functions as unit pressure control in once-through mode, as recycle gas flow control in recycle mode

B Dual prupose controller, Functions as make-up gas controller in once-through mode, as unit pressure control in recycle mode.

Figure 2.5.4-1 - P88 Wax Finishing Pilot Plant

Results and Discussion

The nickel catalysts used in the pilot plant test program were very susceptible to temperature runaways. Exotherms occurred during every series of tests starting at 561K (550°F), and reaching temperatures above 811K (1000°F). The exotherms could be controlled during pilot plant operations by either quenching or depressuring the unit. The nickel catalyst did not seem to lose activity as a consequence of these exotherms, although the catalyst was physically damaged when subjected to temperatures above 922K (1200°F). Despite these temperature runaways, the nickel alumina-based catalyst was selected as the preferred catalyst for the F-T Heavy Product Upgrading. A commercial-scale unit design operating with a nickel catalyst would utilize inter-bed quenching to control reactor catalyst bed temperatures.

In addition to the pilot plant problem of catalyst bed temperature exotherms the atmospheric distillation column bottoms wax product color was off specification. It was later confirmed that the product wax discoloration was caused by thermal degradation in the pilot plant atmospheric distillation column. Reboiler temperatures were set at 603K (625°F) for the separation of a combined naphtha/diesel finished product as an overhead distillation cut from the distillation bottoms wax product. It was confirmed that the color of the distillation bottom wax product is sensitive to the atmospheric distillation column reboiler temperature.

The pilot plant test program conducted during Subtask 2.5.4 demonstrated that it is not possible to process the naphtha/diesel feed and the wax feed and subsequently separate the products in an atmospheric distillation column. The reboiler temperature of the atmospheric distillation column required for the separation of the naphtha/diesel product from the wax product discolors the distillation bottoms wax product. With the concurrence of the EECP Team, no additional testing was conducted on the naphtha/diesel feed combined with the wax feed. It may be possible to separate the products in a commercial unit design equipped with a vacuum distillation column provided that the vacuum is deep enough to enable separation of products at approximately 436K (325°F). A preliminary estimate was made showing the vacuum required to be one millimeter of mercury (Hg).

The results from Test P88-60-3 charging only the F-T heavy product wax feed component are presented as the basis for design confirmation run. **Table 2.5.4-4** presents the operating parameters for Test P88-60-3.

During Test P88-60-3, no naphtha/diesel feed component was charged to the unit, the atmospheric distillation column was not operated, and the naphtha/distillate product was not removed. **Table 2.5.4-5** presents the analysis of the analytical testing performed on the total liquid wax product from Test P88-60-3. The total liquid product wax has not been stabilized to remove light ends. The wax product from Test P88-60-3 meets the food-grade wax specifications for UV Adsorption and Saybolt color. Since the total liquid product wax has not been stabilized, it is not surprising that the oil content exceeds the specification. The light ends may be removed by employing vacuum distillation.

Table 2.5.4-4 Design Basis Confirmation Operating Conditions – Wax Blend Feed

Test	**P88-60-3 Selected as Basis for Design Run**
Catalyst	Nickel catalyst (alumina based)
Feed Type	Blended FT Start-Up Wax
Feed ASTM Color	7.5
Run no. P88-60-3	
LHSV	0.5
Pressure, kPa (psig)	13891 (2000)
Temperature, K (°F)	603 (625)
H_2 circulation, Nm^3/m^3 (scf/bbl) Once thru	674 (4000)

Table 2.5.4-5

Basis for Design - Product Testing for Feed Composed of F-T Heavy Product Liquid

Analytical Tests	Test Method	Food Grade Wax Cut	Measured Results
		Specification Tests	
Melting Point, K (°C/°F)	(ASTM D-87)	>326 (54.4°C/130°F)	376 (103/217)
Oil Content, wt. %	(ASTM D-721) If >15wt% Oil see D-3235	0.5 Max	28.48
Solvent Extractables, wt%	(ASTM D-3235)	Report if D-721 >15 wt%	32.75
Color, Saybolt	(ASTM D-156)		
Initial		Plus 30 Min	+30
30 Days Storage		Plus 30 Min	+30
FDA UV Absorbance	(21CFR 172.886)		
	Part One	Pass	Fail
	Part Two,		
	280-289 nm	0.150 Max	0.123 (pass)
	290-299 nm	0.120 Max	0.089 (pass)
	300-359 nm	0.080 Max	0.058 (pass)
	360-400 nm	0.020 Max	0.012 (pass)
Metals, Iron, ppmw	(ChevronTexaco to Specify)	1 Max	<4.0
Yield, wt% FF	Mass Balance Closure ± 2%	Report	97.5
Yield, vol% FF	Mass Balance Closure ± 2%	Report	-
Gravity, API	(ASTM D-1298)	Report	37.8
Gravity, Specific	(Calculated)	Report	0.8358
Distillation	(ASTM D-2887 or D-2887M High Temp)	Report	
Durasyn By-Products	(ASTM D-5542 Modified)		
Yield, wt% FF	GC Carbon Number Distribution-Extended	Report	
		Characterization Tests	
Congealing Point, K (°C/°F)	(ASTM D-938)	Report	366 (93/199)
Penetration @ 350K (77 °C/170°F), mm	(ASTM D-1321)	Report	73
Viscosity, cSt @ 373 K (100°C/212°F)	(ASTM D-445)	Report	Solid

Table 2.5.4-5
Basis for Design - Product Testing for Feed Composed of F-T Heavy Product Liquid

Analytical Tests	Test Method	Food Grade Wax Cut	Measured Results
Viscosity, cSt @ 394K (121°C/250°F)	(ASTM D-445)	Report	11.35
Sulfur, ppmw	(ASTM D-2622 if >30 ppmw)	Report if > 30 ppmw	<30
Sulfur, ppmw	(ASTM D-5430 if <30 ppmw)	Report if <30 ppmw	0.3
Nitrogen, ppmw	(ASTM D-4629)	Report	4.4

Major results of the wax finishing pilot plant tests include:

1. A wax product meeting Saybolt Color and FDA UV Absorbance Part II food grade wax product specifications can be made from a soft wax/hard wax feed blend using a Nickel Alumina-based catalyst at the following reactor conditions:

   Reactor Temperature - 603K (625°F)
   Reactor Pressure - 13891 kPa (2000 psig)
   Hydrogen Treatgas Rate - 674 Nm^3/m^3 (4000 scf/bbl) H_2/oil
   LHSV – 0.5

   The catalyst is very susceptible to temperature runaway.

2. The wax meets the food grade specification tests, except for oil content and FDA UV Absorbance Part One, although it passes Part Two. Since the total liquid wax product has not been stabilized, it is not surprising that the oil content exceeds the limit. The light ends may be removed by vacuum distillation.

3 It has not been proven that a ratio-of-production feed blend can be Hy-Finished^{SM} in one reactor. Attempts to treat the ratio-of-production feed blend at conditions required for on-specification food grade wax product resulted in unstable reactor catalyst bed temperatures and temperature excursions.

4. It is not possible to Hy-Finish^{SM} a ratio-of-production feed blend resulting in a full range F-T total liquid product and separate the finished naphtha/diesel product from the finished wax product using an atmospheric distillation column. The required reboiler temperature of the atmospheric distillation column discolors the wax product.

5. It may be possible to Hy-Finish^{SM} the full range F-T Product and obtain the required separation in a vacuum column at a lower reboiler temperature. The estimated vacuum required is 1 mm Hg at 436K (325°F).

Subtask 2.5.5 ASTM Testing for Naphtha, Diesel, Wax Properties and Development Tests

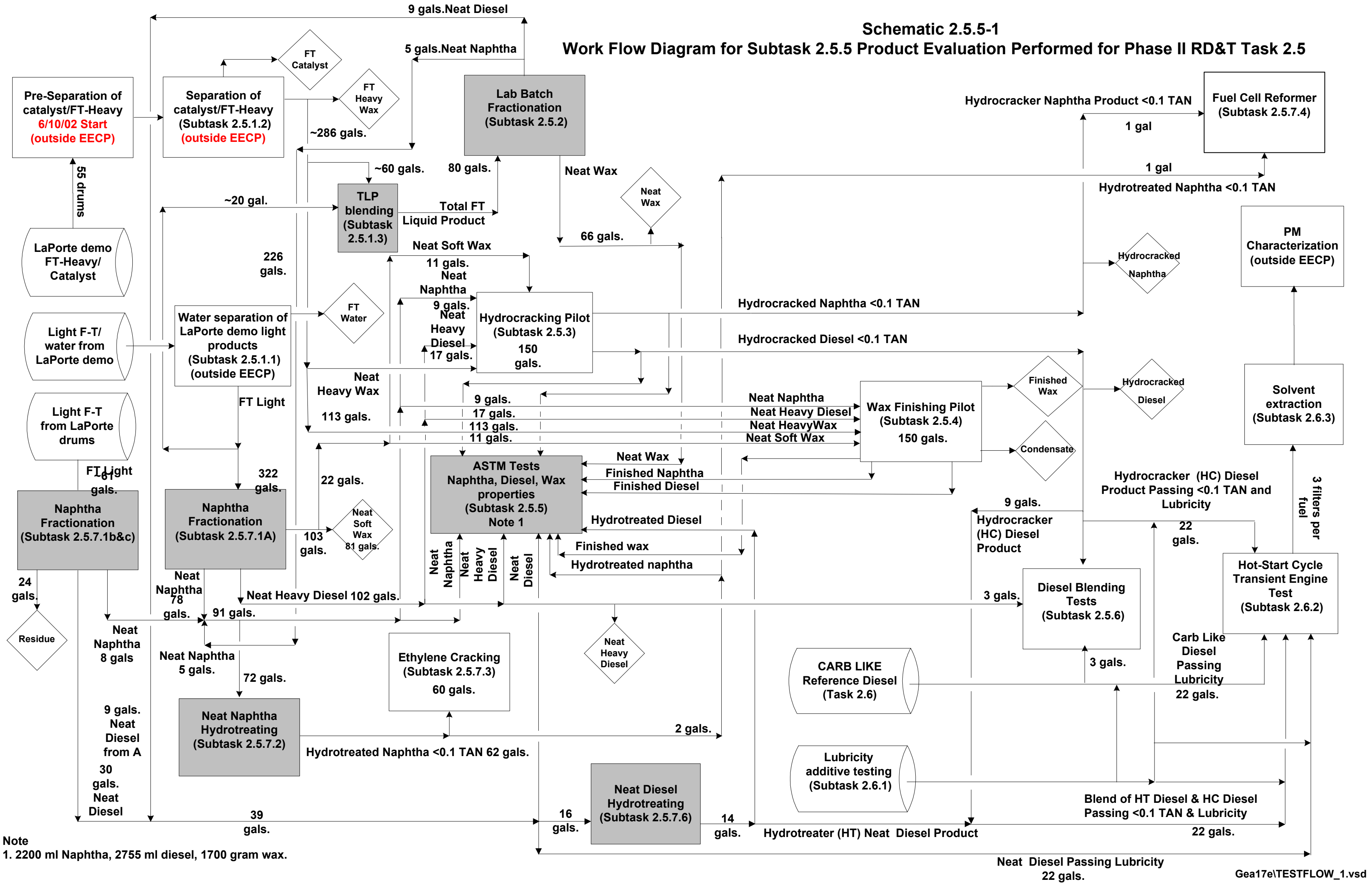
Inspection testing was conducted as a continuing quality assurance check that fuel and specialty wax product specifications were being met for Task 2.5 product evaluations. The flow of work for Subtask 2.5.5 is illustrated in **Schematic 2.5.5-1**. Subtask 2.5.5 entitled "ASTM Naphtha, Diesel, Wax Properties and Development Tests" consists of three individual inspection test schedules and are presented as **Table 2.5.5-1** for naphtha, **Table 2.5.5.-2** for diesel, and **Table 2.5.5-3** for wax. Inspection tests were routinely requested on Task 2.5 products generated from the Subtask 2.5.2 entitled "Lab Batch Fractionation", Subtask 2.5.3 entitled "Hydrocracking Pilot", Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating", and Subtask 2.5.7.6 entitled "Neat Diesel Hydrotreating." The available test results obtained with these test schedules are summarized in the individual Subtask Test Reports appended to this Topical Report. The presence of olefins, acids, and oxygenates in the neat naphtha and diesel products resulted in interference and sometimes questionable results with some of the petroleum industry accepted ASTM test methods employed in **Table 2.5.5-1** and **Table 2.5.5-2**. Additional RD&T developmental work would be required to resolve these interference issues. The lack of solubility of the F-T wax products in the specified ASTM Test Method limited testing from the **Table 2.5.5-3** test schedule for wax products. Additional RD&T developmental work would be required resolve these solvent/wax solubility issues.

Oxygen Concentration Determination

The neat F-T naphtha and neat F-T diesel products are designated as end-use products in Task 2.5 and Task 2.6 product evaluations. The neat F-T naphtha and neat F-T diesel products contains reactive oxygenates which represent potential coke precursors in the end-use products for the Task 2.5 and Task 2.6 product evaluations. These potential coke precursors may contribute to a negative outcome if not reduced to low ppmw oxygen concentrations by hydrotreating. No ASTM test currently exists which claims detection levels in the low ppmw oxygen range. Test method development for oxygen concentration determination was carried out under Subtask 2.5.5.b entitled "Oxygen Concentration Determination for F-T Naphtha and Diesel Boiling Range Fractions" by the Southwest Research Institute (SwRI).

A summary statement is presented herein on the results obtained during Subtask 2.5.5.b product evaluations. The low ppmw oxygen detection levels for oxygenates in hydrotreated F-T distillate products were not achieved at this stage of the SwRI test method development. Documentation of the work and detailed discussions are to be found in the Subtask 2.5.5.b Test Report which is included as Appendix D of this Task 2.5 Topical Report. Subtask 2.5.5.b was intended to mitigate the technical risks to the EECP identified with these potential coke precursors in the form of reactive oxygenates present in the neat F-T naphtha product. Documenting the removal of the reactive oxygenates during Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating" was required prior to undergoing product evaluations in Subtask 2.5.7.3 entitled "Ethylene Cracking" and Subtask 2.5.7.4 entitled "Fuel Cell Reformer."

Schematic 2.5.5-1
Work Flow Diagram for Subtask 2.5.5 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Table 2.5.5-1
Naphtha Characterization Testing Schedule for Subtask 2.5.5

Test Standard	Test Name
ASTM D287	**API Gravity, Specific Gravity, Density**
ASTM D86 or ASTN D2887	**Distillation or Simulated Distillation of Fuel Oils**
ASTM D3120	**Sulfur Content by Coulometric Titration**
ASTM D4629	**Nitrogen by Chemiluminescence**
ASTM D2699	**Research Octane Number**
ASTM D2700	**Motor Octane Number**
ASTM D3242	**Total Acid Number (TAN)**
Developmental Task 2.5.5.b	**Oxygenates and/or Total Oxygen Content see Note 1**
Developmental	**Paraffins, Iso-Paraffins, Aromatics, Naphthenes, and Olefins (PIANO) see Note 1**
	Note 1 – Additional RD&T Test method development required to achieve detection levels desired or due to test interference from compounds present.

Table 2.5.5-2
Diesel Characterization Testing Schedule for Subtask 2.5.5

Test Standard	Test Name
ASTM D287	API Gravity, Specific Gravity, Density
ASTM D86 or ASTM D2887	Distillation or Simulated Distillation of Fuel Oils
ASTM D1500	Color, ASTM
ASTM D130	Copper Corrosion
ASTM D3120	Sulfur Content by Coulometric Titration
ASTM D4629	Nitrogen by Chemiluminescence
ASTM D613	Cetane Number
ASTM D4737	Calculated Cetane Index
ASTM D6078	Scuffing Load (Ball on Cylinder
ASTM D6079	Lubricity of Diesel Fuel by HFRR
ASTM D93	Pensky-Marten (PM) Flash Point
ASTM D445	Kinematic Viscosity at 40°C
ASTM D97	Pour Point
ASTM D2500	Cloud Point
ASTM D482	Ash Content
ASTM D524	Ramsbottom Carbon, 10% Bottoms
ASTM D3242	Total Acid Number (TAN)
Developmental	ASTM D2425 Hydrocarbon Types in Middle Distillates by MS, Aromatics see Note 1
Developmental	Hydrocarbon Type analysis by Clay-Gel Absorption Chromatography see Note 1
ASTM D 5542	Carbon Number Distribution
Developmental Task 2.5.5.b	Oxygenates and/or Total Oxygen see Note 1
	Note 1 – Additional RD&T Test method development required to achieve lower detection levels desired or due to test interference from compounds present.

Table 2.5.5-3
Wax Characterization Testing Schedule for Subtask 2.5.5

Test Standard	Test Name
Developmental	**ASTM D287 API Gravity, Specific Gravity, Density see Note 1**
ASTM D2887	**Simulated Distillation**
ASTM D156	**Color, Saybolt**
ASTM D1500	**Color, ASTM**
ASTM D3120	**Sulfur Content by Coulometric Titration**
ASTM D4629	**Nitrogen by Chemiluminescence**
21CFR 172.886	**FDA approval for Wax, Part 1 and 2**
Developmental	**ASTM D721 Oil in Wax see Note 1**
ASTM D87	**Melting Point of Wax**
ASTM D127	**Drop Melting Point**
ASTM D937	**Cone Penetration of Petrolatum**
ASTM D1321	**Needle Penetration**
ASTM D445	**Kinematic Viscosity at 100°C**
ASTM D938	**Congealing Point of Wax**
ASTM D1832	**Peroxide Number of Petroleum Wax**
ASTM D5185	**ICP Elemental Analysis**
Developmental	**Paraffins, Iso-Paraffins, Aromatics, Naphthenes, and Olefins (PIANO) see Note 1**
Developmental Task 2.5.5.b	**Oxygenates or Total Oxygen Content see Note 1**
Developmental	**Extended ASTM D 5542 Carbon Number Distribution see Note 1**
	Note 1 – Additional RD&T test method development required to achieve lower detection levels desired or due to lack of solubility of wax in solvents specified in ASTM Methods.

Subtask 2.5.5.b was also intended to mitigate the technical risks to the EECP by documenting the removal of reactive oxygenates during Subtask 2.5.7.6 entitled “Neat Diesel Hydrotreating” prior to undergoing F-T diesel product evaluations. The low ppmw oxygen detection levels for oxygenates in hydrotreated F-T distillate products were not achieved at this stage of the SwRI test method development. The ASTM test method for TAN was used as an indication of the removal of reactive olefins, acids, and oxygenates compounds present in the hydrotreated F-T naphtha product from Subtask 2.5.7.2, the hydrotreated diesel product from Subtask 2.5.7.6, and the hydrocracked naphtha and diesel products from Subtask 2.5.3.

Subtask 2.5.6 Diesel Blending Tests

Experimental

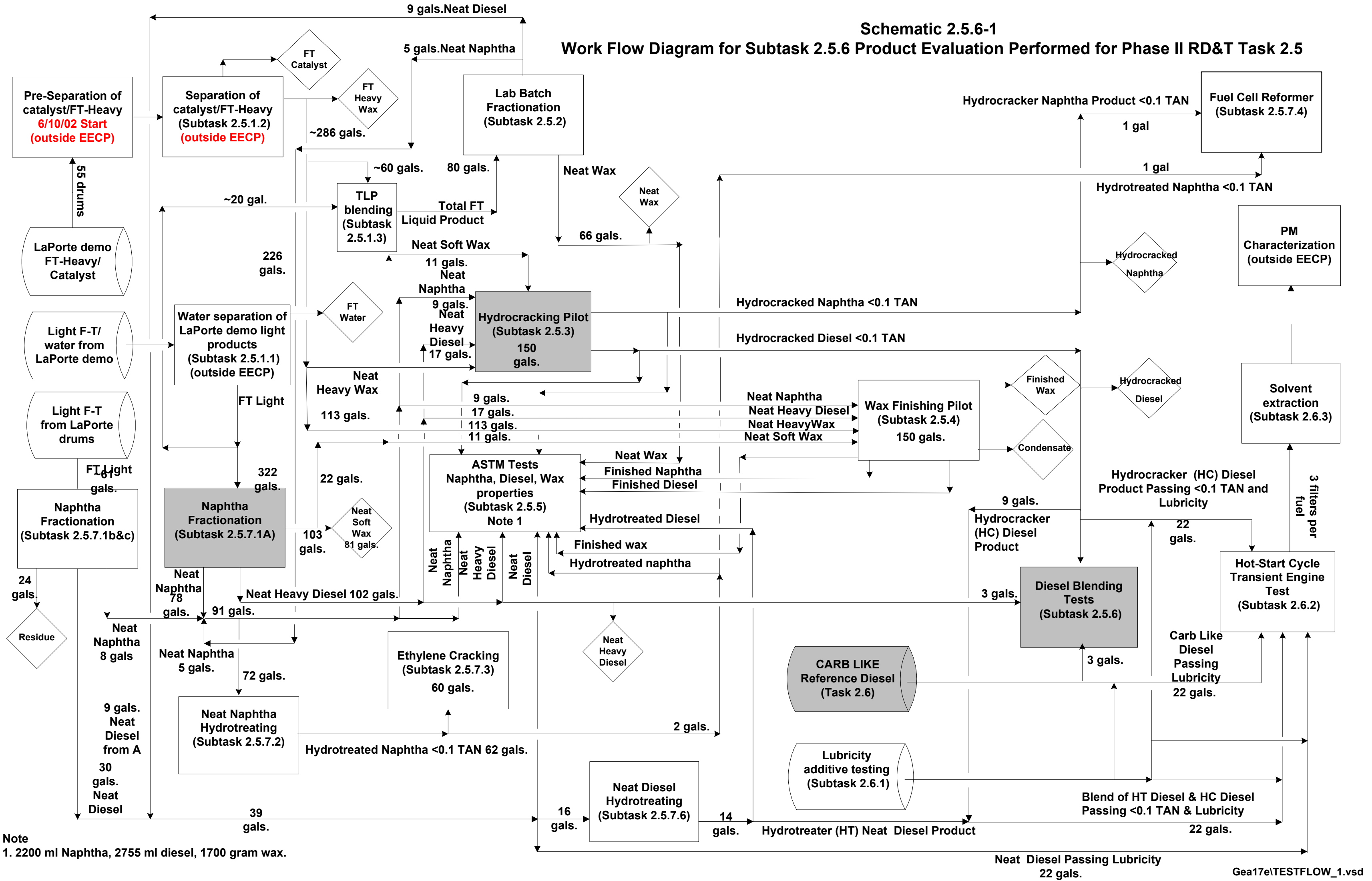
A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.6 entitled "Diesel Blending Tests" are found in the Subtask 2.5.6 Test Report which is included as Appendix E to this Topical Report. The flow of work for Subtask 2.5.6 is illustrated in **Schematic 2.5.6-1**.

Potential risks were identified with using F-T diesel products as direct blending components in transportation diesel. There is the potential for unexpected adverse effects on cetane, pour point, cloud point, Kinematic viscosity at 277K (39°F), storage stability, and lubricity properties when F-T diesel products are used as direct blending components in transportation diesel. The blending responses of two F-T diesel products with a Tier II CARB-like diesel reference fuel were evaluated and a summary of the results are presented herein. The neat F-T heavy diesel distillation product from Subtask 2.5.7.1.a entitled "Naphtha Fractionation" and the Hydrocracker (HC) F-T diesel product from Subtask 2.5.3 entitled "Hydrocracker Pilot" were evaluated. The open literature claims that the presence of oxygenate compounds similar to those compounds that may exist in the neat F-T heavy diesel product may enhance the lubricity property of a fuel.

Neat F-T Diesel Direct Blending to Transportation Fuel

To mitigate the risk of using F-T diesel products as direct blending components in transportation diesel, the neat F-T heavy diesel product from Subtask 2.5.7.1.a entitled "Naphtha Fractionation" underwent product evaluation in Subtask 2.5.6 entitled "Diesel Blending Tests." The neat F-T heavy diesel product contains reactive olefins, oxygenates, and acids which can lead to the risks of corrosion and instability in transportation diesel. The flow of work for the Subtask 2.5.6 Neat F-T Diesel Blending product evaluation is illustrated in **Schematic 2.5.6-2**. Three test fuel blends were prepared with volumetric concentrations of 25, 50, and 75 percent neat F-T heavy diesel in a Tier II CARB-like diesel reference fuel. The cetane, pour point, cloud point, Kinematic viscosity at 313K (104°F), stability, and lubricity properties of the neat F-T heavy diesel, the Tier II CARB-like diesel reference fuel, and the three volumetric blend compositions were evaluated.

Schematic 2.5.6-1
Work Flow Diagram for Subtask 2.5.6 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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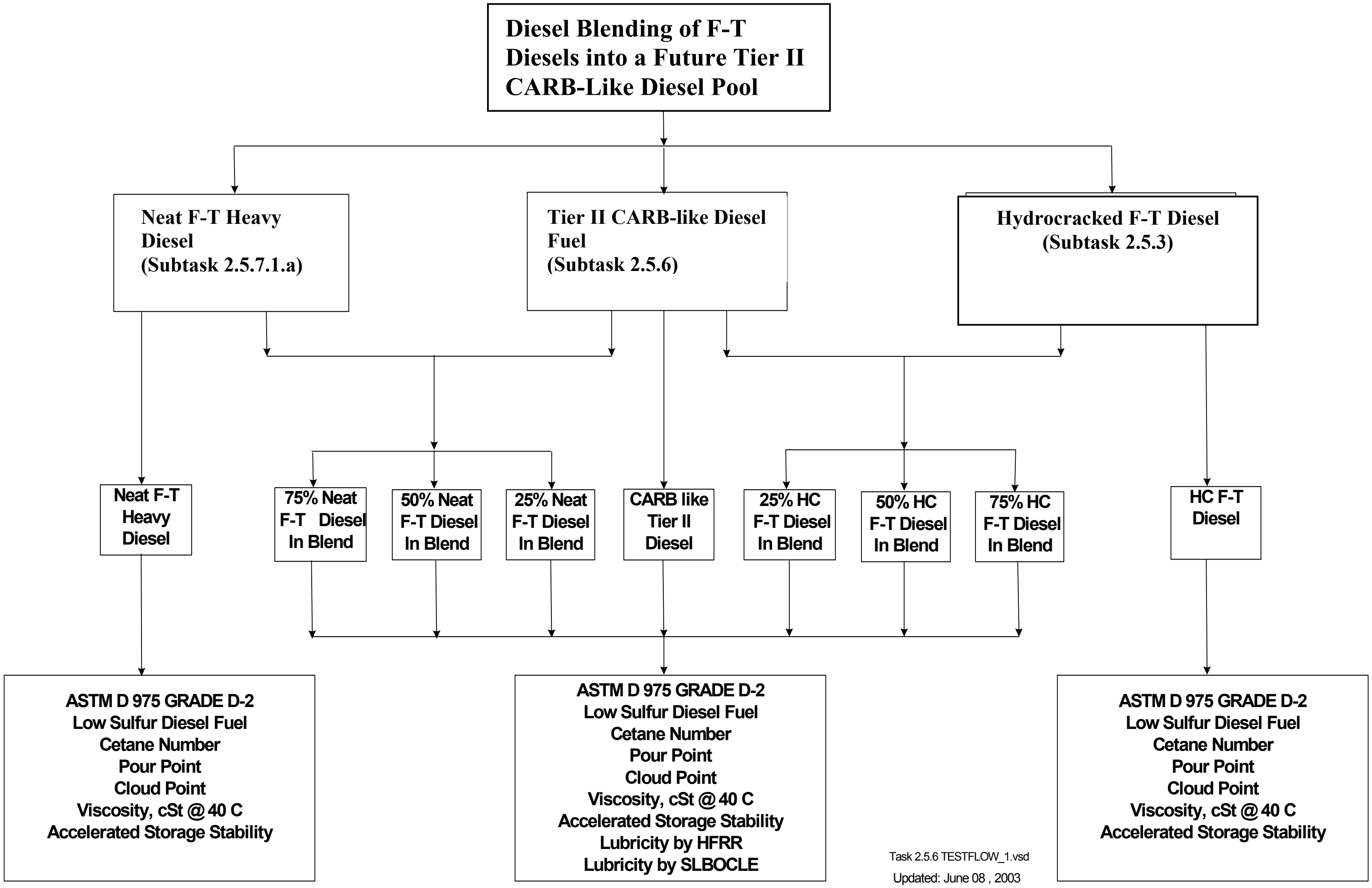
Updated: June 08 , 2003

Schematic 2.5.6-2
Flow of Work for Subtask 2.5.6 Diesel Blending Testing



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Updated: June 08 , 2003

Hydrocracker F-T Diesel Direct Blending to Transportation Fuel

To mitigate the risk of using F-T diesel products as direct blending components in transportation diesel, the hydrocracker (HC) F-T diesel product from Subtask 2.5.3 entitled “Hydrocracking Pilot” underwent product evaluation in Subtask 2.5.6 entitled “Diesel Blending Tests.” The flow of work for the Subtask 2.5.6 hydrocracker F-T Product evaluation is illustrated in **Schematic 2.5.6-2**. Three blends were prepared with volumetric concentrations of 25, 50, and 75 percent hydrocracker F-T diesel product in a Tier II CARB-like diesel reference fuel. The cetane, pour point, cloud point, Kinematic viscosity at 313K (104°F), stability, and lubricity properties of the HC F-T diesel product, the Tier II CARB-like diesel reference fuel, and the three volumetric blend compositions were evaluated.

Results and Discussions

Figure 2.5.6-1 presents the results of the blending responses on the ASTM D-613 cetane number of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The ASTM D-613 cetane number is a standardized measure of fuel ignition quality. It is influenced by the time interval between the beginning of injection and auto ignition of the fuel in the piston cylinder of a designated engine: the shorter the delay time interval, the higher the cetane number. The cetane number scale ranges from zero to 100, but typical values lie in the range of 30 to 65. Diesel engines operate better on fuels with high cetane numbers. Values above 50 begin to produce noticeably better operation than fuels which merely meet the ASTM D-975 minimum specification of a 40 cetane index. Furthermore, higher cetane number produced lower hydrocarbon emissions while allowing engine settings that have smaller increases of nitrogen oxides than would be obtained with average fuels. The neat F-T heavy diesel product exhibits a 76 cetane number, the Hydrocracker F-T diesel product exhibits a cetane number of 74.5, and the Tier II CARB-like diesel reference fuel exhibits a 51 cetane number. The Tier II CARB-like diesel blends with either the neat F-T heavy diesel or the HC F-T diesel product exhibited cetane numbers more like the higher cetane number of the F-T diesel component. This is an unexpected result in that normally when mixing diesel blend stocks with dissimilar cetane numbers, the blends exhibit cetane numbers more like the low cetane number blend component. This represents an attractive economic incentive associated with the direct blending of these F-T diesel products into transportation fuel. All the F-T test fuel blends exhibited excellent ignition quality as measured by cetane number.

Figure 2.5.6-2 presents the results of the blending responses on ASTM D-97 pour point of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. This cold flow property gives an indication of how well a fuel will perform at low temperature in the fuel system as it flows. The test provides the low temperature near which a test fuel will not flow. There is no single

Figure 2.5.6-1 – Cetane Number Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

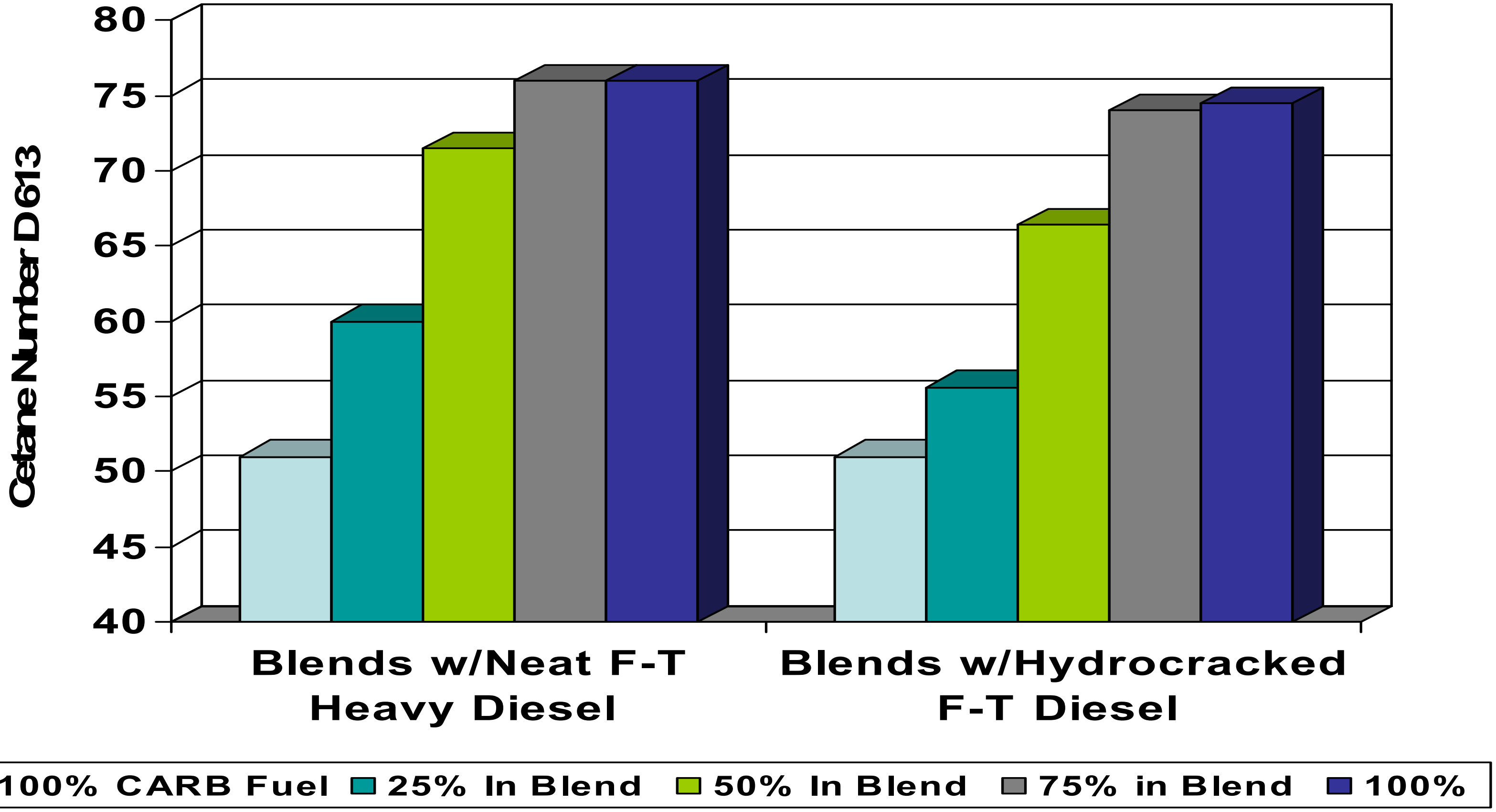
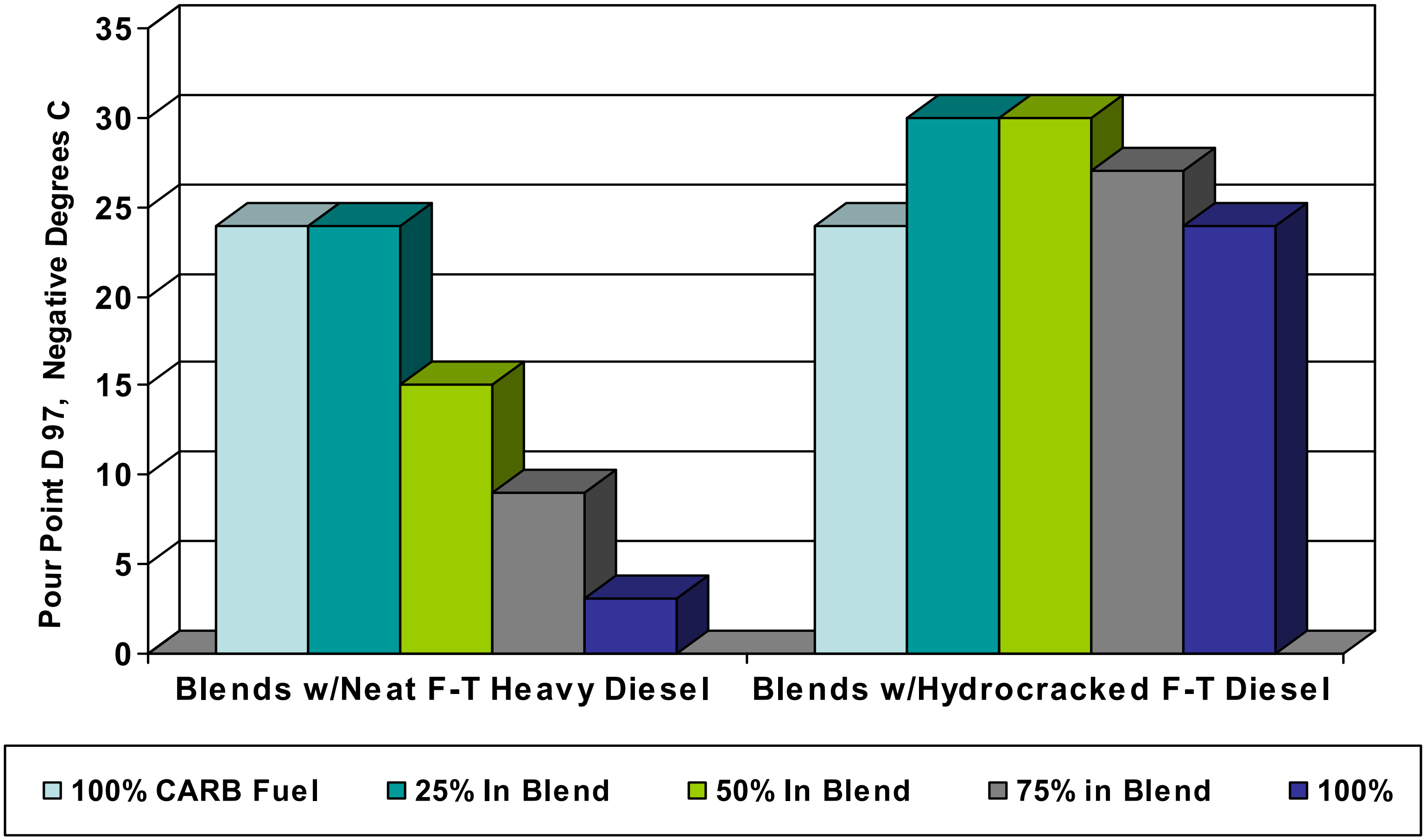


Figure 2.5.6-2 – Pour Point Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



ASTM D-975 specification value for diesel fuel pour point because of the wide variability of prevailing low temperatures across the United States. The intended geographical market area for the F-T diesels will determine their blending amounts and the pour point requirement of transportation diesel fuel blend. The neat F-T heavy diesel product exhibits a 270K (27°F) pour point, the HC F-T diesel product exhibits a pour point of 249K (-11°F) and the Tier II CARB-like diesel reference fuel also exhibits a 249K (-11°F) pour point similar to the HC F-T diesel product. The positive pour point depression exhibited by the volumetric blends containing 25 and 50 percent HC F-T diesel product is very unusual and unexpected positive advantage for the inclusion of F-T diesels at these concentrations.

Figure 2.5.6-3 presents the results of the blending responses on ASTM D-2500 cloud point of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The cloud point is the temperature at which wax is first seen coming out of solution. The wax crystals thus formed revert to the liquid state as the temperature rises. This property of the diesel fuel helps to assess low temperature operability. Cloud point may predict the temperature that would give high pressure drop across diesel fuel filters on start-up. There is no single ASTM D-975 specification value for diesel fuel cloud point because of the wide variability of prevailing low temperatures across the United States. The intended geographical market area for the F-T diesels will determine their blending amounts and the cloud point requirement of the transportation diesel fuel blend. The neat F-T heavy diesel product exhibits a 271K (28°F) pour point, the HC F-T diesel product exhibits a pour point of 256K (1°F) and the Tier II CARB-like diesel reference fuel exhibits a 247K(-15°F) pour point. The positive cloud point “dip” exhibited by the volumetric blends containing 25% of the neat F-T heavy diesel or HC F-T diesel products in the Tier II CARB-like diesel reference fuel blend is an unexpected advantage for the inclusion of F-T diesels at this concentration.

Figure 2.5.6-4 presents the results of the blending responses on diesel fuel lubricity by the ASTM D-6079 High-Frequency Reciprocating Rig (HFRR) test method of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The HFRR lubricity test relies upon the measurement of the width of a wear scar produced by a pin moving back and forth across a test block immersed in the test fuel. The ASTM D-975 diesel fuel specifications do not set a limit for acceptable HFRR wear scar, but its appendix X3.3.3 presents the findings of the ISO interlaboratory study that nominate a wear scar no larger than 450 microns as adequate to protect all fuel injection equipment. The neat F-T heavy diesel product exhibits a passing HFRR wear scar width of 230 microns, the HC F-T diesel product exhibits a failing HFRR wear scar width of 585 microns and the Tier II CARB-like diesel reference fuel exhibits a failing HFRR wear scar width of 605 micron. All of the test fuel blends containing the neat F-T diesel blend component passed the maximum HFRR wear scar width of 450 microns.

Figure 2.5.6-3 – Cloud Point Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

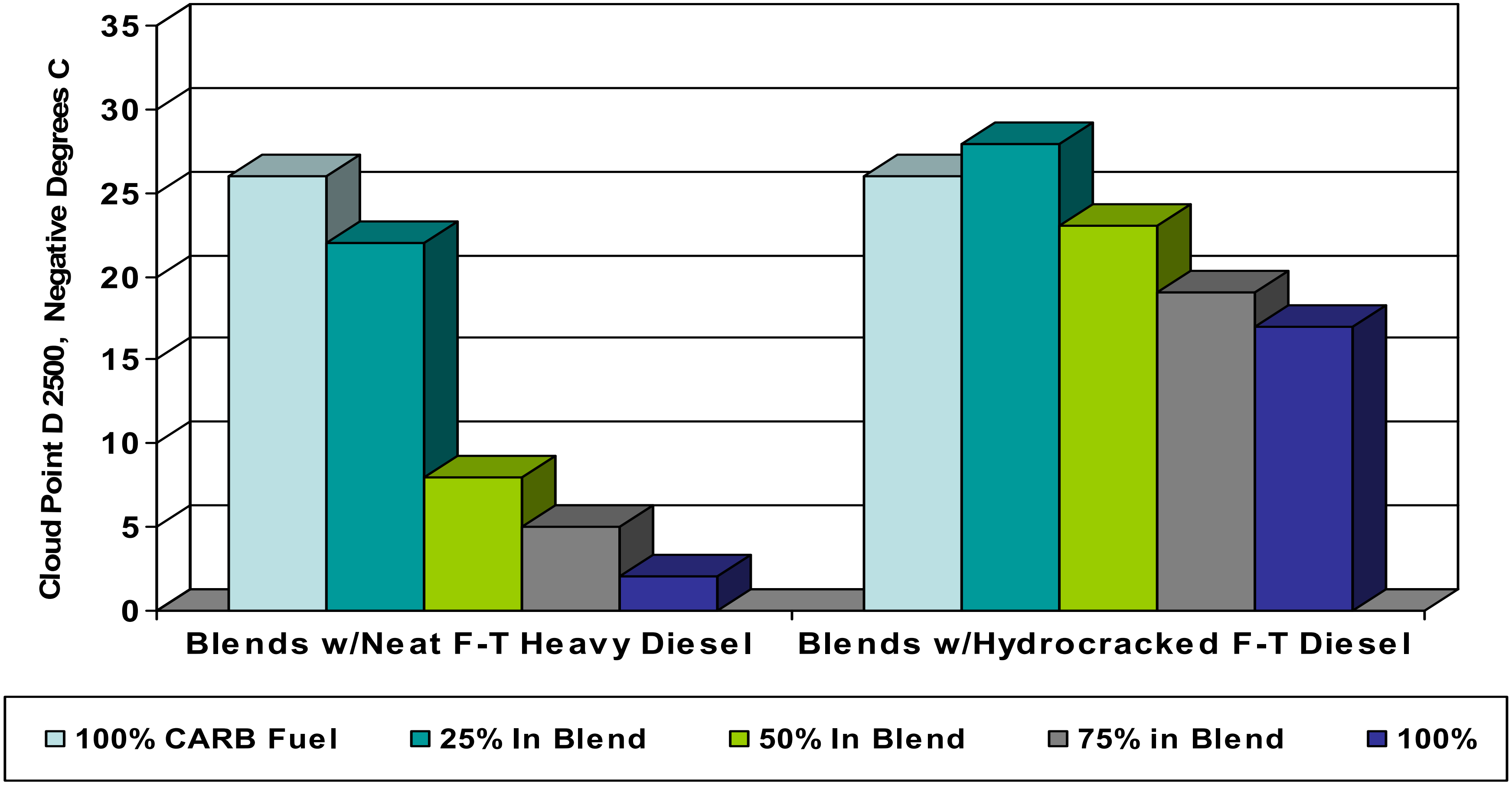
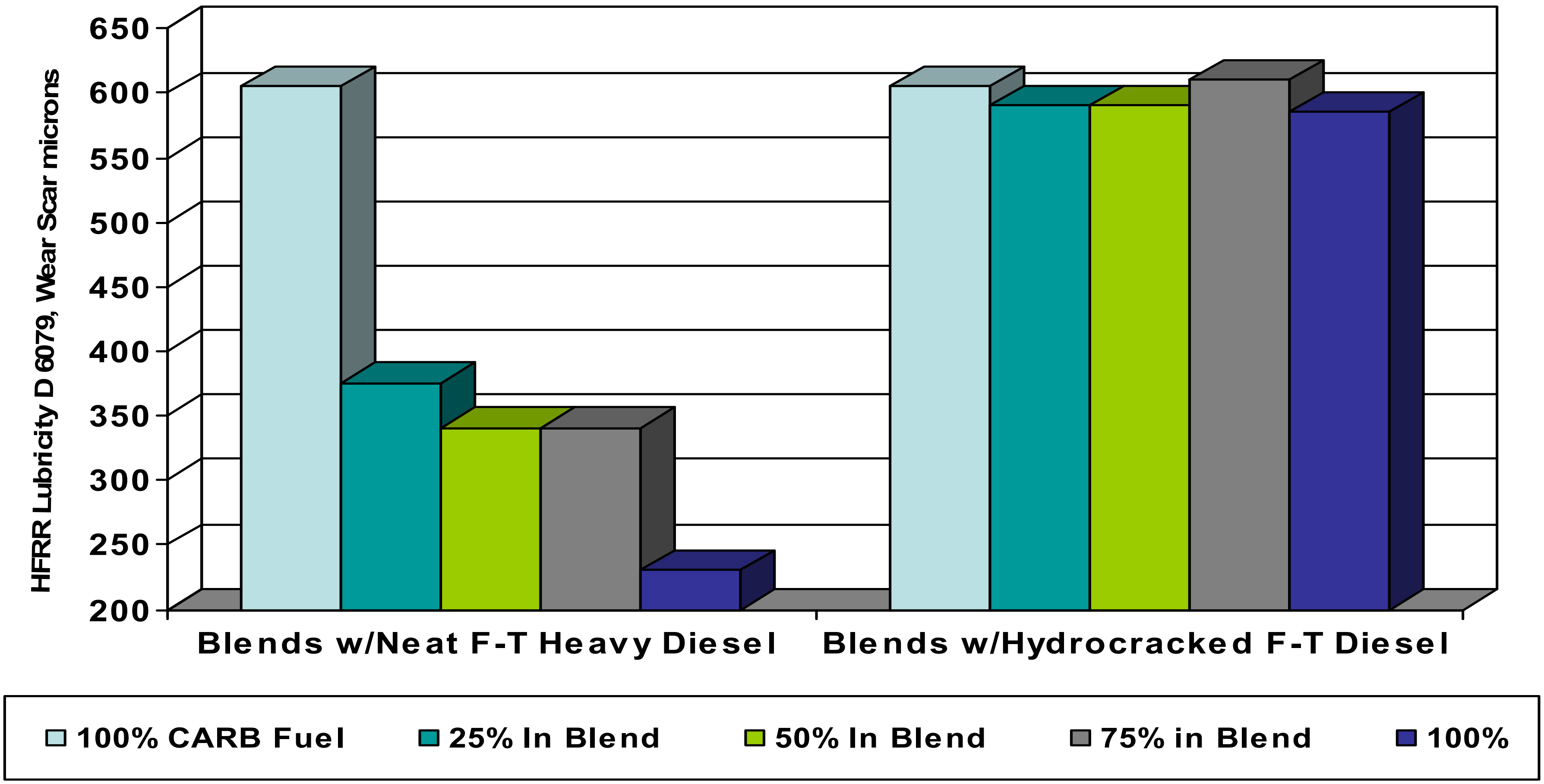


Figure 2.5.6-4 – HFRR Lubricity Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



The HFRR lubricity results indicate that the composition of the neat F-T diesel behaves similar to a chemical lubricity additive. None of the test fuel blends containing the HC F-T diesel passed the maximum HFRR wear scar width of 450 microns. It should be noted that the Tier II CARB-like diesel reference fuel component of the test fuel blends had previously failed the HFRR lubricity test specification as well.

Figure 2.5.6-5 presents the results of the blending responses on diesel fuel lubricity by the ASTM D-6078 Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE) test method of adding a neat F-T heavy diesel to a Tier II CARB Like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB Like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The SLBOCLE lubricity test applies a variable weight to the holder of a captive ball bearing as it bears upon a turning cylinder bathed in the diesel test fuel at controlled temperature. Weight is added in 100 gram increments until a scar appears on the cylinder. Diesel fuel injectors rely on the lubricating properties of the fuel for acceptable operation and service life. ASTM D-975 diesel fuel specifications do not set a limit for an acceptable SLBOCLE scuffing load, but its appendix X3.3.3 cites guidelines for acceptable service from fuels whose minimum scuffing load is 2000-2800 grams. The Engine Manufactures' Association (EMA) have adopted a more rigorous guideline. Under the EMA recommendation, a scuffing load weight of 3100 grams is needed to pass a fuel. The neat F-T heavy diesel product exhibits a passing EMA SLBOCLE scuffing load of 5250 grams, the HC F-T diesel product exhibits a failing EMA SLBOCLE scuffing load of 2350 grams and the Tier II CARB-like diesel reference fuel exhibits a failing EMA SLBOCLE scuffing of 2850. All of the test fuel blends containing the neat F-T diesel blend component passed the minimum EMA SLBOCLE scuffing load specification. The SLBOCLE lubricity results indicate that the composition of the neat F-T diesel behaves similar to a chemical lubricity additive. None of the test fuel blends containing the HC F-T diesel passed the minimum EMA SLBOCLE scuffing load specification of 3100 grams. It should be noted that the Tier II CARB-like diesel reference fuel component of the test fuel blends had previously failed the EMA SLBOCLE lubricity test specification as well.

Figure 2.5.6-6 presents the results of the blending responses on ASTM D-445 Kinematic viscosity at 313K (104°F) of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The ASTM D-445 test measures the time for a volume of fuel to flow under gravity through a rated glass capillary viscometer. The property of viscosity reflects the inner (intrinsic) resistance of a fuel to applied pressure that would result in flow. The ASTM D-975 diesel fuel specifications set an acceptable range for a Kinematic viscosity at 313K (104°F) between a minimum 1.9 centistokes to a maximum 4.1 centistokes. The neat F-T heavy diesel product exhibits a passing ASTM D-975 centistokes value of 3.14, the HC F-T diesel product exhibits a passing ASTM D-975 centistokes value of 3.73 and the Tier II CARB-like diesel reference fuel exhibits a passing ASTM D-975 centistokes value of 2.3.

Figure 2.5.6-5 – SLBOCLE Lubricity Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

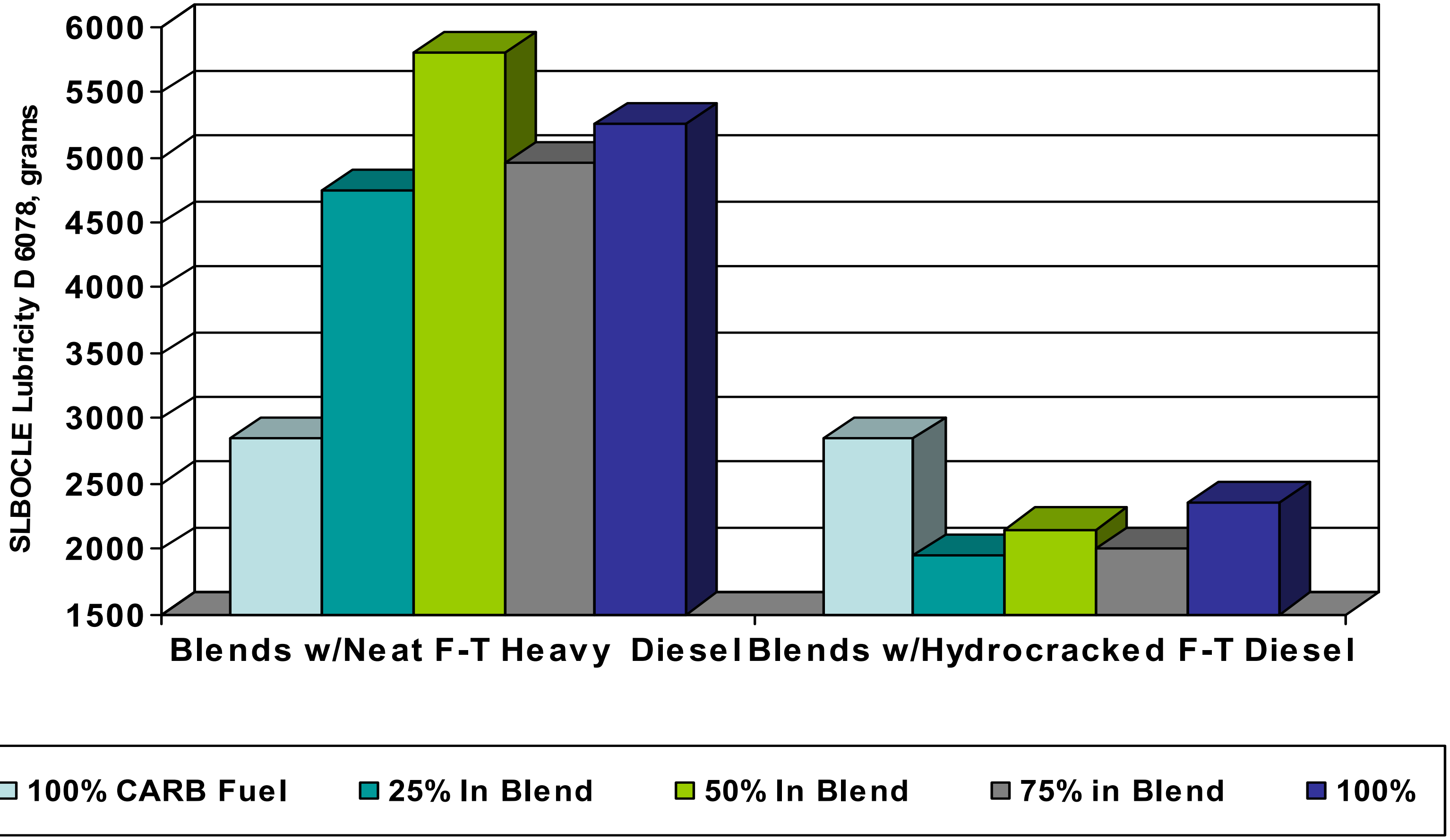
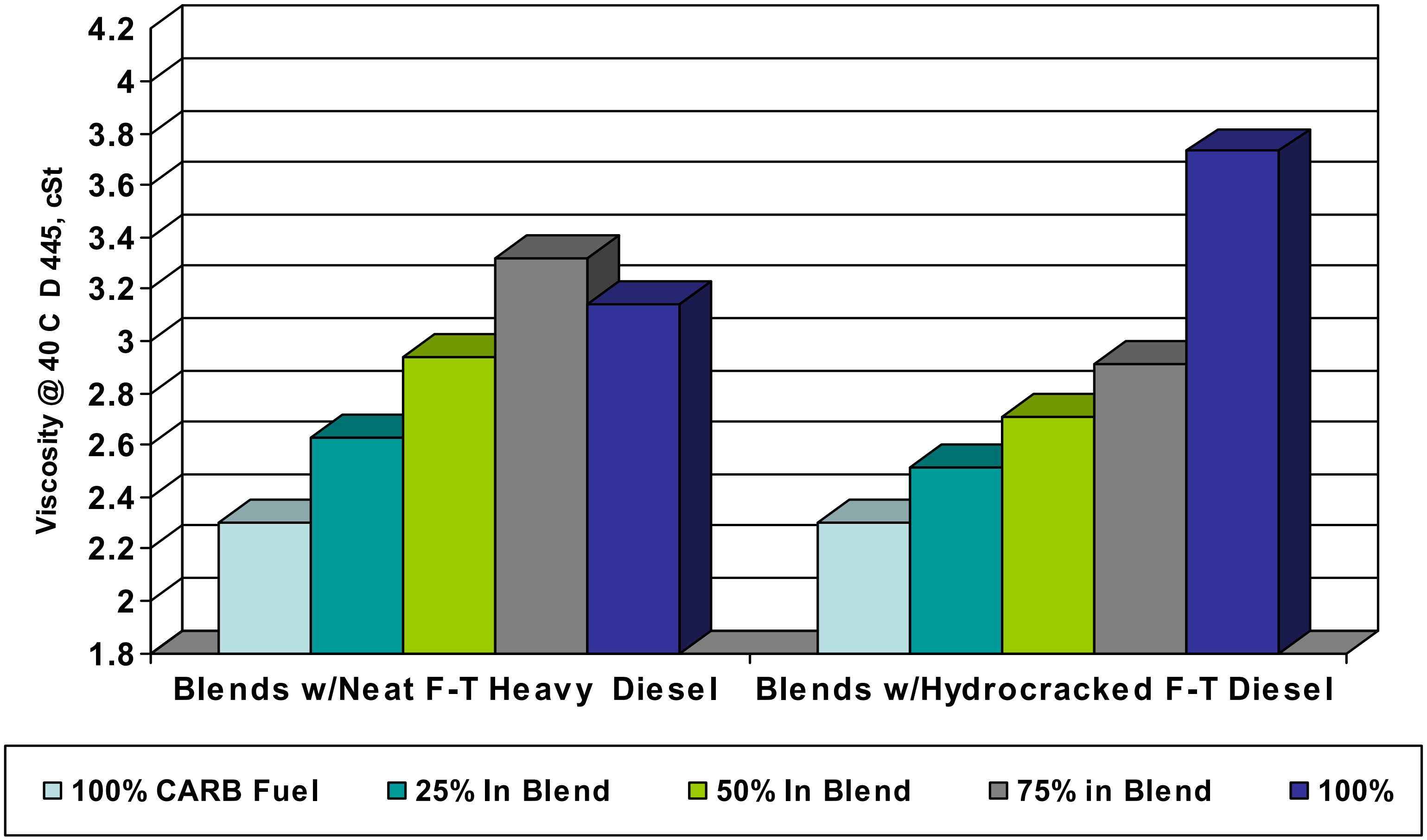


Figure 2.5.6-6 – Viscosity @ 313K (40°C) Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

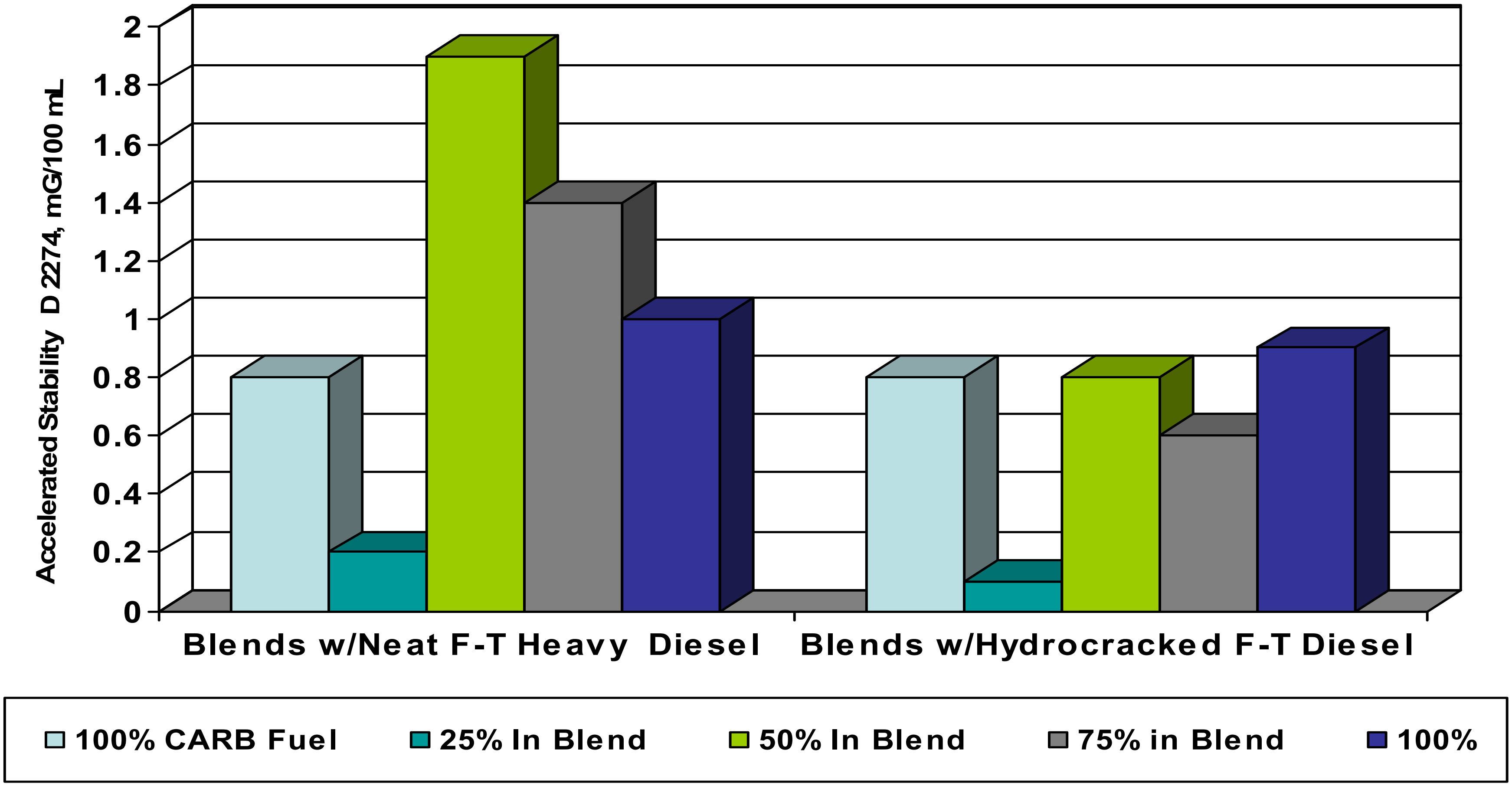


All of the test fuel blends composed of the neat F-T diesel, the HC F-T diesel, and the Tier II CARB-like diesel reference fuel had passing ASTM D-975 centistokes values for kinematic viscosity at 313K (104°F).

Figure 2.5.6-7 presents the results of the blending responses on ASTM D-2274 Oxidation Stability of Distillate Fuel Oil (Accelerated Method) of adding a neat F-T heavy diesel to a Tier II CARB-like diesel reference fuel in volumetric concentrations of 25, 50, and 75 percent and the addition of a HC F-T diesel product to a Tier II CARB-like diesel reference fuel in the same volumetric concentrations of 25, 50, and 75 percent. The ASTM D-2274 test is used internationally to monitor the tolerance of a fuel to its storage conditions. In the test, the fuel is exposed to oxygen for sixteen hours under specified conditions; afterward the oxidation products are separated by filter and measured. Reactive compounds such as the possible ethers and oxygenates that might be present in the neat F-T diesel are likely to combine with the dissolved oxygen of ASTM D-2274 much as they would combine with oxygen in the air during storage. Following activation by molecular oxygen, the reactive compounds begin to further combine with olefins and branched paraffins that may be present in the neat F-T diesel to form heavier compounds. These heavy components grow heavy enough to precipitate from the fuel during storage. Further, these polymeric impurities are susceptible to condensation reactions on hot diesel engine metal surfaces leading to varnishes and plug-causing solids. The ASTM D-975 diesel fuel specifications do not set a specification for ASTM D-2274 oxidation products measured in units of milligrams per 100 milliliter of fuel (mg/100ml). A maximum ASTM D-2274 value of 2.5 mg/100ml is under consideration for adoption by New Zealand. Fuels that exhibit unacceptably high values under D-2274 may require more severe or alternate upgrading to remove reactive compounds. The neat F-T heavy diesel product exhibited a desirable low ASTM D-2274 value of 1.0 mg/100ml, the HC F-T diesel product exhibits a desirable low ASTM D-2274 value of 0.9 mg/100ml and the Tier II CARB-like diesel reference fuel exhibits a desirable low ASTM D-2274 value of 0.8 mg/100ml. All of the test fuel blends composed of the neat F-T diesel, the HC F-T diesel, and the Tier II CARB-like diesel reference fuel had desirable low ASTM D-2274 values below the maximum 2.5 mg/100ml value under consideration for adoption by New Zealand.

The two test fuels, the neat F-T diesel and the Hydrocracker F-T diesel, and all of their test fuel blends prepared with the Tier II CARB-like diesel fuel reference fuel performed very well during testing of cetane engine, pour point, cloud point, lubricity, viscosity, and storage stability. The Subtask 2.5.6 product evaluations mitigated the technical and economic risks initially identified with direct blending of F-T diesels into transportation fuels.

Figure 2.5.6-7 – Accelerated Stability Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



Subtask 2.5.7.1.a, b, and c Naphtha Fractionation

Experimental

The risks to be mitigated by distillations conducted under Subtask 2.5.7.1.a, b, and c distillations were the maximum recoveries of an IBP-466K (380°F) neat F-T naphtha, a 466K (380°F) to 644K (700°F) neat F-T diesel, and a 644K (700°F) plus neat F-T soft wax product. These fractions meet fuel and specialty wax product boiling range and quality specifications with the minimal introduction of background contaminants from equipment and handling. A summary is presented below of the important findings which mitigated potential risks to the EECP as result of the work conducted in Subtask 2.5. 7.1a, b, and c entitled "Neat Naphtha Fractionation." The flow of work for Subtask 2.5.7.1a, b, and c is illustrated in **Schematic 2.5.7.1a, b, and c-1**. Documentation of the work and detailed discussions are included in the Subtask 2.5. 7.1a, b, and c Test Report in Appendix F to this Task 2.5 Topical Report. Subtask 2.5.7.1.a, b, and c fractionated the F-T Light Product after the presence of free water was successfully removed. As illustrated in the flow of work in **Schematic 2.5.7.1a, b, and c-1**, Subtask 2.5.7.1.a, b, and c performed the fractionation of three different sample sizes of F-T light product recovered from the LaPorte AFDU. SubTask 2.5.7.1.a fractionated approximately 322 gallons (1219 liters) of F-T Light Product collected in a commercial ISOtainer vessel receiver at the LaPorte AFDU to maximize the recovery of a IBP-466K (380°F) neat F-T naphtha, a 466K (380°F) to 644K (700°F) neat F-T diesel, and a 644K (700°F) plus neat F-T soft wax product. SubTask 2.5.7.1.b and c fractionated approximately 227 liters (60 gallons) of F-T light product collected in two 208 liter (55 gallon) drums from the drain of an overhead product vessel receiver on the LaPorte AFDU to maximize the recovery of a IBP-466K (380°F) neat F-T naphtha, a 466K (380°F) to 644K (700°F) neat F-T diesel, and a 644K (700°F) plus neat F-T soft wax product.

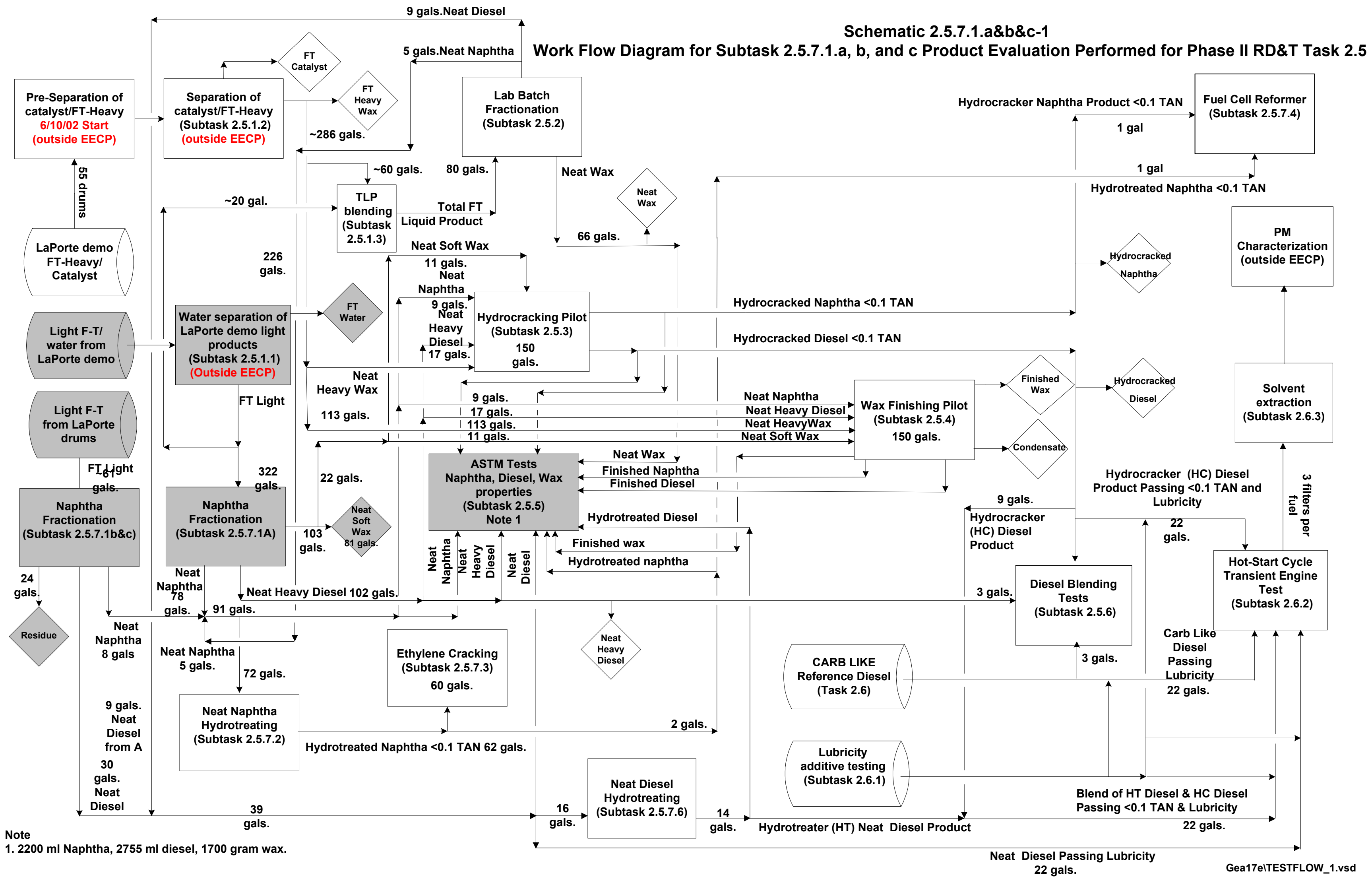
Results and Discussion

Table 2.5.7.1-1 presents the results from the inspection testing conducted on the 1016.1 kilograms (2235.5 pounds) of the composite blend prepared from the eight drums of F-T light product originally recovered from the LaPorte AFDU ISOtainer product receiver. This material was collected prior to an atmospheric batch distillation to recover a neat F-T naphtha product followed by a continuous distillation under vacuum to recover a neat F-T diesel product and a neat F-T soft wax product.

Inspection testing was done on each of the distillation products obtained from Subtask 2.5.7.1.a, 2.5.7.1.b, and 2.5.7.1.c before composite blending was done to maximize the recoveries of end-use products. **Table 2.5.7.1-2** presents the yields and quality inspection test results on the distillation products from Subtask 2.5.7.1a. Inspection testing found the neat F-T diesel product from Subtask 2.5.7.1.a to have some loss of front-end boiling range components due to operating the continuous distillation column overhead product diesel receiver too hot which resulted in the flashing and loss of diesel vapors to the vacuum system. The505K (450°F) to 644K (700°F) neat F-T heavy diesel yield and quality was considered satisfactory end-use product.

Schematic 2.5.7.1.a&b&c-1

Work Flow Diagram for Subtask 2.5.7.1.a, b, and c Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Table 2.5.7.1-1-Subtask 2.5.7.1.a F-T Light Product from ISOtainer

Composite Blend of F-T Light Product	
Inspection Tests	**Results**
Gravity,	
API	43.4
Specific	0.8090
Sulfur, ppmw	0.14
Nitrogen, ppmw	16.4
Aromatics, wt%	Not detected
Karl Fisher Water, wt%	0.22
D2887 Distillation, K (°F)	
IBP	336 (146)
5%	396 (253)
10%	422 (300)
30%	488 (419)
50%	570 (566)
70%	651 (713)
90%	699 (798)
95%	706 (811)
EP	787 (957)

Table 2.5.7.1-2-Subtask 2.5.7.1.a Batch and Continuous Distillation Product Results

SubTask 2.5.7.1a **Fraction Analyses**	**Composite Blend of F-T Light Product**	**Lab Scale Distillation Trial Naphtha Product**	**Batch Distillation Naphtha Product Composite**	**Lab Scale Distillation Trial Diesel Product**	**Continuous Distillation Diesel Product Composite**	**Lab Scale Distillation Trial Soft Wax Product**	**Continuous Distillation Soft Wax Product Composite**
API Gravity	43.4	53.2	54.8	43.6	40.8	37.7	36.7
Specific Gravity	0.8090	0.7661	0.7595	0.8081	0.8212	0.8363	0.8413
Fraction, wt% basis Feed		23.7	22.1	41.8	30.7[1]	33.2	32.2
Karl Fischer Water, wt%	0.22	0.40	0.23	na	Na	Na	Na
Nitrogen, Other ppmw	16.35	1.471		7.067		42.07	
Nitrogen, Chemiluminescene, ppmw			<1		9.9		39.7
Sulfur, Chemiluminescene, ppmw			2		2.4		11.4
Sulfur, Dohrmann, ppmw	<1			<1			
Sulfur, Antek, ppmw				<1		1.2	
Sulfur, Other, ppmw		<6.0		<6.0		<6.0	
Aromatics, wt%			None detected		None detected		None detected
D2887/D86/D1160, K (°F)	D2887	D2887/D86	D2887/D86	D2887/D86	D2887/D86	D2887/D1160	D2887/D1160
IBP	336 (146)	86 (303) /162	131 (328) /172	371(461) /424	402(479)/491	679(632) /747	641(611) /641
5	253 (396)	193(362) /232	201(367) /244	401(478) /448	452(506) /510	715(652) /755	701(645) /733
10	300 (422)	204(369) /250	209(371) /257	419(488) /456	482(523) /519	734(663) /760	729(660) /750
20	369 (460)	254(396) /262	254(396) /270	454(507) /471	519(544) /533	767(681) /771	768(682) /764
30	419 (488)	275(408) /277	285(414) /283	488(526) /492	549(560) /549	784(691) /778	785(691) /778
40	487 (526)	300(422) /287	300(422) /295	520(544) /514	577(576) /565	793(696) /784	794(696) /786
50	566 (570)	304(424) /299	305(425) /306	552(562) /537	603(590) /581	799(699) /787	800(700) /788
60	642 (612)	333(440) /309	340(444) /317	593(585) /563	629(605) /597	805(702) /793	806(703) /794
70	713 (651)	344(446) /320	343(446) /328	625(602) /588	653(618) /612	813(707) /809	813(707) /801
80	782 (690)	349(449) /331	366(459) /339	652(617) /609	675(630) /628	834(719) /870	827(715) /810
90	798 (699)	382(467) /346	382(467) /352	677(631) /630	699(644) /647	912(762) /937	907(759) /880
95	811 (706)	384(469) /355	385(469) /362	694(641) /643	717(654) /664	1003(812) /----	983(801) /-----
EP	957 (787)	434(496) /375	540(555) /382	724(657) /656	781(689) /682	1240(944) /----	1269(960) /953
ICP Metals, ppmw							
Iron (FE)	16.6						125

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[1] Weight percent low by approximately 12% due to front-end of diesel lost during processing

The neat F-T heavy diesel was a feed component in a ratio-of-production feed blend representing the LaPorte AFDU F-T light product and F-T heavy product streams. **Table 2.5.7.1-3** presents the results of the inspection testing done on the Subtask 2.5.7.1.a neat F-T heavy diesel product. The 505K (450°F) to 644K (700°F) neat F-T heavy diesel product was designated as an acceptable end-use product. The neat F-T heavy diesel was a feed component in a ratio-of-production feed blend representing the LaPorte AFDU F-T light and heavy product streams. The ratio-of-production feed blend was employed in Subtask 2.5.3 entitled "Hydrocracking Pilot" and Subtask 2.5.4 entitled "Wax Finishing Pilot." The 505K (450°F) to 644K (700°F) neat F-T heavy diesel was not used in the product evaluations conducted under Task 2.6 entitled "Fuel/Engine Performance and Emissions." The poor 83.4 weight percent (wt%) mass balance closure reported for Subtask 2.5.7.1.a was the result of the lost of neat F-T light diesel product that falls outside desired performance standards.

Subtask 2.5.7.1.b and Subtask 2.5.7.1.c each fractionated the contents of a partial filled 55-gallon drum receiver from the drains of a LaPorte AFDU overhead product receiver to maximize the recoveries of neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products. The drums of F-T light product were designated as Drum One for Subtask 2.5.7.1.b and Drum Two for Subtask 2.5.7.1.c. **Table 2.5.7.1-4** and **Table 2.5.7.1-5** present the results of the inspection testing conducted on the F-T light product from Drum One and Drum Two of the LaPorte AFDU after the free water was removed, but prior to distillation.

Inspection testing was done on each of the distillation products obtained from Subtask 2.5.7.1.a-c before composite blending was done to maximize the recoveries of end-use products. The 466K (380°F) to 644K (700°F) neat F-T diesel product from Subtask 2.5.7.1.b and c is designated as end-use product for the Task 2.6 product evaluations. **Table 2.5.7.1-6** presents the results of the product yields and quality inspection tests performed on the IBP to 466K (380°F) neat F-T naphtha product, the 466K (380°F) to 644K (700°F) neat F-T diesel product, and on the644K (700°F) plus neat F-T soft wax products obtained on the composite products from the three batch distillation runs performed on the F-T light product from Subtask 2.5.7.1b Drum One. The mass balance closure of the 99.7 weight percent for Subtask 2.5.7.1.b was within acceptable standards and is an indication of maximum recovery of products. **Table 2.5.7.1-7** below presents the results of the product yields and quality inspection tests performed on the IBP to 466K (380°F) neat F-T naphtha product, the 466K (380°F) to 644K (700°F) neat F-T diesel product, and on the 644K (700°F) plus neat F-T soft wax products obtained on the composite products from the four batch distillations performed on the F-T light product from Subtask 2.5.7.1.c Drum Two after free water and particulate removal. The Subtask 2.5.7.1.c results on the naphtha, diesel, and soft wax products obtained from the distillation of the F-T light product from Drum Two are in close agreement with the previously reported Subtask 2.5.7.1.b results on the naphtha, diesel, and soft wax products obtained from the distillation of the F-T light product from Drum One. The Subtask 2.5.7.1.c product yields and quality are acceptable for end-product use in Task 2.5 and Task 2.6 product evaluations. The mass balance closure of 99.6 wt% for Subtask 2.5.7.1.c was within acceptable standards.

Table 2.5.7.1-3 – Subtask 2.5.7.1.a Continuous Distillation Heavy Diesel Test Results

SubTask 2.5.7.1a Inspection Tests	**Continuous Distillation of F-T Light Product Neat F-T Heavy Diesel Product Composite**
API Gravity	40.8
Specific Gravity	0.8212
Nitrogen, ppmw	9.9
Sulfur, ppmw	2.4
Aromatics, wt%	None detected
D2887/D86, °F (K)	D2887/D86
IBP	402(479)/491
5	452(506) /510
10	482(523) /519
30	549(560) /549
50	603(590) /581
70	653(618) /612
90	699(644) /647
95	717(654) /664
EP	781(689) /682

Table 2.5.7.1-4 – Subtask 2.5.7.1.b F-T Light Product from Drum One Test Results

Subtask 2.5.7.1.b F-T Light Product from Drum One Inspection Tests	
Gravity, API	41.2
Gravity, Specific	0.8193
Karl Fisher Water, wt%	0.46
Nitrogen, ppmw	7
Sulfur, ppmw	1.5
Aromatics, wt%	Not detected
D2887 Simulated Distillation, °F (K)	
IBP	206 (370)
5%	297 (420)
10%	342 (445)
30%	494 (530)
50%	628 (604)
70%	785 (691)
90%	819 (710)
95%	902 (756)
EP	1229 (938)

Table 2.5.7.1-5 – Subtask 2.5.7.1.c F-T Light Product from Drum Two Test Results

Subtask 2.5.7.1.c F-T Light Product from Drum Two Inspection Tests	
Gravity, API	42.2
Gravity, Specific	0.8146
Karl Fisher Water, wt%	0.46
Nitrogen, ppmw	8.3
Sulfur, ppmw	<1
Aromatics, wt%	Non detected

Table 2.5.7.1-6- Subtask 2.5.7.1.b Batch Distillation Product Results

Task 2.5.7.1.b F-T Light Product from Drum One after water and particulate removal	Batch Distillations Composite of Naphtha Products	Batch Distillations Composite of Diesel Products	Batch Distillations Composite of Soft-Wax Products
Gravity, API	55.2	43.7	38.3
Gravity, Specific	0.7579	0.8076	0.8333
Yield, wt%	12.4	45.1	42.2
Karl Fisher water, wt%	0.9	No test	No test
Sulfur, ppmw	<1	1.3	4.1
Nitrogen, ppmw	1.0	2	18
Aromatics, wt%	Not detected	Not detected	Not detected
D2887/D86/D1160, °F (K)	D2887/D86	D2887/D86	D2887/D1160
IBP	134(330) / 189	341(445) / 426	672(629) / 403
5%	201(367) / 245	384(469) / 447	724(657) / 696
10%	232(384) / 257	417(487) / 454	749(671) / 766
30%	284(413) / 281	489(527) / 498	789(694) / 779
50%	305(425) / 302	558(565) / 543	800(700) / 791
70%	343(446) / 322	618(599) / 585	814(707) / 803
90%	380(466) / 348	675(630) / 631	920(766) / 866
95%	384(469) / 360	695(641) / 652	1028(826) / 905
EP	453(507) / 374	745(669) / 663	1220(933) / 932

Table 2.5.7.1-7 – Subtask 2.5.7.1.c Batch Distillation Product Test Results

Task 2.5.7.1.c F-T Light Product from Drum Two after water and particulate removal	Batch Distillations Composite of Naphtha Products	Batch Distillations Composite of Diesel Products	Batch Distillations Composite of Soft-Wax Products
Gravity, API	54.7	43.7	37.1
Gravity, Specific	0.7599	0.8076	0.8393
Yield, wt%	12.6	49.7	37.3
Karl Fisher water, wt%	3.97	No test	No test
Sulfur, ppmw	<1	<1	<2
Nitrogen, ppmw	<1	2	22
Aromatics, wt%	Not detected	Not detected	Not detected
D2887/D86/D1160, °F (K)	D2887/D86	D2887/D86	D2887/D1160
IBP	155(341) / 202	343(446) / 423	680(633) / 747
5%	202(367) / 261	384(469) / 444	715(652) / 755
10%	242(390) / 271	417(487) / 454	736(664) / 761
30%	297(420) / 292	488(526) / 494	786(692) / 778
50%	318(432) / 311	550(561) / 539	801(700) / 790
70%	343(446) / 329	611(595) / 580	816(709) / 805
90%	381(467) / 353	672(629) / 622	939(777) / 897
95%	385(469) / 364	691(639) / 640	1040(833) / 953
EP	455(508) / 385	734(663) / 656	1215(930) / 1023

The Subtask 2.5.7.1.b and c IBP to 466K (380°F) neat F-T naphtha and 466K (380°F) to 644K(700°F) neat F-T diesel products for Task 2.5 and Task 2.6 product evaluations were tested and approved prior to blending with the neat F-T naphtha and neat F-T diesel products from Subtask 2.5.2 entitled "Lab Batch Fractionation." The IBP to 466K (380°F) neat F-T naphtha product composite blend from Subtask 2.5.7.1.a, b, and c and Subtask 2.5.2 was the designated end-use product for Task 2.5 product evaluations. **Table 2.5.7.1-8** presents the inspection test results of the IBP to 466K (380°F) neat F-T naphtha products in the composite blend that were used for Task 2.5 product evaluations. The neat F-T naphtha was a feed component in a ratio-of-production feed blend representing the LaPorte AFDU F-T light product and F-T heavy product streams. The ratio-of-production feed blend was employed in to Subtask 2.5.3 entitled "Hydrocracking Pilot" and Subtask 2.5.4 entitled "Wax Finishing Pilot."

The 466K (380°F) to 644K (700°F) neat F-T diesel product composite blend from Subtask 2.5.7.1.b and c and Subtask 2.5.2 distillations was the designated end-use product for Task 2.6 product evaluations. **Table 2.5.7.1-9** presents the results of the inspection tests performed on the 466K (380°F) to 644K (700°F) neat F-T diesel products in the composite blend for use in Task 2.5 and Task 2.6 product evaluations. The composite blend of Subtask 2.5.7.1.b and c and Subtask 2.5.2 466K (380°F) to 644K (700°F) neat F-T diesel distillation products took two routes for Task 2.6 product evaluations. A designated quantity of the combined blend of Subtask 2.5.2 and Subtask 2.5.7.1.b and c neat F-T diesel overhead distillation products were used directly in product evaluations conducted under Subtask 2.6.1 entitled "Lubricity Additive Testing." These products were used to measure the lubricity property of the neat F-T diesel and determine the need for treatment with a commercial additive to pass lubricity. A Subtask 2.6.1 neat F-T diesel product passing lubricity qualified for product evaluation in Subtask 2.6.2 entitled "Hot-Start Cycle Transient Engine Test" and in Subtask 2.6.3 entitled "Solvent Extraction of Particulate Matter." A second designated quantity of the composite blend of Subtask 2.5.7.1.b and c and Subtask 2.5.2 466K (380°F) to 644K (700°F) neat F-T diesel overhead distillation products under went product evaluation in Subtask 2.5.7.6 entitled "Neat Diesel Hydrotreating."

Inspection testing found the neat soft-wax product from Subtask 2.5.7.1.b and Subtask 2.5.7.1.c. to be contaminated with a high concentration of iron solids (>2000 ppmw). The two Subtask 2.5.7.1.b and c neat soft wax products found to be contaminated with high solids levels were discarded. The neat F-T soft-wax product from Subtask 2.5.7.1.a is the designated end-use product for Task 2.5 product evaluations. **Table 2.5.7.1-10** presents the results of the inspection testing performed on the Subtask 2.5.7.1.a neat F-T soft-wax product. The neat F-T soft-wax was a feed component in a ratio-of-production feed blend representing the LaPorte AFDU F-T light product and F-T Heavy Product streams. The ratio-of-production feed blend was employed in Subtask 2.5.3 entitled "Hydrocracking Pilot" and to Subtask 2.5.4 entitled "Wax Finishing Pilot."

Table 2.5.7.1-8				
Inspection Tests on Neat F-T Naphtha Products Task 2.5.2 and Subtask 2.5.7.1a, b, and c Distillation Products Blending for End-use Product for Task Sub 2.5.7.2 Neat F-T Naphtha Hydrotreating				
Subtask	**2.5.2**	**2.5.7.1.a**	**2.5.7.1.b**	**2.5.7.1.c**
Product Identification	**Naphtha IBP-380°F IBP- 466K**	**Naphtha IBP-380°F IBP- 466K**	**Naphtha IBP-380°F IBP- 466K**	**Naphtha IBP-380°F IBP- 466K**
Analyses				
Gravity, API	**57.1**	**55**	**55.2**	**54.7**
Specific Gravity	**0.7503**	**0.7587**	**0.7579**	**0.7599**
Sulfur, ppmw	**<6**	**2.1**	**0.6**	**0.3**
Nitrogen, ppmw	**2.5**	**1**	**1**	**0.6**

Table 2.5.7.1-9

Inspection Tests on Neat F-T Diesel Products
Task 2.5.2 and Subtask 2.5.7.1a, b, and c Distillation Products

Blending for End-use Product for Task Sub 2.5.7.6 Neat F-T Diesel Hydrotreating

Subtask	**2.5.2**	**2.5.7.1.b**	**2.5.7.1.c**
Product Identification	**Diesel 466K-644K (380°F-700°F)**	**Diesel 466K-644K (380°F-700°F)**	**Diesel 466K-644K (380°F-700°F)**
Analyses			
Gravity, API	**43.5**	**43.7**	**43.7**
Specific Gravity	**0.8086**	**0.8076**	**0. 8076**
Sulfur, ppmw	**<6**	**1.3**	**<1**
Nitrogen, ppmw	**11**	**2**	**2**

Table 2.5.7.1-10- Subtask 2.5.7.1.a Continuous Distillation Soft-Wax Test Results

SubTask 2.5.7.1a Inspection Testing	**Continuous Distillation of F-T Light Product Neat F-T Soft Wax Product Composite**
API Gravity	36.7
Specific Gravity	0.8413
Fraction, wt% basis Feed	32.2
Nitrogen, ppmw	39.7
Sulfur, ppmw	11.4
Aromatics, wt%	None detected
D2887/D86/D1160, °F (K)	D2887/D1160
IBP	641(611) /641
5	701(645) /733
10	729(660) /750
30	785(691) /778
50	800(700) /788
70	813(707) /801
90	907(759) /880
95	983(801) /-----
EP	1269(960) /953
ICP Metals, ppmw Iron (Fe)	125

Major results of the naphtha fractionation tests include:

1. The distillation of a three different sample sizes representing the LaPorte AFDU F-T Light Product was successfully completed under Subtask 2.5.7.1.b and c on the two, 208 liter (55-gallon) drum samples and resulted in the maximum recovery of neat F-T naphtha product, neat F-T diesel, and neat F-T soft-wax products for Task 2.5 and Task 2.6 product evaluations. Subtask 2.5.7.1.b and c distillation products met necessary fuel and specialty wax product boiling range and quality specifications with the minimal introduction of background contaminants from equipment and handling.

2. The atmospheric batch distillation of the 1219 liters (322 gallons) representing the LaPorte AFDU F-T light product collected in a commercial ISOtainer product receiver to recover a IBP-466K (380°F) neat F-T naphtha was successfully completed under Subtask 2.5.7.1.a and resulted in the maximum recovery of neat F-T naphtha product for Task 2.5 product evaluations. The neat F-T naphtha product met the necessary boiling range and quality specifications with the minimal introduction of background contaminants from equipment and handling.

3. The continuous distillation under vacuum of the 466K (380°F) plus atmospheric distillation bottoms to recovery a 466K (380°F) to 644K (700°F) neat F-T diesel product and a 644K (700°F) plus neat F-T soft-wax product encountered problems which resulted in the loss of front-end boiling components of the neat F-T diesel. The resulting 505K (450°F) to 644K (700°F) neat F-T heavy diesel product was deemed suitable for Task 2.5 product evaluations but was not used in Task 2.6 product evaluations.

4. Work conducted under Subtask 2.5.7.1.a resulted in the maximum recovery of neat F-T soft-wax product for Task 2.5 product evaluations. Under Subtask 2.5.7.1.a, a neat F-T soft-wax product met necessary boiling range and quality specifications with the minimal introduction of background contaminants from equipment and handling.

Subtask 2.5.7.2 Neat Naphtha Hydrotreating

Experimental

A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating." The flow of work for Subtask 2.5.7.2 is illustrated in **Schematic 2.5.7.2-1**. Documentation of the work and detailed discussions are included in the Subtask 2.5.7.2 Test Report in Appendix G of this Topical. The composition and type of hydrotreating catalyst used and the specific operating parameters employed in the Subtask 2.5.7.2 product evaluation are proprietary technology licensor information and are not disclosed herein. Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating" will mitigate the technical risk identified as being low associated with the removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T naphtha product. Removed of these precursors is required to generate end-use products of acceptable quality to carry out ethylene cracking for chemicals production and for hydrogen fuel generation from a fuel cell reformer.

Feed Composition

The IBP to 466K (380°F) neat F-T naphtha feed for Subtask 2.5.7.2 is a composite blend of the IBP to 466K (380°F) naphtha distillation products from Subtask 2.5.2 entitled "Lab Batch Fractionation" and Subtask 2.5.7.1a, b, and c entitled "Naphtha Fractionation." A summary of the distillation results for Subtask 2.5.2 and Subtask 2.5.7.1.a, b, and c are presented in sections of this report. A Subtask 2.5.2 Test Report is included as Appendix A in this Topical Report. A Subtask 2.5.7.1a, b, and c Test Report is included as Appendix F of this Topical Report. **Table 2.5.7.2-1** presents the results of the inspection testing carried out on the feed to Subtask 2.5.7.2.

Equipment

ChevronTexaco TEMA performed Pilot Plant Test 34-91 for the F-T naphtha hydrotreating test. **Figure 2.5.7.2-1** presents the schematic diagram of the pilot plant used for the Subtask 2.5.7.2 hydrotreating test. The naphtha feed combined with the make-up hydrogen and recycle gas is fed to the hydrotreating reactors. The two hydrotreating reactors are in series. The reactor effluent is separated into liquid and vapor in the high pressure separator (HPS). The liquid is then fractionated in a debutanizer where the naphtha product is collected on the bottom and the C4's and lighter go overhead. The separated vapor from the HPS, composed mainly of the hydrogen, is scrubbed with water to remove the traces of ammonia that is formed from nitrogen present in the feed. The vapor is then recycled back to the reactors.

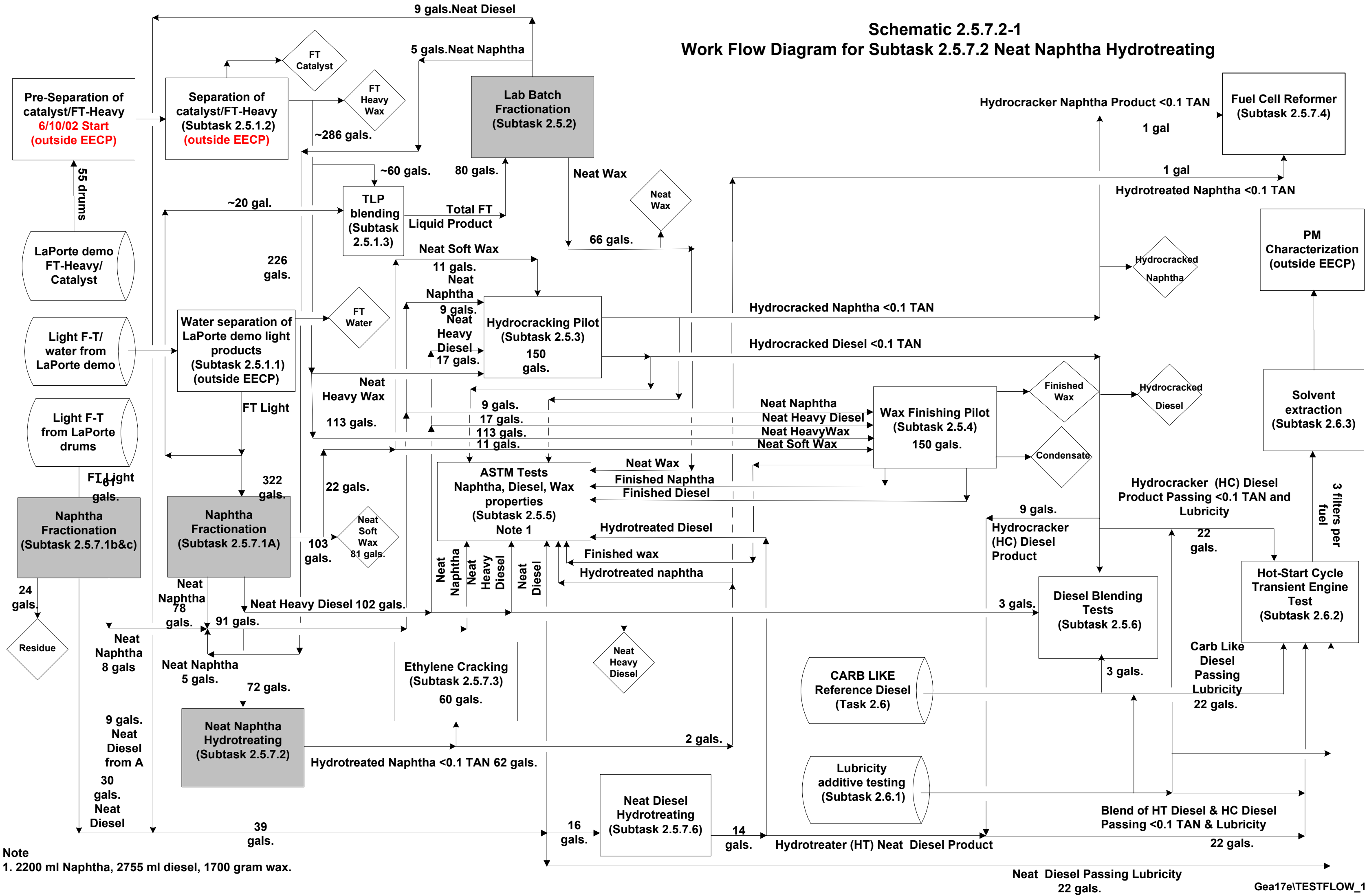
Results and Discussion

The upgrading conducted under Subtask 2.5.7.2 product evaluation entitled "Neat Naphtha Hydrotreating" was successful in the removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T naphtha. A TAN specification of less than 0.1 milligrams of potassium hydroxide (KOH) titrated per gram of hydrotreater F-T naphtha product was established for the hydrotreated F-T naphtha product. The neat F-T naphtha feed had a TAN of 13 mg KOH/g. **Table 2.5.7.2-2** presents mass balance closures, product yield slates, and qualities of the hydrotreated F-T naphtha product representative of the production test. Acceptable mass balance closures were obtained during the course of the production test. The removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T naphtha resulted in the consumption of 865 standard cubic feet of hydrogen per barrel of naphtha feed (SCFB) or 154 standard cubic meters of hydrogen per cubic meter of naphtha feed (m3/m3). Approximately 219 liters (58 gallons) of hydrotreated F-T naphtha product was generated during the hydrotreater production test. **Table 2.5.7.2.-3** presents the results on the composite blend of the hydrotreated F-T naphtha product. The TAN of the blended hydrotreated F-T naphtha product was 0.09 mg KOH/g, acceptable for Task 2.5 product evaluations.

Approximately 212 liters (56 gallons) of hydrotreated F-T naphtha was designated as end-use product for Subtask 2.5.7.3 entitled “Ethylene Cracking.” One gallon (3.785 liters) of hydrotreated F-T naphtha product was designated as end-use product for Subtask 2.5.7.4 entitled “Fuel Cell Reformer.” One gallon (3.785 liters) was designated for product inspection testing.

Subtask 2.5.7.2 product evaluation entitled “Neat Naphtha Hydrotreating” was successful in the removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T naphtha feed. The desired quantity of hydrotreated F-T naphtha was generated for end-use in the Task 2.5 product evaluations. The hydrotreated F-T naphtha performed well in Subtask 2.5.7.4 as a fuel cell reformer feed generating the highest yield of hydrogen among the four feeds tested. The hydrotreated F-T naphtha performed well in Subtask 2.5.7.3 as an ethylene cracker feed generating commercial ethylene and propylene yield predictions from the licensor model.

Schematic 2.5.7.2-1
Work Flow Diagram for Subtask 2.5.7.2 Neat Naphtha Hydrotreating



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Table 2.5.7.2-1

Naphtha Feed Properties for Hydrotreating Pilot Plant

ID		WOW9288	
Gravity, °API		54.7	
Specific Gravity		0.76	
Nitrogen	wt, ppm	1.3	
Sulfur	wt, ppm	3.3	
Oxygen By NAA	wt %	4.3	
AED Analyses			
Oxygen	wt %	not available	
Alcohol	wt %	not available	
Olefins	wt %	not available	
TAN	mg KOH / g	13	
Simulated Distillation, LV%		Temperature (K)	(°F)
	IBP	311	101
	0.5%	334	142
	5%	366	199
	10%	371	208
	30%	411	281
	50%	424	303
	70%	445	341
	90%	466	380
	95%	468	383
	99%	485	413
	EP	530	494

Figure 2.5.7.2-1
Naphtha Hydrotreating Pilot Plant Block Flow Diagram

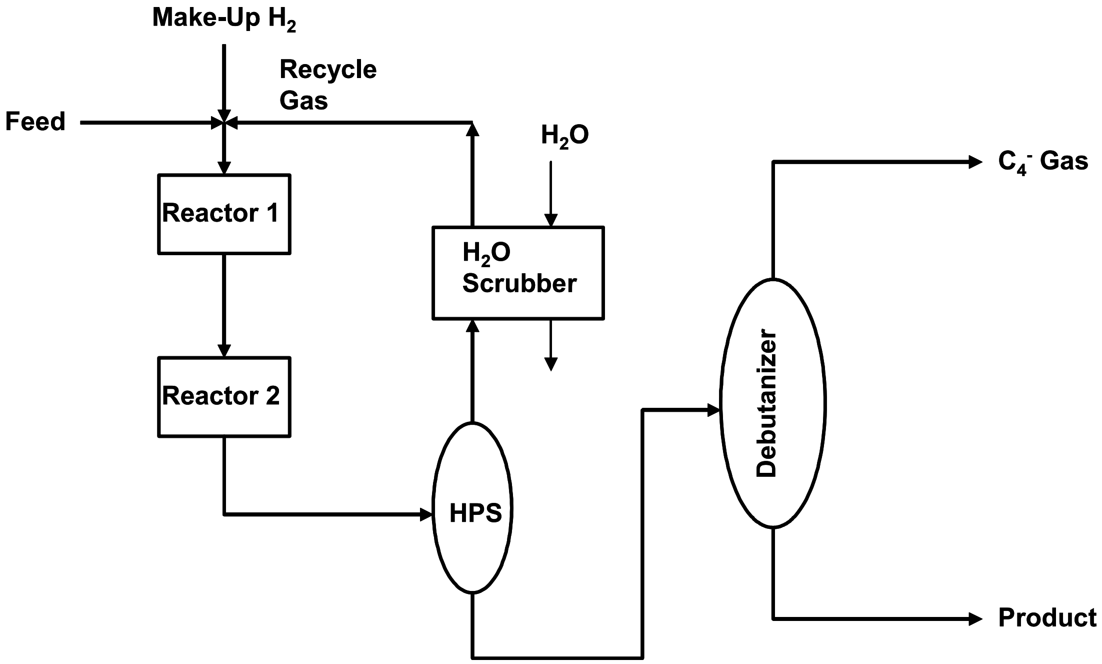


Table 2.5.7.2-2

Yields (Calculated by D2887) for Hydrotreating Naphtha

Feed	**WOW9288**				
Test Number	34-91			34-91	
Test Duration, Hours	114-126			426-438	
No Loss Prod. Yields	WT. %	VOL. %		WT. %	VOL. %
Total C4-	1.0			1.6	
Total C5+	95.9	100.8		95.3	100.4
H2 Consumption SCF/B	(sm^3/m^3)	(SCF/B)		(sm^3/m^3)	(SCF/B)
	154	865		153	861
Material Balance Closure, wt%	100			101	
Product Properties					
Specific Gravity	0.72			0.72	
Gravity, °API	64.6			64.2	
TAN, mg KOH / g	<0.05			0.07	
Simdist (D2887) (Volume %)	Temperature				
	(K)	(°F)		(K)	(°F)
St	271	28		269	25
5	332	139		329	132
10	347	165		341	155
30	399	259		398	257
50	424	303		423	302
70	447	345		446	344
90	469	384		467	382
95	470	386		469	384
99.5	479	403		478	401

Table 2.5.7.2-3

Hydrotreated Naphtha Properties

ID		WOW9307	
Gravity, °API		64.2	
Specific Gravity		0.723	
Sulfur	wt, ppm	pending	
Nitrogen	wt, ppm	0.2	
TAN	mg KOH/g	0.09	
PONA	Aromatic (vol %)	pending	
	Olefin (vol %)	2.0	
	Par/Np (vol %)	95.8	
Research Octane		<40	
Simulated Distillation	LV%	Temperature (K)	(°F)
	IBP	295	71
	0.5%	340	153
	5%	369	205
	10%	371	208
	30%	412	282
	50%	425	306
	70%	447	346
	90%	469	384
	95%	476	398
	99%	486	415
D86 Distillation	IBP	340	152
	5%	377	219
	10%	390	242
	30%	413	284
	50%	428	311
	70%	441	334
	90%	452	355
	95%	459	366
	EP	479	403

Subtask 2.5.7.3 Ethylene Cracking

Experimental

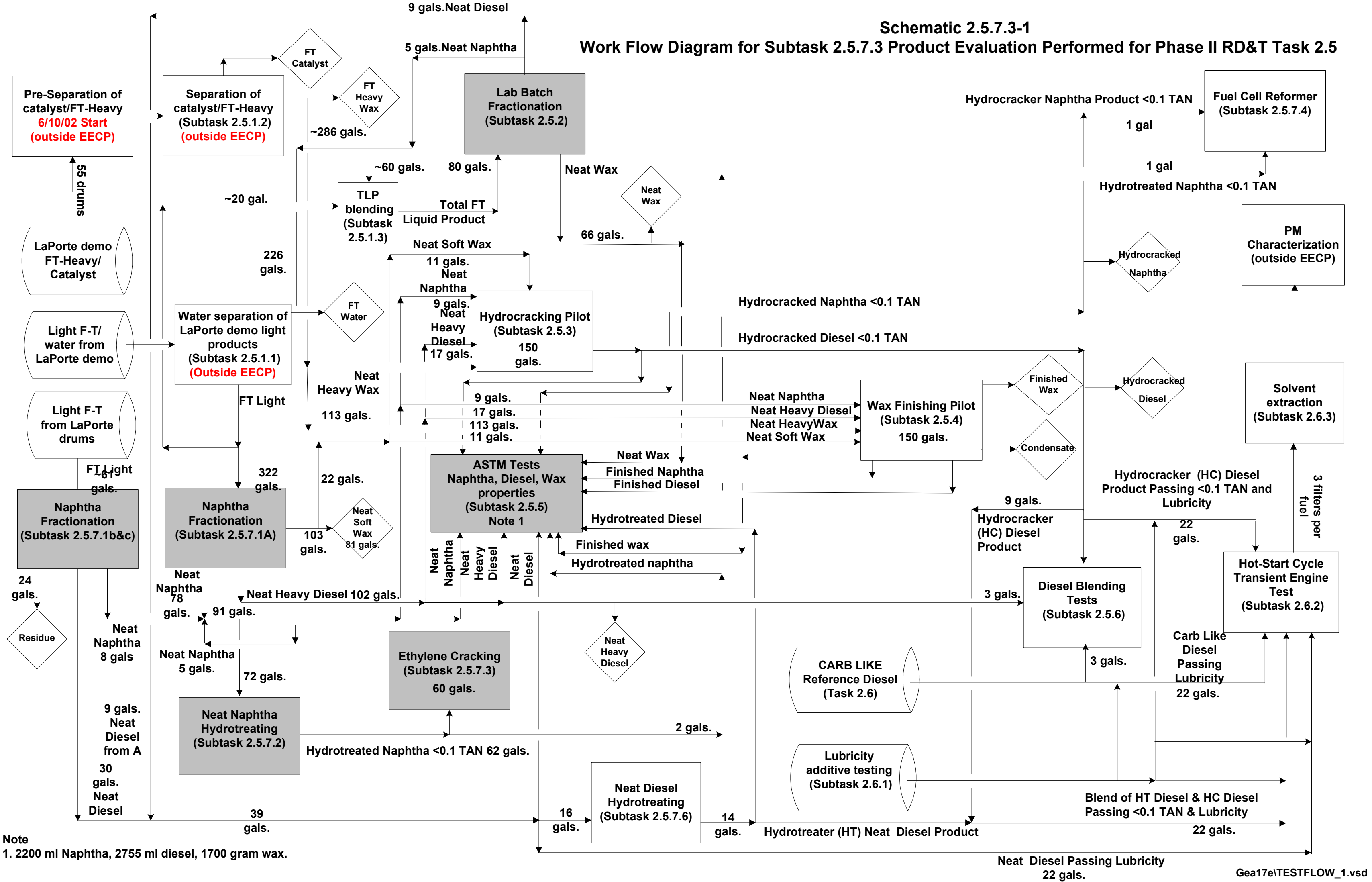
The potential technical and economic risks to the EECP from Task 2.5 can be mitigated by demonstrating that the F-T naphtha end-use product derived from the upgrading of the total F-T liquid product can meet or exceed current specifications for the manufacture of ethylene and propylene chemicals. A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.7.3 entitled "Ethylene Cracking." The flow of work for Subtask 2.5.7.3 is illustrated in **Schematic 2.5.7.3-1**. Documentation of the work and detailed discussions are included in the Subtask 2.5.7.3 Test Report in Appendix H to this Topical Report. The F-T synthesis total liquid product contains a very small yield (< 5 wt %) of neat F-T naphtha that, after hydrotreating to remove thermal or ethylene cracker feed coke precursors, is a very desirable highly paraffinic petrochemical feed stock component. Ethylene is a basic building block for many organic chemicals, plastics, and synthetic fibers. Ethylene is a very important petrochemical due to its production volume, number of product derivatives, and market value.

As illustrated in **Schematic 2.5.7.3-1** Subtask 2.5.2 entitled "Lab Batch Fractionation" and Subtask 2.5.7.1.a, b, and c entitled "Naphtha Fractionation" were successfully carried out to maximize the yield and quality of a full range IBP- 466K (380°F) neat F-T naphtha present in the LaPorte AFDU F-T light product. Work conducted under Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating" successfully removed the risks of coke precursors in the ethylene cracker feed present in the form of reactive olefins, oxygenates, and acids in the neat F-T naphtha. Kellogg Brown & Root (KBR) predicted commercial ethylene and propylene output yields for the hydrotreated F-T naphtha feedstock from proprietary technology licensor models.

Thermal or ethylene cracking of a hydrocarbon feedstock in the presence of steam is the most dominant and universally applied process technology for ethylene production. While steam is not a reactant in the thermal cracking reaction, the presence of steam enhances product selectively to ethylene and reduces coking in commercial ethylene cracking furnaces. Industry interchanges the terms ethylene cracking, thermal cracking and steam cracking to refer to this process technology. The chemistry of the thermal or ethylene cracking reactions is complex, involving many chain reactions of decomposition, dehydrogenation, polymerization, and condensation. The complexity of thermal or ethylene cracking increases with the molecular weight of the ethylene cracking feed stock component. The complexity is the result of multiple reactions and subsequent production of numerous by-products. The cracked gas product stream is composed of mainly hydrocarbon compounds with two carbon atoms (C2's), hydrocarbon

Schematic 2.5.7.3-1

Work Flow Diagram for Subtask 2.5.7.3 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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compounds with three carbon atoms (C3's), and methane (CH_4) along with some C4's, H_2, CO, CO_2, pyrolysis naphtha, and water vapor.

Feedstock Component

Thermal or ethylene cracker distillate hydrocarbon feedstock components can be complex petroleum-based or F-T synthesis hydrocarbons. Thermal or ethylene cracker distillate hydrocarbon feeds in the naphtha boiling range are classified by the industry according to their boiling range with full range naphtha typically in the 300K-494K (80°F-430°F) range, a light naphtha feed in the 300K-422K (80°F-300°F) range and a heavy naphtha in the 422K-494K (300°F-430°F) range. The hydrotreated F-T naphtha originally distilled from the LaPorte AFDU F-T Light Product and the KBR petroleum-based reference naphtha feed would tend to fall into the heavy naphtha feed classification.

Petroleum-based naphtha is a complex mixture of paraffins, isoparaffins, naphthenes, and aromatics. In general for petroleum-based naphtha feedstocks, as the API gravity decreases or the specific gravity increases, the paraffin content decreases. F-T naphthas are a mixture of normal paraffins, straight chain alpha olefins, isoparaffins, with some oxygenates and acids. The aromatic contents are very low or not detected. Hydrogenation converts the straight chain alpha olefins to normal paraffins while removing oxygenates and acids. The group properties of these hydrocarbon type compounds have an important effect on the yield slate of the cracked gas products. Normal paraffins produce more ethylene, while isoparaffins generate more propylene. An ethylene cracker feedstock component with high naphthenes content combined with low paraffins content favors the generation of hydrocarbon compounds with four carbon atoms (C_4) containing butadiene. An ethylene cracker feedstock component with a high naphthenic content generates more aromatics during high severity cracking. Therefore, the choice of thermal or ethylene cracker naphtha feedstock and the selection of operating conditions is based on the types of by-products desired by the customer.

Reaction Mechanism

The reaction mechanism in thermal or ethylene cracking is believed to involve the formation of free radicals and chain reactions. In cracking ethane, for example, a C_2H_6 molecule is split into two CH_3 free radicals first:

$$C_2H_6 \rightarrow CH_3\cdot + CH_3\cdot$$

These free radicals then proceed to interact with other molecules and cause a chain of reactions:

$$\begin{aligned}
CH_3\cdot + C_2H_6 &\rightarrow CH_4 + C_2H_5\cdot \\
C_2H_5\cdot &\rightarrow C_2H_4 + H \\
H\cdot + C_2H_6 &\rightarrow H_2 + C_2H_5\cdot \\
H\cdot + H\cdot &\rightarrow H_2 \\
H\cdot + CH_3\cdot &\rightarrow CH_4 \\
H\cdot + C_2H_5\cdot &\rightarrow C_2H_6 \\
C_2H_5\cdot + CH_3\cdot &\rightarrow C_3H_8 \\
C_2H_5\cdot + C_2H_5\cdot &\rightarrow C_4H_{10}
\end{aligned}$$

The reactants are more complex for distillate hydrocarbon feedstocks but the reaction mechanism is believed to be the same. From a process point of view, ethane gives the highest yield of ethylene and the least amount of by-products, whereas at the cracking of distillate hydrocarbon feedstocks results in a lower yield of ethylene and a higher yield of by-products.

Kinetics

The generally accepted kinetic model for hydrocarbon cracking to produce ethylene is based on the observation that the disappearance of a simple compound is unimolecular and first-order, and can be represented by the following equation:

$$K_t\Theta = 2.3 \log (1/(1-\alpha))$$

Where: K_t = reaction rate constant, sec^{-1}, at temperature t
Θ = time, sec
α = fractional disappearance of the feedstock.

In a complex feedstock system, such as naphtha, the reaction rate constants for use in predicting conversions or yields are based on the properties of the component groups, such as normal paraffins, branched paraffins, alkyl cyclohexanes, and alkyl cyclopentanes. Prediction methods for product yields based on kinetic models are considered the proprietary intellectual property of technology licensors and are not discussed. Designers of ethylene plants rely heavily on pilot plant data to update, as needed their commercial yield prediction models on new feedstocks such as F-T naphthas where commercial operating experience is not available.

Cracking Severity

Cracking severity is a loosely defined term to describe the combined effects of time, temperature, pressure, and time-temperature history of feedstock on product yields. For the purpose of the Subtask 2.5.7.4 entitled “Ethylene Cracking,” cracking severity is defined by KBR in terms of a propylene/ethylene product ratio.

Cracking severity has a very important effect on product yields. Those products whose yields increase with cracking severity are hydrogen, ethylene, methane, aromatic tar, benzene, toluene, xylene (BTX aromatics), and cyclopentadiene. Those products whose yields decrease with cracking severity are propylene, isobutylene, isoprene, naphthalenes, and pyrolysis gasoline. The butadiene content may increase or decrease, depending on cracking severity.

Residence Time

Although residence time is one of the major process variables in the cracking process, a precise definition does not appear to exist, largely because of variations in choosing the terminal conditions.

Residence time is related to other process variables by the following equation:

Equation Number 1: Residence time = VcMP/GRT

Where:
Vc = volume of cracking coil
M = molecular weight of hydrocarbon and steam
P = total pressure
G = total mass flow in coil per unit time
T = absolute temperature
R = universal gas constant

Since system pressure, temperature, and molecular weight change continuously throughout a cracking coil, Equation Number One must be integrated to obtain the real residence time. Sometimes, however, an average gas density, d_{avg}, based on the coil inlet conditions in the radiant zone and coil outlet conditions, is used in calculating the residence time.

Equation Number 2: Residence time = d_{avg} (L/G)

Where:
d_{avg} = average gas density, lb/cu ft
L = coil length, ft
G = fluid mass flow, lb/square feet/second

Residence time has also been expressed as the interval between the time when the feed stock in the radiant section of the thermal or ethylene cracker coil is above a certain temperature, e.g., 922K (1200°F) and the time it arrives at the thermal or ethylene cracker furnace outlet, or as the interval of time in the radiant coil starting when 1 percent of the distillate feedstock is cracked and ending when the distillate feed stock reaches the thermal or ethylene cracker furnace outlet.

Effect of Operating Variables on Yields

Factors affecting product yields are type of feedstock, hydrocarbon partial pressure, cracking severity, and residence time. As mentioned earlier, feedstock selection is usually based on availability and cost. Hydrocarbon partial pressure depends on the total system pressure and the steam dilution ratio. Generally, the higher the steam dilution ratio, the lower the hydrocarbon partial pressure and the higher the ethylene yield. In commercial operating applications, steam dilution ratios are limited by economic considerations to narrow ranges, and are varied with the type of feedstock. The composition of the feedstock has an important effect on yields of ethylene and co-products. For naphtha feedstocks, the hydrogen content has a very important effect on ethylene yield. In general, ethylene yield increases with the hydrogen content of the naphtha feed stock.

Feedstock Hydrogen Content

ASTM Test Method D 3343 provides a method for calculating the hydrogen content of a light distillate feedstock. The equation for estimating hydrogen content inputs an average boiling point range, the API gravity, and the aromatic content of the feedstock. The aromatic contents of F-T naphthas are quite low, therefore the selection of the boiling range and corresponding API gravity of the thermal or ethylene cracker feed are significant parameters in the determination of its hydrogen content. The boiling range of the F-T naphtha and its corresponding API gravity are significant factors which determine its hydrogen content.

D 3343 Equation: %Hydrogen = + (0.06317*Gravity)
- (0.041089*Aromatics)
+ (0.000072135*Aromatics*D86 Distillation Average)
+ (0.00005684*Gravity*D86 Distillation Average)
- (0.000496*Gravity*Aromatics)
+10.56

Where:
Gravity = gravity, API
Aromatics = volume percent aromatics
D86 Distillation Average = average of 10, 50, and 90 percent distillation data, °F

Other operating process parameters that have significant impacts on yields are residence time, cracking severity, and hydrocarbon partial pressure. For a given cracking severity, ethylene yield increases rapidly as residence time decreases. Ethylene yield, at a constant cracking severity, can be increased by decreasing the hydrocarbon partial pressure at the thermal or ethylene cracker furnace outlet. The hydrocarbon partial pressure is the difference between the total pressure and the partial pressure of steam. From a technical basis, the hydrocarbon partial pressure is the cracked gas partial pressure because of the presence of hydrogen and acid gases at the thermal or ethylene cracker furnace outlet. The industry recognizes that all cracked products are derived from the hydrocarbon feed stock; therefore the industry term hydrocarbon partial pressure is interchanged with cracked gas partial pressure. Hydrocarbon partial pressure, within commercial operating constraints, can be decreased by increasing the steam-to-feed stock dilution ratio and by decreasing the total pressure at the thermal or ethylene cracker furnace outlet.

Decoking

Carbon deposition or coking on the inner surface of the tubular coils of a commercial thermal or ethylene cracker is an unavoidable commercial operating problem in thermal cracking. Commercial cracking furnaces are generally built in multiple units. The number of cracking furnaces required for a given plant capacity depends on the composition of the feed stock and the cracking severity. Therefore, a feed stock composition exhibiting a low coking tendency is economically attractive. With short-residence-time, high severity cracking, typically one commercial operating cracking furnace can produce about 49,951,600 kg(110 million lb)/year ethylene with gas oil as the feedstock, and up to 81,646,900 (180 million lb)/year with ethane as feedstock. The ethylene yield from a naphtha feedstock would fall within this range. In addition to the operating cracking furnace in commercial service, one or two extra commercial cracking furnaces are generally provided as spares to be brought online during decoking of the cracking furnace that is being brought down for service. The optimum spare ratio is generally considered to be about 10 to 15 percent of the operating capacity. The run length for a commercial thermal or ethylene cracker furnace depends on the feedstock composition, maximum tubular coil metal temperature exposed, the tube coil diameter, and the average rise in tubular coil skin temperature per day. Mathematical models for predicting coke formation rates are the proprietary intellectual property of the technology licensors. For smaller diameter coils the commercial furnace run length is limited by the increase in pressure drop due to coke buildup, while for larger diameter coils, coil metal temperature rise is the limiting factor. A typical run length for a paraffinic petroleum-based naphtha feedstock between the need for commercial cracking furnace decoking could be 65 days.

Results and Discussion

Subtask 2.5.2 entitled “Lab Batch Fractionation” and Subtask 2.5.7.1.a, b, and c entitled “Naphtha Fractionation” were successfully carried out to maximize the yield and quality of a full range IBP- 466K (380°F) neat F-T naphtha present in the LaPorte AFDU F-T light product stream for end-use product evaluations. Work conducted under Subtask 2.5.7.2 entitled “Neat Naphtha Hydrotreating” successfully removed the risks of coke precursors in the ethylene cracker feed present in the form of reactive olefins, oxygenates, and acids in the neat F-T naphtha. The IBP- 466K (380°F) hydrotreated F-T naphtha along with a petroleum-based reference naphtha supplied by KBR and designated as Alpha-7 naphtha were each thermally cracked in a KBR pilot plant consisting of a conditioned 9.5 millimeter (3/8-inch) diameter 800H Schedule (SHC) 40 reactor for the purpose of obtaining product yields, mass balance closure, and successful unit operability. The smaller reactor was fabricated for this test program in order to achieve 24 hour operations at a 200 millisecond residence time with the limited amount of hydrotreated F-T naphtha feedstock available. KBR commercial cracking furnaces (the SCORE furnace technology design provided by KBR) are designed to operate at commercial residence times closer to 120 milliseconds. Operation at lower residence time has been shown to produce higher yields of ethylene. There was insufficient hydrotreated F-T naphtha feedstock to carry out the proposed technology licensor 24-hour test program at the lower commercial residence time. KBR predicted commercial ethylene and propylene output yields which are presented herein for the both the hydrotreated F-T naphtha feedstock and the KBR Alpha-7 petroleum-based reference naphtha feedstock from KBR proprietary technology licensor models. These models were adjusted with the pilot plant test data obtained from Subtask 2.5.7.3 entitled “Ethylene Cracking.” Prediction methods for product yields based on kinetic models are considered the proprietary intellectual property of technology licensors and are not discussed. Designers of ethylene plants rely heavily on pilot plant data to update as needed their commercial yield prediction models on new feedstocks such as F-T naphthas where commercial operating experience is limited or not available.

Feedstock Composition Results

The composition of the feedstock for thermal or ethylene cracking applications has an important effect on the yields of ethylene and co-products. Neat F-T naphtha is a mixture of normal paraffins, straight chain alpha olefins, isoparaffins, with some oxygenates and acids. Hydrogenation converts the straight chain alpha olefins to normal paraffins while removing oxygenates and acids.

The group properties of these hydrocarbon type compounds have a significant effect on the yield slate of the cracked gas products. Normal paraffins produce more ethylene, while isoparaffins generate more propylene. A thermal or ethylene cracker feedstock component with high naphthenes content combined with low paraffins content favors the generation of C_4 hydrocarbons containing butadiene. A thermal or ethylene cracker feedstock component with a high naphthenic content generates more aromatics during high severity cracking. For thermal or ethylene cracking naphtha feed stocks, the hydrogen content has a very important effect on ethylene yield. A general correlation published in the open literature relating single-pass ethylene yield with the hydrogen content of the naphtha feedstock is illustrated in **Figure 2.5.7.3-1**. In general, ethylene yield increases with the hydrogen content of the naphtha feed stock.

Table 2.5.7.3-1 presents the results of the inspection testing conducted on the hydrotreated F-T naphtha and the petroleum-based KBR reference naphtha feed designated as Alpha-7 naphtha. These two feedstocks underwent thermal cracking in the KBR pilot plant test program. Shown, in **Table 2.5.7.3-1**, only for thermal and ethylene cracking feed comparison purposes is the composition of a lighter boiling range hydrocracker F-T naphtha product from another technology licensor reported in the open literature. Thermal or ethylene cracker distillate hydrocarbon feeds in the naphtha boiling range are classified by the industry according to their boiling range with full range naphtha typically in the 300K-494K (80°F-430^{o}F) range, a light naphtha feed in the 300K-422K (80°F-300°F) range, and a heavy naphtha in the 422K-494K (300°F-430°F) range. The hydrotreated F-T naphtha distilled from the LaPorte AFDU F-T light product and the KBR petroleum based reference naphtha feed (Alpha-7 naphtha) would tend to fall into the heavy naphtha feed classification. Whereas the lighter boiling range hydrocracker F-T naphtha product from another technology licensor reported in the open literature would tend to fall in the light naphtha feed classification. **Figure 2.5.7.3-2** shows that the ASTM D-3343 hydrogen content of the hydrotreated F-T naphtha is 15.6 weight percent compared to the lower 15.2 weight percent for the KBR Alpha-7 petroleum based reference naphtha. The lower boiling range of the hydrocracker F-T naphtha product from another technology licensor reported in the open literature results in a higher 16 wt% ASTM D-3343 hydrogen content. Base on the general correlation illustrated in **Figure 2.5.7.3-1** published in the open literature relating single-pass ethylene yield with the hydrogen content of a naphtha feedstock, a delta 0.4 weight percent increase in thermal or ethylene cracking feed hydrogen content may result in a delta 3 weight percent increase in ethylene product yield. **Figure 2.5.7.3-3** shows that the hydrotreated F-T naphtha has a desirable 6 to 1 ratio of normal to isoparaffins which compose 92 weight percent of its composition. The hydrotreated F-T naphtha contains insignificant amounts of the less desired naphthenes, olefins, or aromatics. The KBR Alpha-7 naphtha has a 0.7 to 1 ratio of normal to isoparaffins which compose 72 weight percent of its composition. The KBR Alpha-7 naphtha contains 21 weight percent naphthenes and insignificant amounts of olefins and aromatics. For feed comparisons only, the lighter boiling range hydrocracker F-T naphtha product from another technology licensor reported in the open literature has a 1.2 to 1.0 ratio of normal to isoparaffins which compose 93 weight percent of its composition. Its naphthene content is 7 weight percent and contains insignificant amounts of olefins or aromatics.

Figure 2.5.7.3-1

Relationship Between Hydrogen Content of Feedstock and Single-Pass Ethylene Yield

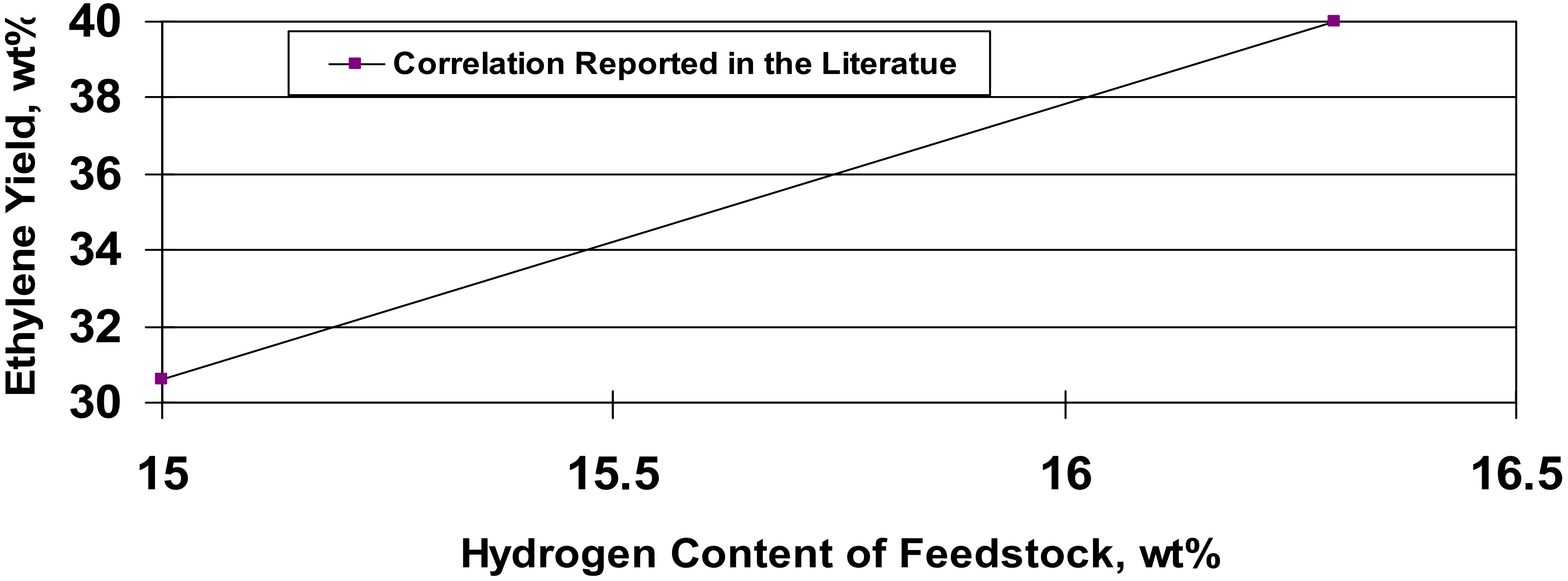


Table 2.5.7.3-1

Feed Inspection Tests on F-T Naphthas and KBR Petroleum-Based Naphtha

Properties/Feed Type	KBR Petroleum-Based Reference Naphtha Alpha-7	Hydrotreated F-T Naphtha	HC F-T Naphtha Reported in Open Literature
Density @20 ºC/68ºF (293K)	0.7406	0.7168	0.687
PIONA (wt.%)			
N-Paraffins	28.7	78.7	49.9
I-Paraffins	43.7	13.2	42.9
Olefins	0.4	0.4	0
Naphthenes	21.3	2.3	7.2
Aromatics	1.0	4.1	0
Unknown	5.0	1.3	0
Aromatics by ILT Lab	No test	None detected	No test
D86 K (°F)			
10%	365 (197)	390 (243)	327 (129)
50%	401 (262)	421 (298)	348 (167)
90%	461 (371)	453 (356)	380 (225)
ASTM D-3343 Hydrogen Content, wt%	15.2	15.6	16.0

Figure 2.5.7.3-2- Hydrogen Contents of F-T Naphthas And KBR Reference Petroleum Naphtha

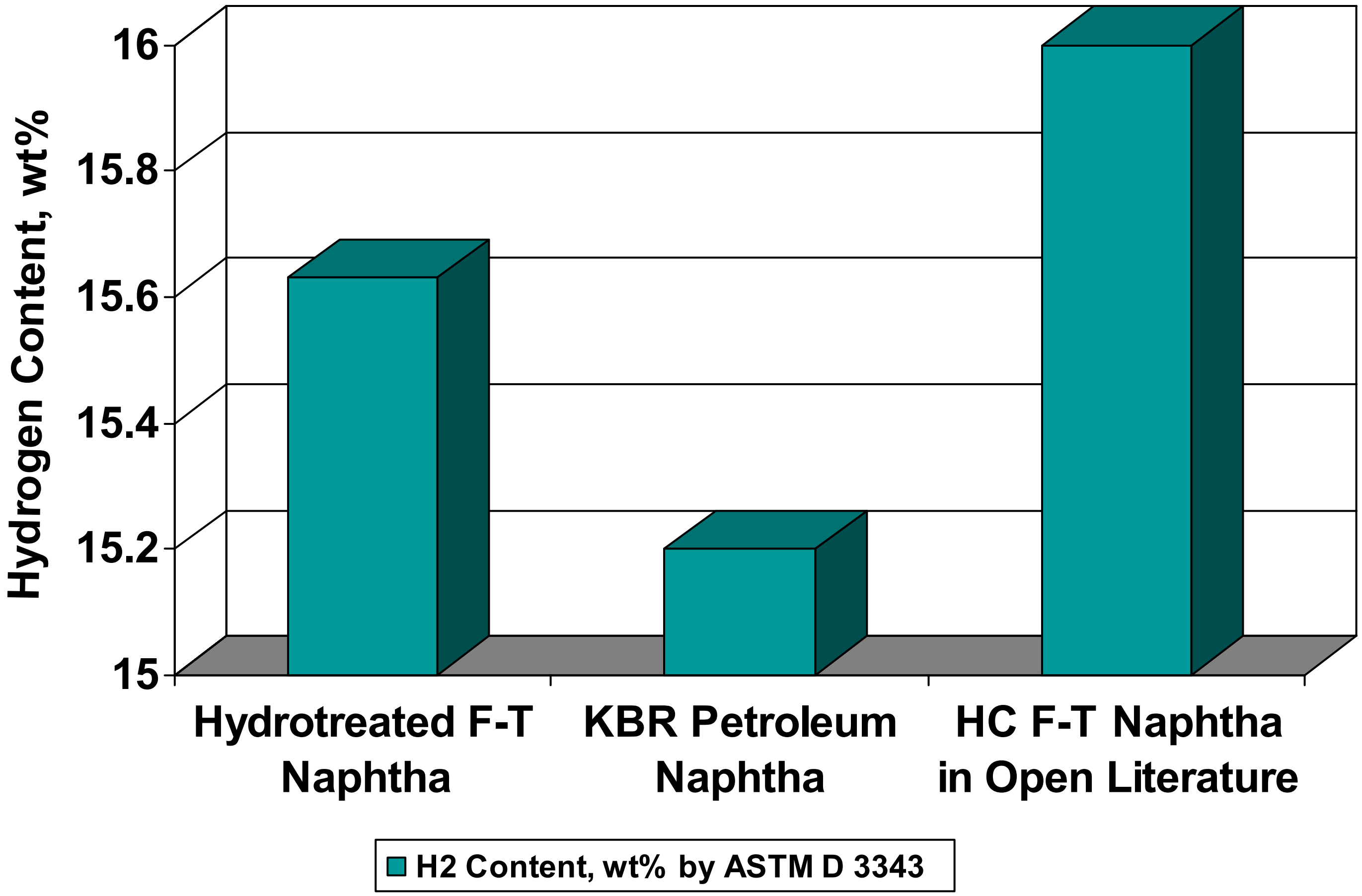
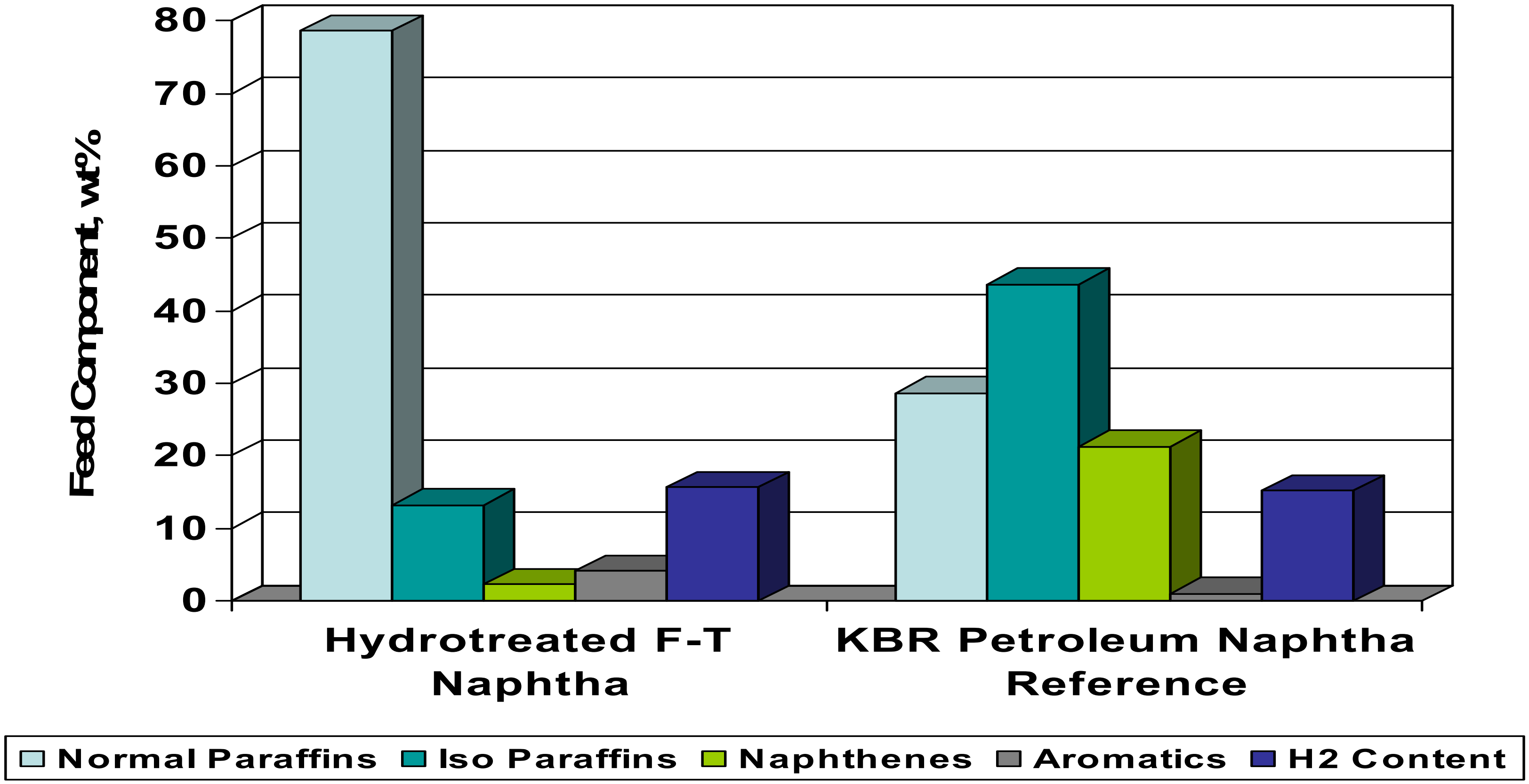


Figure 2.5.7.3-3 – Feed Inspection Tests on Hydrotreated F-T Naphtha versus KBR Petroleum Naphtha Reference



Commercial Ethylene and Propylene Yield Predictions

KBR commercial cracking furnaces (the SCORE furnace technology design provided by KBR) are designed to operate at commercial residence times closer to 120 milliseconds. Lower residence time was previously shown to produce higher yields of ethylene product. A small KBR pilot plant reactor was fabricated for the Subtask 2.5.7.3 product evaluation to achieve a 24-hour operation at a 200 millisecond residence time. These test were conducted over a range of cracking severities defined by KBR in terms of a propylene/ethylene product ratio with the limited amount of hydrotreated F-T naphtha feedstock available. There was insufficient hydrotreated F-T naphtha feedstock to carry out the proposed technology licensor 24-hour test program at the lower 120 millisecond commercial residence times. Therefore, KBR predicted commercial ethylene and propylene output yields are presented herein for the both the hydrotreated F-T naphtha feedstock and the KBR Alpha-7 petroleum-based reference naphtha feedstock from KBR proprietary technology licensor models tuned with the pilot plant test data obtained from Subtask 2.5.7.3 entitled “Ethylene Cracking.” Prediction methods for product yields based on kinetic models are considered the proprietary intellectual property of technology licensors and are not discussed in this report. Designers of thermal or ethylene cracking plants rely heavily on pilot plant data to update as needed their commercial yield prediction models on new feedstocks such as F-T naphthas where commercial operating experience is limited or not available. Documentation of the KBR thermal or ethylene cracking pilot plant test results are included in the Subtask 2.5.7.3 Test Report in Appendix H.

Figure 2.5.7.3-4 presents the results from a comparison of the predicted commercial ethylene yields over a range of cracking severities defined by KBR in terms of a propylene/ethylene product (P/E) ratio for both the hydrotreated F-T naphtha and the KBR petroleum-based reference naphtha. Those products whose yields increase with cracking severity are hydrogen, ethylene, methane, aromatic tar, benzene, toluene, xylene (BTX aromatics), and cyclopentadiene. The higher normal paraffins content and higher hydrogen content of the hydrotreated F-T naphtha feed resulted in higher ethylene product yields compared to the ethylene product yields for the KBR petroleum-based reference fuel.

Figure 2.5.7.3-5 presents the comparison of the predicted commercial propylene product yields over a range of cracking severities defined KBR in terms of a P/E ratio for both the hydrotreated F-T naphtha and the KBR petroleum-based reference naphtha. Those products whose yields decrease with cracking severity are propylene, isobutylene, isoprene, naphthalenes, and pyrolysis gasoline. The higher normal paraffins content and higher hydrogen content of the hydrotreated F-T naphtha feed resulted in higher propylene product yields compared to the propylene product yields for the KBR petroleum-based reference fuel.

Figure 2.5.7.3-4

Prediction of Commerical Ethylene Yields for Hydrotreated F-T Naphtha and KBR Petroleum Naphtha

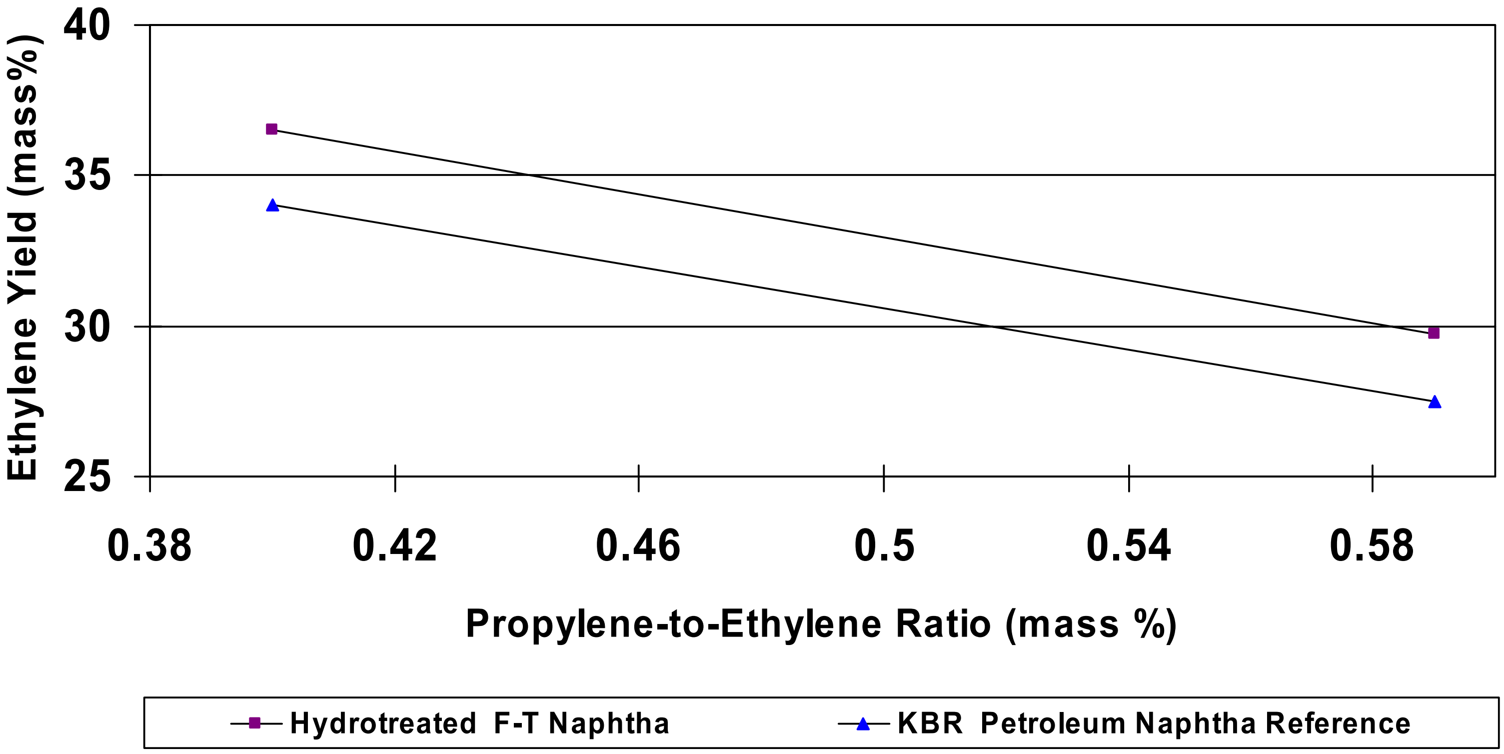
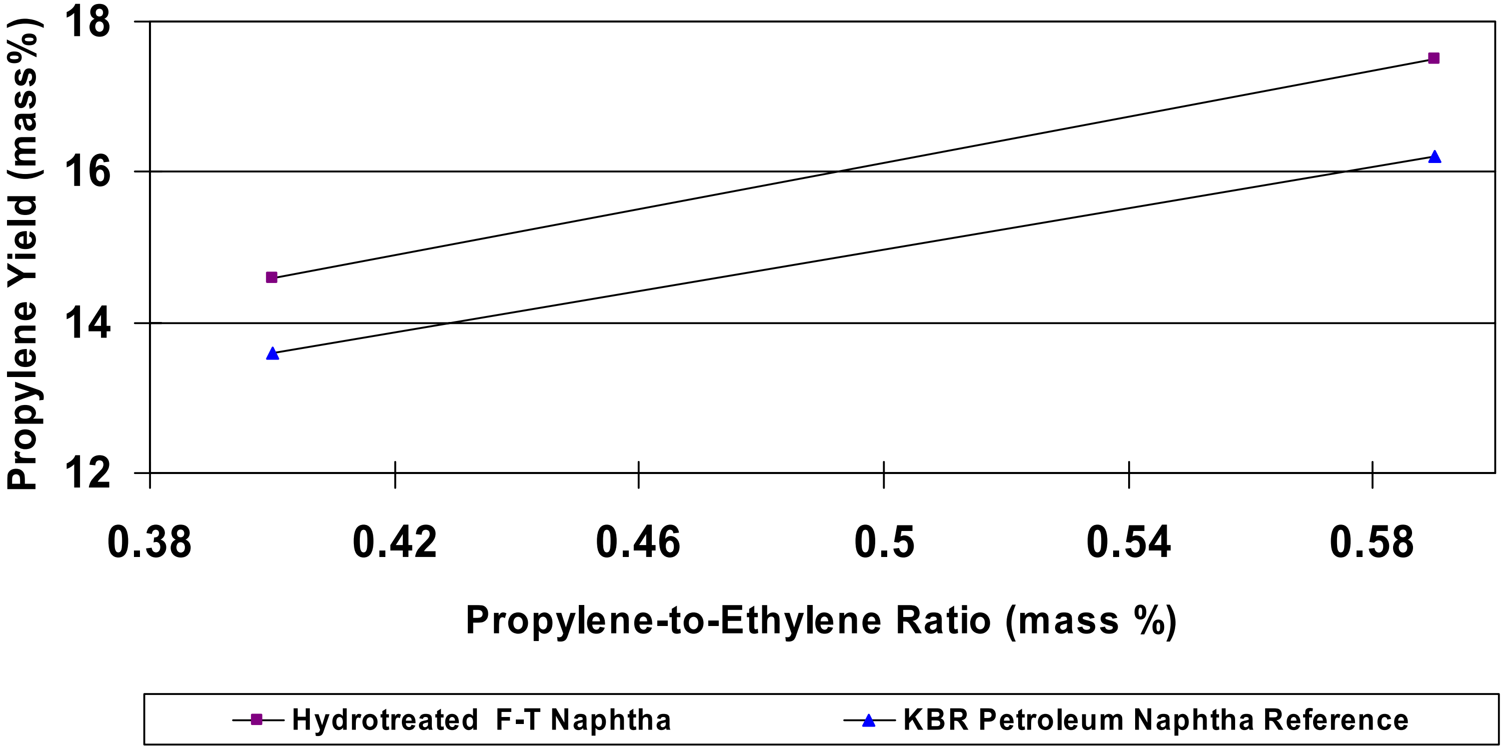


Figure 2.5.7.3- 5

Prediction of Commerical Propylene Yields for Hydrotreated F-T Naphtha and KBR Petroleum Naphtha



The two thermal or ethylene cracking feeds, the hydrotreated F-T naphtha and the KBR petroleum-based reference naphtha performed as expected at the 200 millisecond residence time and at the highest cracking severity defined by KBR in terms of a propylene to ethylene product ratio on the small pilot plant reactor fabricated for Subtask 2.5.7.3. The technology licensor, KBR, was able to predicted commercial ethylene and propylene output yields for both the hydrotreated F-T naphtha feedstock and the KBR Alpha-7 petroleum-based reference naphtha feedstock from KBR proprietary technology licensor models. The product evaluation conducted under Subtask 2.5.7.3 mitigated the technical and economic risks initially identified with the production of ethylene and propylene chemicals from an F-T naphtha product.

Subtask 2.5.7.4 Fuel Cell Reformer

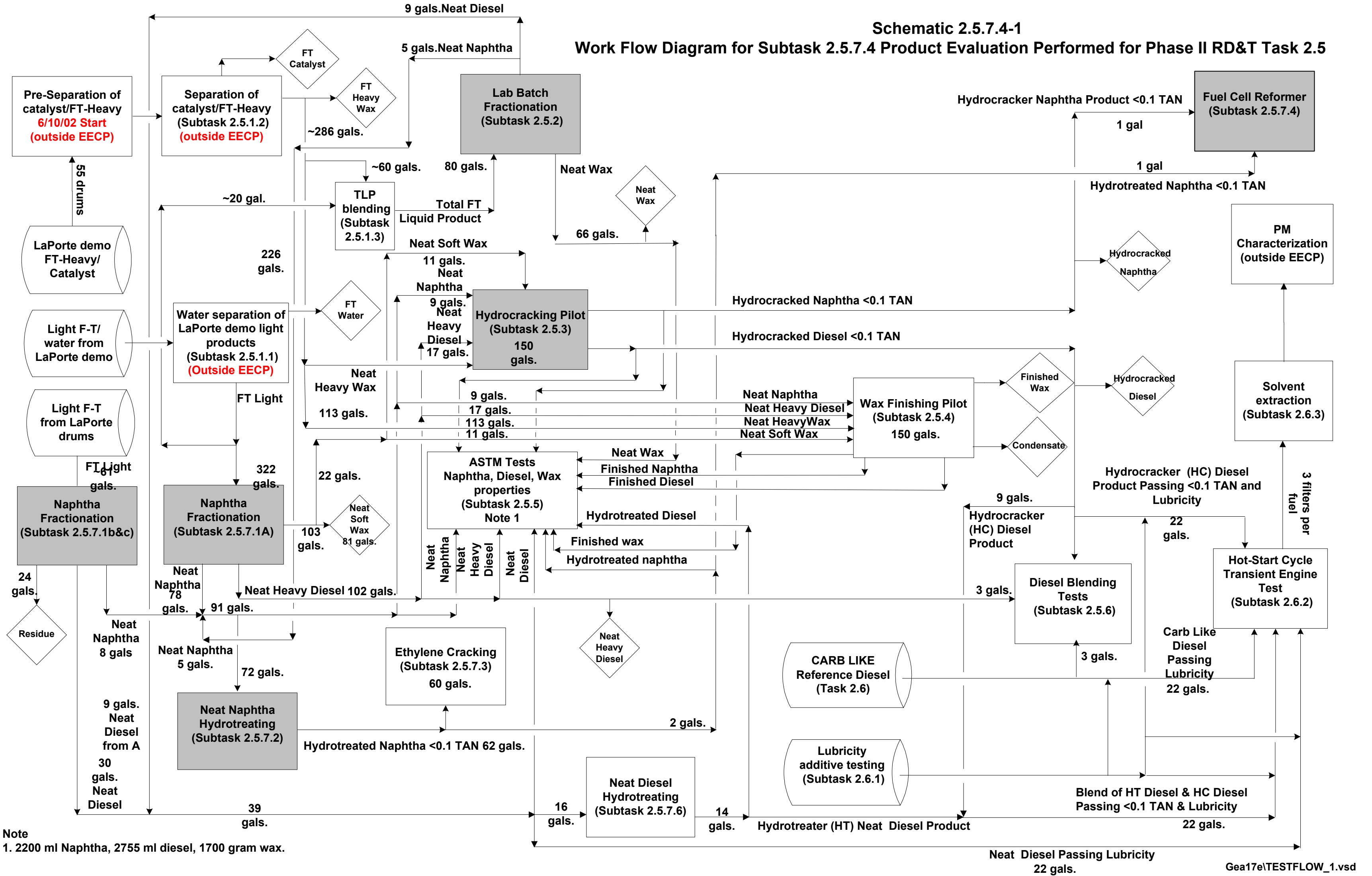
There are several technical and economic risks that need to be mitigated to determine the final product market disposition of the neat F-T naphtha product, hydrotreater F-T naphtha product, and hydrocracker F-T naphtha products. A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.7.4 entitled "Fuel Cell Reformer." The flow of work for Subtask 2.5.7.4 is illustrated in **Schematic 2.5.7.4-1**. Documentation of the work and detailed discussions included in the Subtask 2.5.7.4 Test Report in Appendix I. The LaPorte AFDU F-T light and heavy product streams contain a very small yield (< 5 wt %) of neat F-T naphtha. Subtask 2.5.2 entitled "Lab Batch Fractionation" and Subtask 2.5.7.1.a, b, and c entitled "Naphtha Fractionation" were successfully carried out to maximize the yield and quality of a full range IBP- 466K (380°F) neat F-T naphtha present in the LaPorte AFDU F-T light product stream for end-use product evaluations. Work conducted under Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating" successfully removed the risks of coke precursors in the fuel cell reformer feed present in the form of reactive olefins, oxygenates, and acids in the neat F-T naphtha. The hydrocracker F-T naphtha product from Subtask 2.5.3 showed that the maximum conversion of F-T wax to hydrocracker F-T diesel product is expected to be a very desirable highly paraffinic feed for a fuel cell reformer. The technical risk has been identified as high for use of the F-T naphthas as fuel cell reformer feeds.

Replacement for Subtask 2.5.7.5 Catalytic Reforming Pilot

The reactive olefins, oxygenates, and acids present in the neat F-T naphtha product have been identified as a stability risk for direct blending into gasoline transportation fuel. The octane of the neat F-T naphtha product is low and will lower the refinery gasoline pool octane and is therefore identified as an economic risk to the EECP at a time when gasoline octane pool losses are occurring as a result of legislated reductions in benzene content and caps on aromatic and olefin gasoline contents. The removal of the reactive olefins and oxygenates along with some acids by hydrotreating will further lower the octane value of the neat F-T naphtha product. Viable economical end-use product markets for the neat F-T naphtha require hydrotreating and stabilization of the neat F-T naphtha product. Therefore, no product evaluations were carried out under Task 2.5 to address the risks of direct blending of the low octane neat F-T naphtha product directly into the gasoline pool.

The original Phase II RD&T Plan envisioned the use of a designated quantity of the hydrotreated F-T naphtha product from Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating" as feed for a Subtask 2.5.7.5 entitled "Catalytic Reforming Pilot." Work under Subtask 2.5.7.2 will not be carried out. The reasons for the decision not to go forward with Subtask 2.5.7.5 are presented herein. Meetings were held between the EECP Team and several licensors of Catalytic Reforming Unit (CRU) technologies that were considered to be potentially adaptable for upgrading the low octane of the hydrotreated F-T naphtha into a high octane CRU reformate product for addition to transportation gasoline fuel. Based upon a review of inspection tests on the F-T naphtha product streams, the technology licensors contacted

Schematic 2.5.7.4-1
Work Flow Diagram for Subtask 2.5.7.4 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Updated: June 08 , 2003

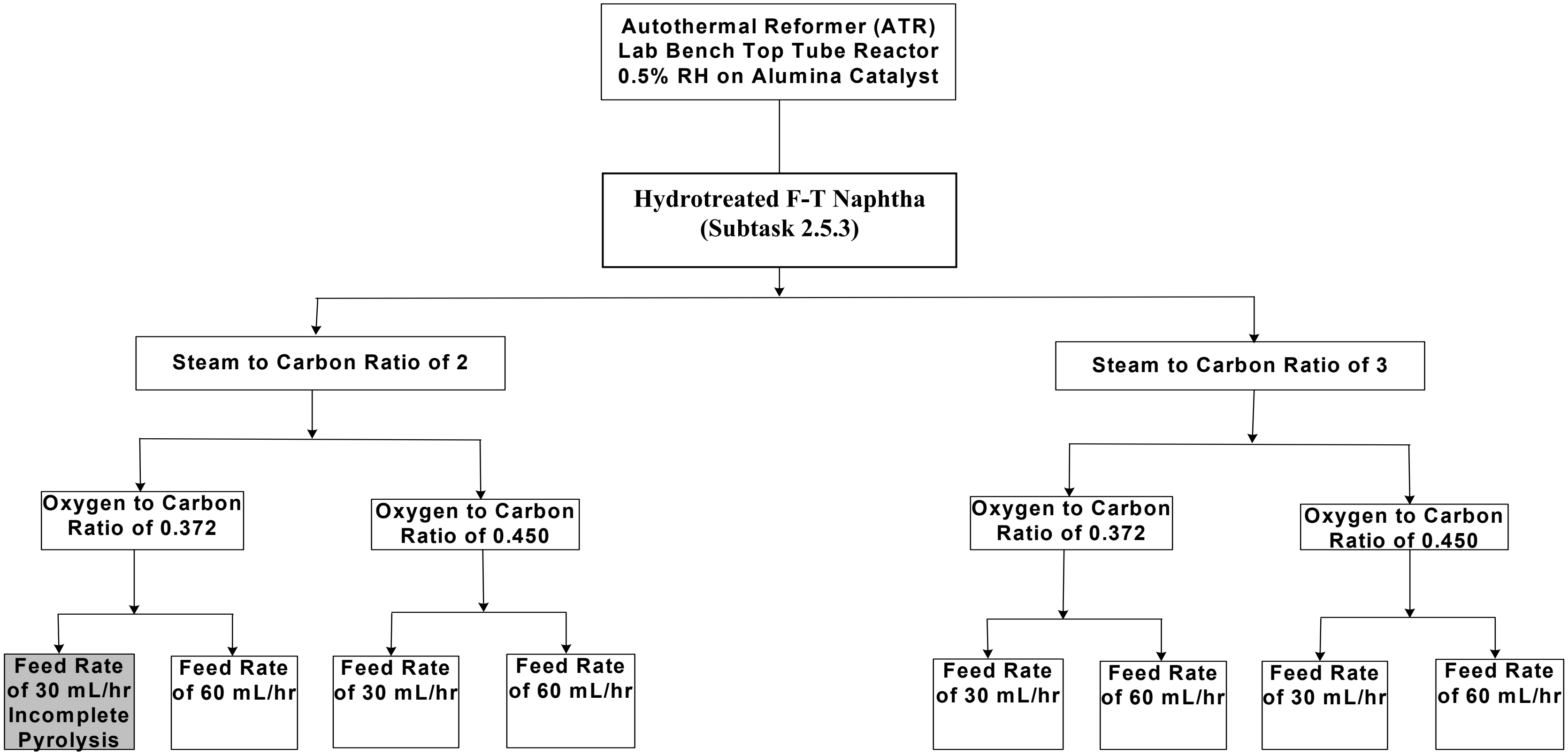
concluded that economical CRU reformate yields could not be obtained with the low octane neat F-T naphtha, hydrotreater (HT) F-T naphtha, or hydrocracker (HC) F-T naphtha products.

To mitigate the technical and economic risks associated with the final product market disposition of F-T naphtha product an alternative product end-use market was identified for F-T naphtha products. A new Subtask 2.5.7.4 entitled “Fuel Cell Reformer” was added to the Phase II to evaluate individually the suitability of two F-T naphtha products, the HT F-T naphtha product and the HC F-T naphtha product as fuel cell reformer feeds. A HC F-T naphtha product was prepared and is expected to be free of fuel cell reformer feed coke precursors. A HT product was also prepared and is expected to remove fuel cell reformer feed coke precursors. The potential to use these two F-T naphtha products as fuel cell reformer feeds is identified as a high technical and economic risk. Overall, the risk to the EECP from the outcome of this Subtask 2.5.7.4 product evaluation is considered to be low.

Experimental

The suitability of the two F-T naphthas, the HT F-T naphtha product and the HC F-T naphtha product, for hydrogen fuel generation was tested under autothermal reforming (ATR) conditions. Petroleum-based naphtha and kerosene reference feeds were included in the product evaluation. A ChevronTexaco Technology Venture (CTTV) ATR bench-scale test apparatus unit was utilized to carry out the product evaluations. Deionized water, air, and the hydrocarbon feedstock were charged to the unit and to a mixer located inside an electric tube furnace. The temperature of the electric furnace was adjusted so that the ATR feed is pre-heated to at least 673K (752°F). The ATR feed then passed to a 25.4 millimeter (1-inch) diameter tube reactor containing ATR catalyst. The tube reactor is in a second electrically heated furnace. The second electronically heated furnace is used to offset heat losses from the small diameter, high temperature tube reactor. In full-scale applications, the ATR reactor has relatively low heat losses and is nearly adiabatic. In the ATR tube reactor the feed passed through a packed catalyst bed. For all the tests in this report 60 grams of a commercially available (Engelhard Escat 326) 0.5 percent rhodium on alumina catalyst was used. After exiting the ATR reactor the ATR reformate passes through a chilled heat exchanger into a knockout vessel used to separate condensed water the ATR reformate. Reformate was discharged into a ventilation hood. A slip stream of the product gas is sent to a gas chromatograph for compositional analysis. For each of the four feeds, the HT F-T naphtha, the HC F-T naphtha, the petroleum-based reference naphtha feed, and the petroleum-based reference kerosene feed, evaluations were conducted under eight sets of test conditions. The tests were conducted at two feed rates of 30 milliliters (ml) and 60 ml, at two steam/carbon ratios of 2 and 3, and two air/fuel (O_2/Carbon (C)) ratios of 0.372 and 0.450. The flow of work and test conditions employed with the HT F-T and HC F-T product evaluations of Subtask 2.5.7.4 are illustrated in **Schematic 2.5.7.4-2** and **Schematic 2.5.7.4-3**, respectively.

Schematic 2.5.7.4-2
Flow of Work for Subtask 2.5.7.4 Fuel Cell Reformer Evaluation of HT F-T Naphtha Feed



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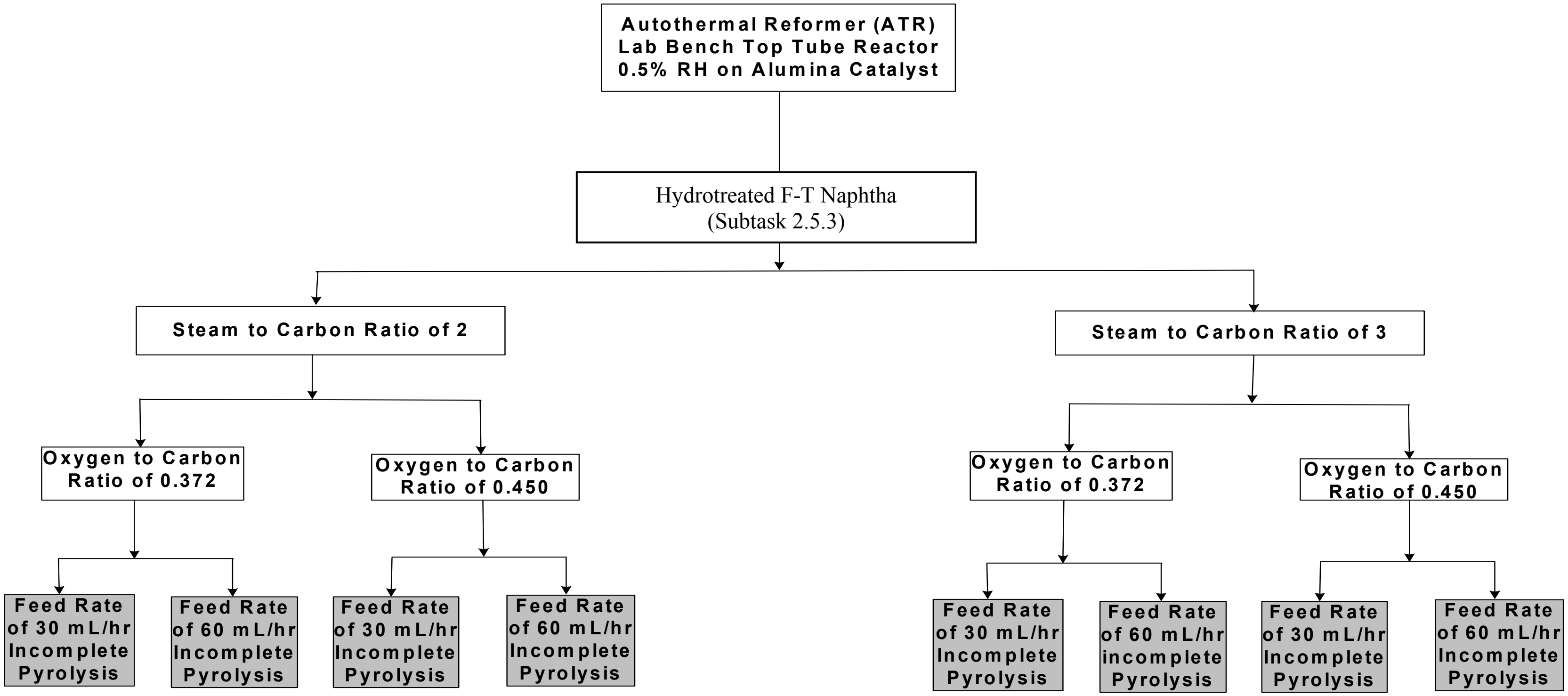
Schematic 2.5.7.4-3
Flow of Work for Subtask 2.5.7.4 Fuel Cell Reformer Evaluation of HC F-T Naphtha Feed



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Results and Discussion

A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.7.4 entitled “Fuel Cell Reformer.” The flow of work for Subtask 2.5.7.4 is illustrated in **Schematic 2.5.7.4-1**. Documentation of the work and detailed discussions are included in the Subtask 2.5.7.4 Test Report in Appendix I. The LaPorte AFDU F-T light and heavy product streams contain a very small yield (< 5 weight percent) of neat F-T naphtha. Subtask 2.5.2 entitled “Lab Batch Fractionation” and Subtask 2.5.7.1.a, b, and c entitled “Naphtha Fractionation” were successfully carried out to maximize the yield and quality of a full range IBP-466K (380°F) neat F-T naphtha present in the LaPorte AFDU F-T light product stream for end-use product evaluations. Subtask 2.5.7.2 entitled “Neat Naphtha Hydrotreating” successfully removed the risks of coke precursors in the fuel cell reformer feed present in the form of reactive olefins, oxygenates, and acids in the neat F-T naphtha. The Subtask 2.5.3 hydrocracker F-T naphtha product from the maximum conversion of F-T wax to hydrocracker F-T diesel product is expected to be a very desirable highly paraffinic feed for a fuel cell reformer. The technical risk has been identified as high for use of the F-T naphthas as fuel cell reformer feeds.

FeedStock Composition Results

The hydrogen to carbon ratio of a fuel cell reformer feed is an important parameter in the generation of hydrogen fuel. **Figure 2.5.7.4-1** presents the carbon and hydrogen test results on the HT F-T naphtha product, the HC F-T naphtha product, the petroleum-based reference naphtha feed, and the petroleum-based reference kerosene feed. The HT F-T naphtha product exhibited a density at 293K (68°F) of 0.719 and hydrogen to carbon ratio of 2.09. The HC F-T naphtha product exhibited a density at 293K (68°F) of 0.703 and hydrogen to carbon ratio of 2.13. The petroleum-based reference naphtha feed exhibited a density at 293K (68°F) of 0.747 and hydrogen to carbon ratio of 2.03. The petroleum-based reference kerosene feed exhibited a density at 293K (68°F) of 0.76 and hydrogen to carbon ratio of 2.17.

ATR Reformer Carbon Balances Results

Figure 2.5.7.4-2 presents the carbon balances obtained with the four feeds at an O_2 to C ratio of 0.372 and a Steam to C ratio of 3 at feed rates of 30 and 60 milliliters (1.83 and 3.66 cubic inches) per hour. Carbon balances (100 times the weight of carbon feed rate divided by the weight of carbon in reformate) of less than 100 percent indicates that the feed is pyrolyzing in the reactor and forms coke. At the test conditions shown for the results presented in **Figure 2.5.7.4-2**, the HT F-T naphtha carbon balances were 100 percent indicating no significant carbon formation with this feed. At the eight test conditions shown in **Schematic 2.5.7.4-3** for the HT F-T naphtha feed, a carbon balance of less than 100 percent indicates that carbon formation was exhibited with the HT F-T naphtha feed only at the lowest feed rate of 30 milliliters (1.83 cubic inches) per hour, the lowest steam to carbon ratio of 2, and the lowest oxygen to carbon ratio of 0.372. This depicts depicted as the single shaded test condition block in **Schematic 2.5.7.4-2**. The HT F-T naphtha is considered a suitable feed for fuel cell reforming based upon its overall satisfactory performance in the test program.

Figure 2.5.7.4-1 – Feed Inspection Tests on F-T Naphthas versus Processed Petroleum Feeds

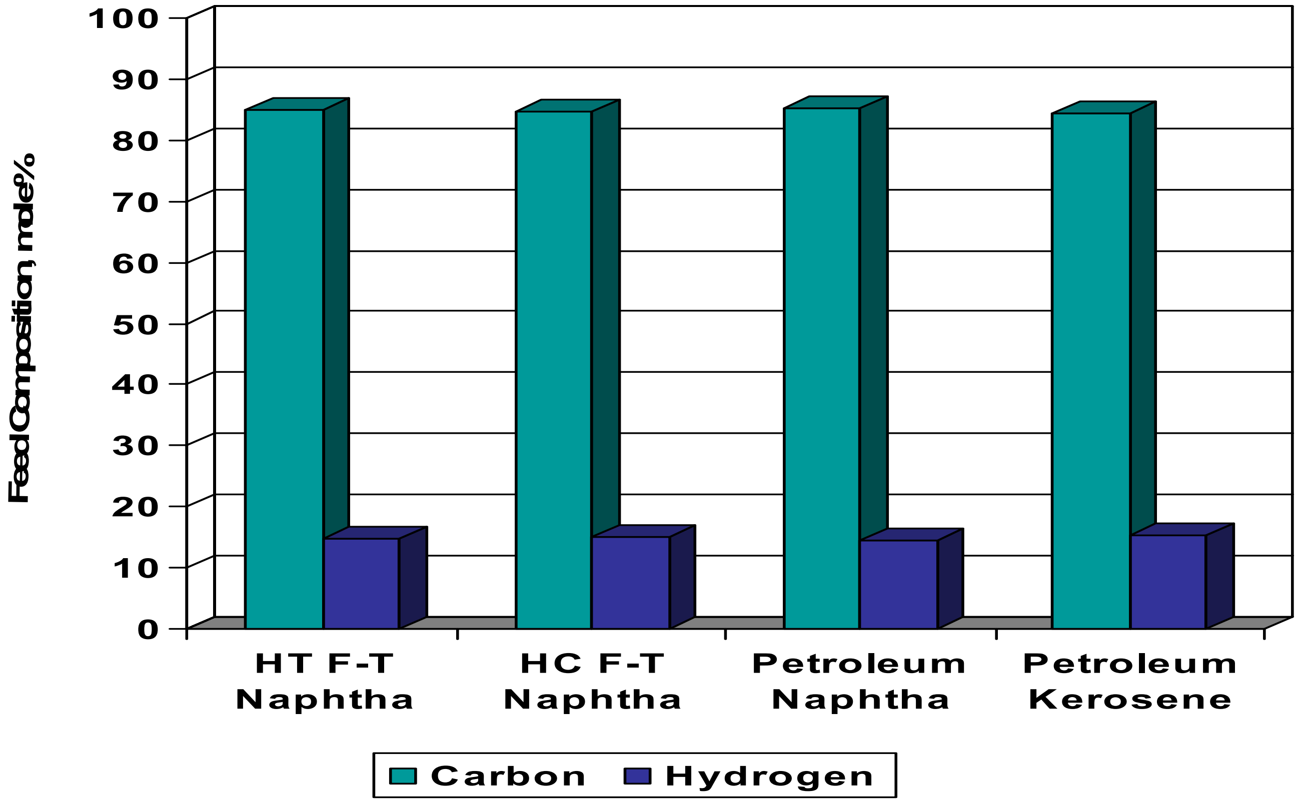
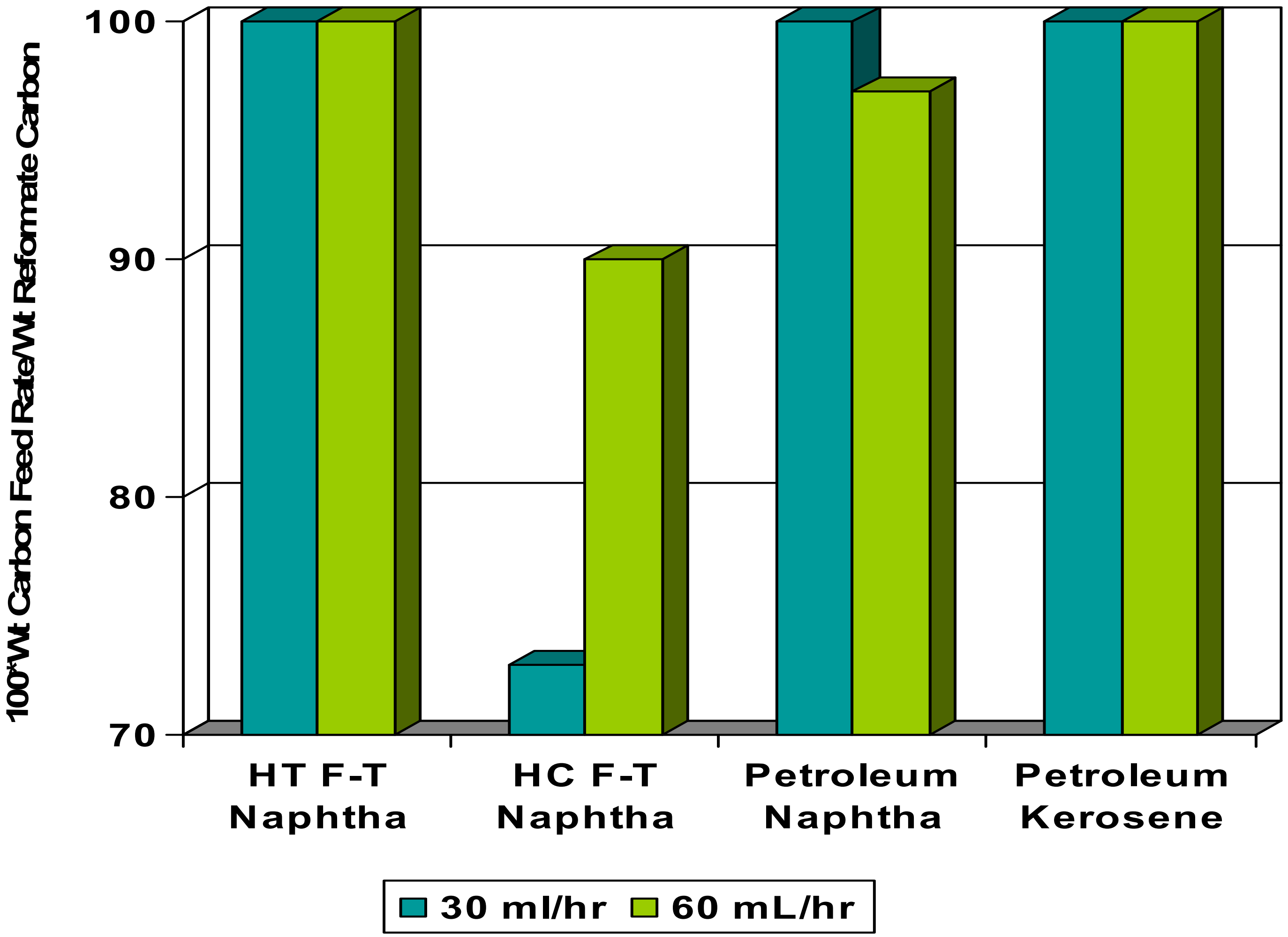


Figure 2.5.7.4-2 – Carbon Balances for F-T Naphthas and Petroleum Feeds

Indication of Complete Pyrolysis of Feed Ahead of ATR Catalyst Bed

Run Conditions of O_2/C = 0.372, Steam/C = 3, Feed Rates of 30 and 60 mL/hr



The HC F-T naphtha carbon balance results presented in **Figure 2.5.7.4-2** range from 70 to 90 percent indicates a high level of pyrolysis and carbon formation for this fuel cell reformer feed. This high level of pyrolysis and carbon formation is an unusual and unexpected result for the HC F-T naphtha feed. The HC F-T naphtha product should be free of fuel cell reformer coke precursors due to the high severity of the hydroprocessing treatment employed in conversion of the neat F-T wax to naphtha and diesel distillate products. The HC F-T naphtha product met a TAN specification of less than 0.1(milligrams of KOH) titrated per gram of HT F-T naphtha product) the same TAN specification the HT F-T naphtha product was required to meet. At the eight test condition blocks shown in **Schematic 2.5.7.4-3** for the HC F-T naphtha feed, carbon balances of less than 100 percent indicates that carbon formation was exhibited in all eight shaded test condition blocks depicted in **Schematic 2.5.7.4-3**. The high level of pyrolysis and coke formation observed at all eight test conditions with the HC F-T naphtha indicates that it would be a difficult feed to reform. Additional work is warranted to determine the exact cause of this coke formation. The carbon balance results presented in **Figure 2.5.7.4-2** for the petroleum-based reference naphtha range from 100 to 95 percent for the 30 milliliter (1.83 cubic inches) per hour and 60 milliliter (3.66 cubic inches) per hour feed rates, respectively. For the petroleum-based reference naphtha feed the carbon balances are less than 100 percent as the feed rate is increased. The carbon balances approach 100 percent as the oxygen to carbon ratio and steam to carbon ratio are increased. This kind of reformer feed behavior is observed when aromatics present in petroleum-based feeds form resins in the ATR catalyst bed. The higher density and lower hydrogen to carbon ratio exhibited by the petroleum-based reference naphtha indicates greater aromaticity in this reformer feed compared to the two F-T naphthas. The carbon balance results presented in **Figure 2.5.7.4-2** for the petroleum based kerosene reference feed were 100 percent. The petroleum based kerosene reference feed has the highest hydrogen to carbon ratio of the four feeds charged to the fuel cell reformer. Feeds with high hydrogen to carbon ratios, low sulfur, and low aromatics would be expected to be good reformer feeds for the generation of hydrogen fuel.

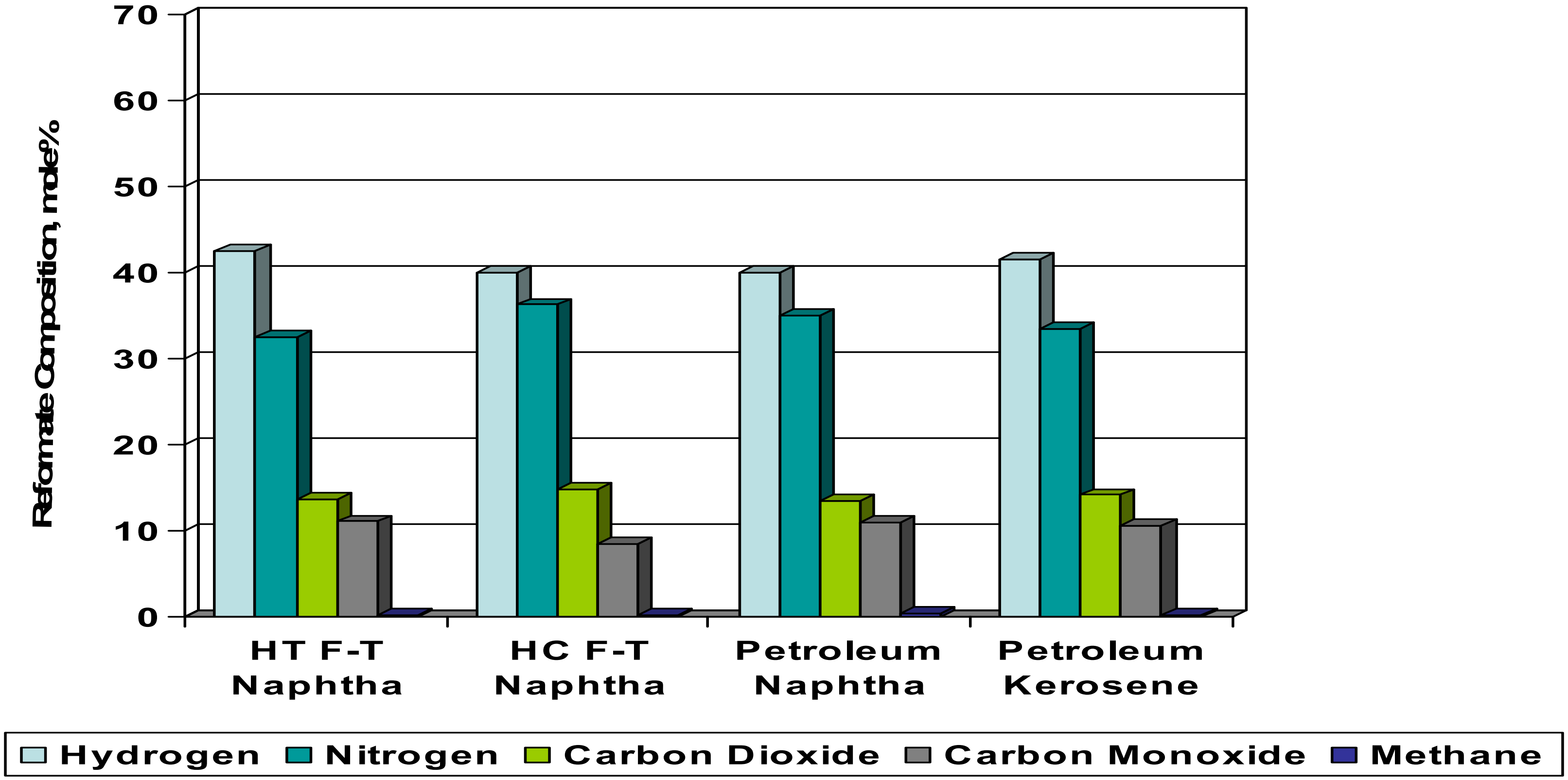
ATR Reformer Hydrogen Fuel Generation Results

Figure 2.5.7.4-3 presents the results of the compositional analyses of the product gases obtained from reforming each of the four feeds at a oxygen to carbon ratio of 0.372, a steam to carbon ratio of 3, and a feed rate of 60 milliliters (3.66 cubic inches) per hour. The product gas from reforming the HT F-T naphtha feed contains 42.5 percent hydrogen, the highest hydrogen production from the four reformer feeds studied. The product gas from reforming the petroleum-based kerosene reference feed had the next highest hydrogen concentration of 41.5 percent. The product gas from reforming the HC F-T naphtha feed contains 40.0 percent hydrogen, while the product gas from reforming the petroleum-based naphtha reference fuel contains 39.95 percent hydrogen.

The HT F-T naphtha is a good reformer feed for the production of hydrogen fuel. The HT F-T naphtha exhibits low levels of sulfur, aromatics, and olefins along with its high hydrogen to carbon ratio which all contribute to reduce ATR catalyst poisoning and carbon formation. The HC F-T naphtha reformer feed performed below expectations and exhibited coke formation tendencies at all ATR reformer test conditions studied.

Figure 2.5.7.4-3 - Reformate Compositions of F-T Naphthas versus Processed Petroleum Based Feeds

Run Conditions of $O_2/C = 0.372$, Steam/C = 3, Feed = 60 mL/hr



Subtask 2.5.7.5 Catalytic Reforming Pilot

Experimental

The original Phase II RD&T Plan envisioned the use of a designated quantity of the HT F-T naphtha product from Subtask 2.5.7.2 entitled “Neat Naphtha Hydrotreating” to be used as feed for Phase II RD&T Subtask 2.5.7.5 entitled “Catalytic Reforming Pilot.”

Results and Discussion

Work to be conducted under Subtask 2.5.7.5 entitled “Catalytic Reforming Pilot” was not performed for the reasons are presented herein. Meetings were held between the EECP Team and two major licensors of CRU technologies that were potentially adaptable for upgrading the low octane of the HT F-T naphtha into a high octane, CRU reformate product for addition to transportation gasoline. Based upon review of inspection tests on the composition of the F-T naphtha product streams, the two technology licensors contacted by the EECP team concluded that economical CRU reformate yields could not be obtained with the low octane neat F-T naphtha, HT F-T naphtha, or the HC F-T naphtha products.

To mitigate the technical and economic risks associated with the final product market disposition of F-T naphtha product an alternative product end-use market was identified for F-T naphtha product**.** A new Phase II RD&T Subtask 2.5.7.4 entitled “Fuel Cell Reformer” was added to evaluate individually the suitability of two F-T naphtha products, the HT F-T naphtha product and the HC F-T naphtha product, as fuel cell reformer feedstocks.

Subtask 2.5.7.6 Neat Diesel Hydrotreating

Experimental

A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.7.6 entitled "Neat Diesel Hydrotreating." Documentation of the work and detailed discussions are included in the Subtask 2.5.7.6 Test Report in Appendix J of this Topical. The composition and type of hydrotreating catalyst used and the specific operating parameters employed in the Subtask 2.5.7.6 product evaluation are proprietary technology licensor information and are not disclosed herein. Subtask 2.5.7.6 entitled "Neat Diesel Hydrotreating" will mitigate the technical risk identified as being low associated with the removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T diesel product to generate end-use product of acceptable quality to carry out Task 2.6 entitled "Fuel/Engine Performance and Emissions" product evaluations. The flow of work for Subtask 2.5.7.6 is illustrated in **Schematic 2.5.7.6-1**.

Feed Composition

The 466K (380°F) to 644K (700°F) neat F-T diesel feed for Subtask 2.5.7.6 is a composite blend of the 466K (380°F) to 644K (700°F) diesel distillation products from Subtask 2.5.2 entitled "Lab Batch Fractionation" and Subtask 2.5.7.1b and c entitled "Naphtha Fractionation." A summary of the distillation results for Subtask 2.5.2 and Subtask 2.5.7.1. b and c are presented in sections of this report. A Subtask 2.5.2 Test Report is included as Appendix A to Topical Report. A Subtask 2.5.7.1 a, b, and c Test Report is attached as Appendix F to this Topical Report. **Table 2.5.7.6-1** presents the results of the inspection testing carried out on the feed to Subtask 2.5.7.6.

Equipment

ChevronTexaco TEMA performed Pilot Plant Test 34-91 for the F-T diesel hydrotreating test. **Figure 2.5.7.6-1** presents the schematic diagram of the pilot plant used for the hydrotreating test. The diesel feed, combined with the make-up hydrogen and recycle gas, is fed to the hydrotreating reactors. The two hydrotreating reactors were in series. The reactor effluent is separated into liquid and vapor in the HPS. The liquid is fractionated in a debutanizer where the hydrotreated products are collect on the bottom and the C4's and lighter goes overhead. The separated vapor from the high pressure separator, composed mainly of the hydrogen, is scrubbed with water to remove trace NH_3 that is formed from nitrogen in the feed. The vapor is then recycled back to the reactors

Results and Discussion

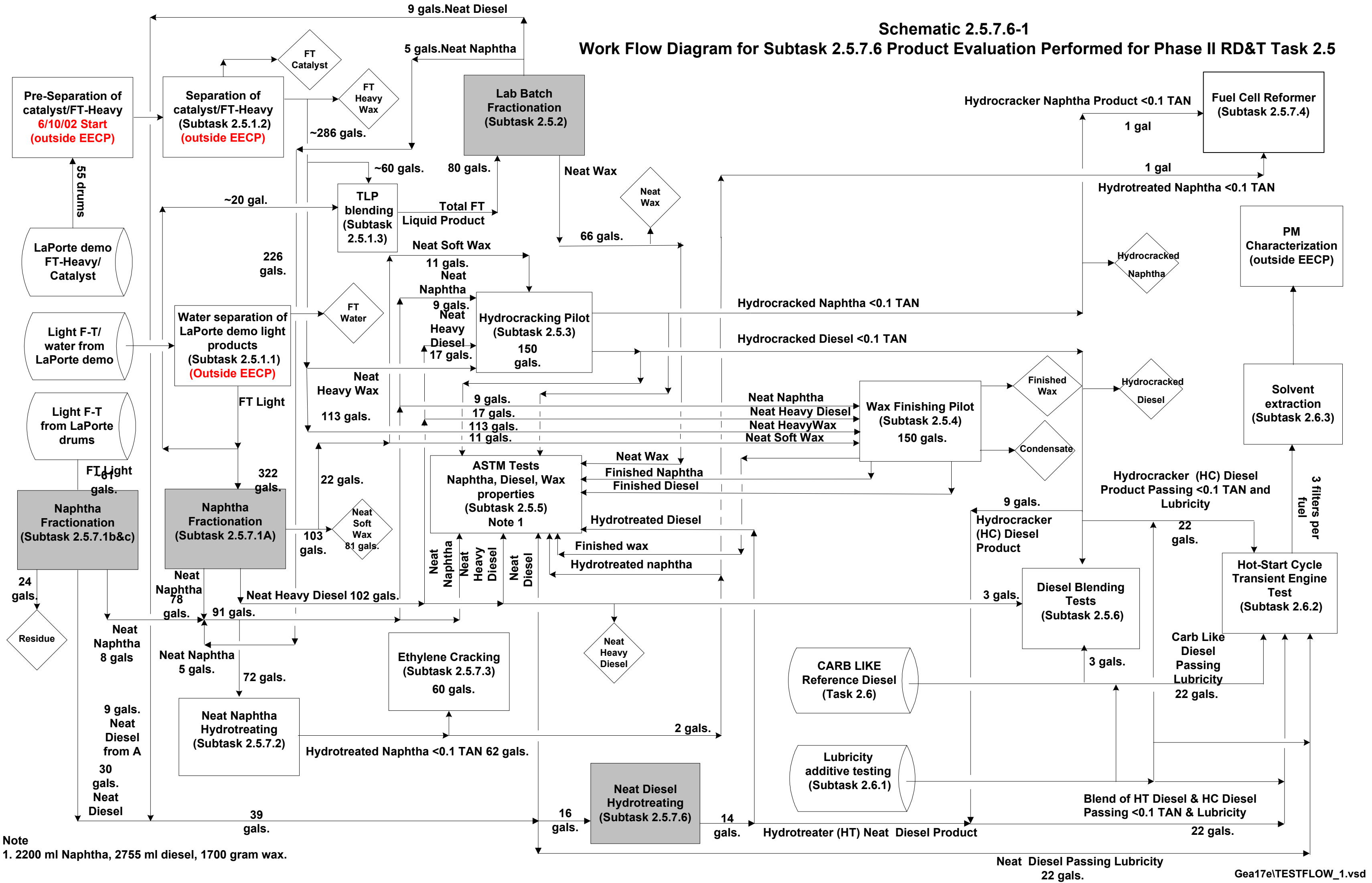
The objective of the Subtask 2.5.7.6 product evaluation entitled "Neat Diesel Hydrotreating" was the successful removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T diesel feed. A TAN specification of less than 0.1 milligrams of KOH titrated per gram of hydrotreater F-T diesel product was established for the HT F-T diesel product. The neat F-T diesel feed had a TAN of 3.69 mg KOH/g. **Table 2.5.7.6-2** presents mass balance closures, product yield slates, and qualities of the HT F-T diesel product representative of the production run. Acceptable mass balance closures were obtained during the course of the production run. The removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T diesel resulted in the consumption of 627 standard cubic feet of hydrogen per barrel of naphtha feed or 112 standard m^3 of hydrogen per m^3 of naphtha feed.

The diesel products were blended and a total of 0.0511 m^3 (13.5 gallons) were recovered. Because the hydrotreated diesel products contained naphtha boiling range material, it was decided to fractionate the product into naphtha range material and diesel boiling range material (466-644 K, 380-700ºF). This was done in three batch distillations. The naphtha cuts from each batch distillation were combined. The diesel cuts from each batch distillation were also combined. The cetane number of the diesel cuts was 74.8. The **Table 2.5.7.6-3** presents the results of the work performed with the product blend and distillation. The product properties of the hydrotreated diesel products, the distilled hydrotreated diesel product blends and the blended diesel are given in **Table 2.5.7.6-4**.

A total of 0.0833 m^3 (22 gallons) of test fuel is needed to perform a hot start cycle transient engine test (Subtask 2.6.2) and solvent extraction (Subtask 2.6.3). Since there was only 0.0397 m^3 (10.5 gallons) of the hydrotreated diesel in the boiling range of 466K to 644K (380ºF to 700ºF), a blend was made with 0.0473 m^3 (12.5 gallons) of F-T diesel product from the hydrocracking pilot plant work (Subtask 2.5.3) for lubricity additive testing (Subtask 2.6.1), hot start cycle transient engine testing (Subtask 2.6.2) and for solvent extraction (Subtask 2.6.3). The properties of the blend are presented in **Table 2.5.7.6-4**. The F-T diesel blend also met the product specification target of a TAN less than 0.1 mg KOH/g.

Work conducted under Subtask 2.5.7.6 product evaluation entitled "Neat Diesel Hydrotreating" was successful in the removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T diesel feed. The desired quantity of hydrotreated F-T diesel was generated for end-use product evaluations. The hydrotreated F-T diesel performed well as a feed component in a blend with HC F-T diesel product which underwent product evaluations in Subtask 2.6.1 entitled "Lubricity Additive Testing," Subtask 2.6.2 entitled "Hot-Start Cycle Transient Engine Emission Test" and Subtask 2.6.3 entitled "Solvent Extraction." The test fuel blend composed of hydrotreater and hydrocracker F-T diesel products passed lubricity with additive addition and reduced the engine emissions of NOx, PM, HC, CO, and SOF by 13, 17, 63, 21, and 39 percent, respectively, compared to a Tier II CARB-like diesel reference fuel.

Schematic 2.5.7.6-1
Work Flow Diagram for Subtask 2.5.7.6 Product Evaluation Performed for Phase II RD&T Task 2.5



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Updated: June 08 , 2003

Table 2.5.7.6-1

Diesel Feed Properties for Hydrotreating Pilot Plant

Sample ID		WOW9289	
Specific Gravity		0.81	
Gravity, °API		43.5	
Sulfur	wt PPM	3.0	
Nitrogen	wt PPM	7.4	
Oxygen by NAA	wt %	2.9	
AED Analyses			
Oxygen	wt %	not available	
Alcohol	wt %	not available	
Olefins	wt %	not available	
TAN	mg KOH/g	3.69	
		Temperature, K	°F
Simulated Distillation, LV%	IBP	395	251
	0.5%	430	314
	5%	466	380
	10%	485	414
	30%	524	484
	50%	564	556
	70%	600	621
	90%	630	674
	95%	639	690
	99%	651	712
	EP	655	720
D86 Distillation, LV%	IBP	437	328
	5%	475	396
	10%	491	425
	30%	530	495
	50%	568	563
	70%	604	627
	90%	632	679
	95%	643	698
	EP	650	710

Figure 2.5.7.6-1
Diesel Hydrotreating Pilot Plant Block Flow Diagram

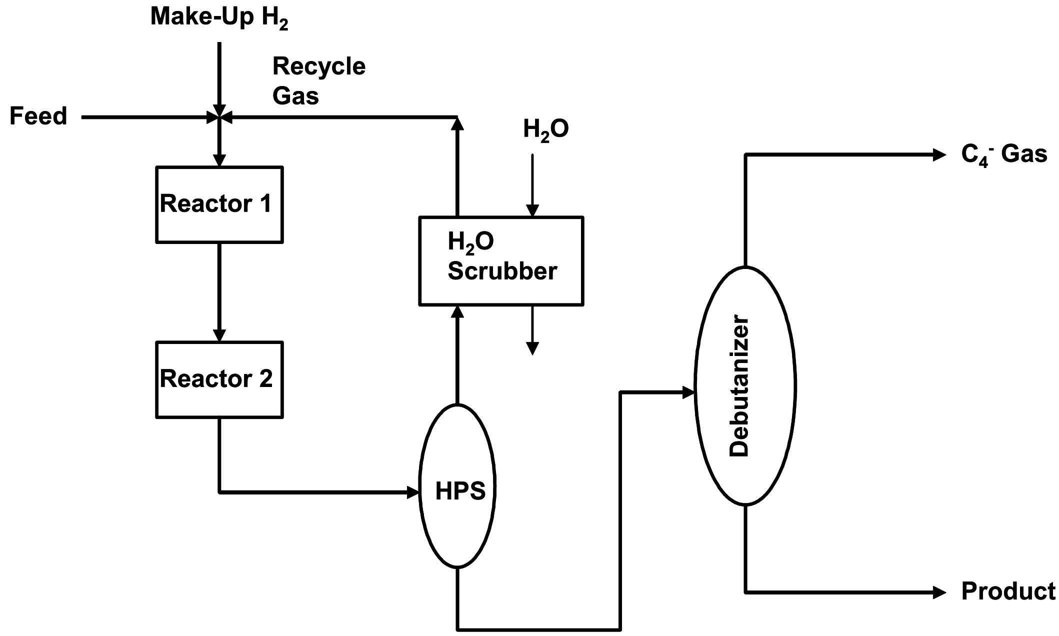


Table 2.5.7.6-2
Yields for Hydrotreating Diesel

Feed		**WOW9289**	
Run Number		34-91	
Run Hours		534-558	
Normalized Prod.Yields		WT. %	VOL. %
Total C4-		0.3	
Total C5+		97.6	101.4
C5-466 K (380°F)		14.5	16.7
466-644 K (380-700°F)		83.1	84.7
H2 Consumption		sm^3/m^3	SCF/B
		111.7	627
Material Balance Closure		101 wt%	
Product Properties			
Specific Gravity		0.78	
Gravity, °API		50.5	
TAN, mg KOH/g		0.05	
		Temperature K	°F
Simdist (D2887) Volume %	St	294	70
	5	370	206
	10	436	325
	30	499	439
	50	544	519
	70	587	598
	90	627	670
	95	637	688
	99.5	651	713

Table 2.5.7.6-3 Diesel Hydrotreating Product Blend & Distillation

	Hydrotreated Diesel Products	Distilled Hydrotreated Diesel Blends (3 Batches)	Blended Naphtha from Distillation	Blended Diesel from Distillation
Boiling Range	~308K-644K (~95-700°F)	St-466K & 466-644K (St-380 & 380-700°F)	St-466K (St-380°F)	466°K-644K (380°F-700°F)
Further Work				Blended with HC Diesel

Table 2.5.7.6-4 Diesel Hydrotreating Product Properties

Sample ID		WOW9302	FSL 9803 Cut 1	FSL 9803 Cut 2	FSL 9804 Cut 1	FSL 9804 Cut 2	FSL 9805 Cut 1	FSL 9805 Cut 2	PGQ 1153	PGQ1142	WOW 9306
Description		Hydrotreated Diesel Products	Distilled Hydrotreated Diesel Product Blends						Composite of naphtha range Fractions	Composite of diesel range Fractions	Diesel Blend 55% HCR'd Diesel 45% HDT'd Diesel
			Batch 1		Batch 2		Batch 3				
Boiling Temp Range	K		IBP-466	466-644	IBP-466	466-644	IBP-466	466-644	IBP-466	466-644	
	°F		IBP-380	380-700	IBP-380	380-700	IBP-380	380-700	IBP-380	380-700	
Specific Gravity		0.78	0.71	0.79	0.71	0.79	0.72	0.79	0.72	0.79	0.79
Gravity, °API		50.5	67.3	48.4	66.8	48.4	64.7	48.3	66.3	48.4	48.6
Sulfur	wt PPM	< 1		0.59		0.53		<1			< 1
Nitrogen	wt PPM	0.2		0.25		0.17		0.19			< 0.15
Astm Color	none	0.0									0
Pour Point	K (°C)	272 (-1)									263 (-10)
Cloud Point	K (°C)	277 (4)								280 (7)	272 (-1)
Cold Filter Plugging Point	K (°C)	274 (1)									270 (-3)
Aromatics	wt %	pending									pending
Ramsbottom Carbon	wt %	0.06									0.05
TAN	mg KOH/g	< 0.05									< 0.05
Viscosity at 40 °C	cSt	2.2									3.0
Ash Oxide, D482	wt %	< 0.005									< 0.005
Flash Pt	K (°C)	<298 (<25)								372 (99)	354 (81)
		Temperature (K)									
Simulated Distillation, LV%	IBP	272									360
	0.5%	309	271	460	271	459	306	450		460	397
	5%	371	309	469	309	469	340	468		470	467
	10%	423	341	489	341	488	342	487		489	487
	30%	499	372	526	372	525	396	525		526	526
	50%	544	414	560	421	560	422	560		560	560
	70%	588	445	596	446	595	446	598		596	595
	90%	627	468	629	469	629	469	629		629	629
	95%	639	469	640	470	640	470	640		640	637
	99%	651	476	651	487	651	486	651		651	647
	EP	654	484	654	487	654	487	655		657	651
D86 Distillation, LV%	IBP	293									444
	5%	402									479
	10%	450									497
	30%	508									534
	50%	552									567
	70%	595									601
	90%	630									630
	95%	641									638
	EP	644									645
		Temperature (°F)									
Simulated Distillation LV%	IBP	31									189
	0.5%	96	29	369	29	367	92	351		369	256
	5%	208	97	385	97	384	153	383		386	382
	10%	302	154	420	155	419	156	418		420	417
	30%	439	210	487	211	486	253	486		487	487
	50%	520	286	549	298	548	301	548		549	549
	70%	599	342	613	344	612	344	617		614	612
	90%	670	383	673	385	672	384	672		673	672
	95%	691	385	692	386	692	386	692		693	688
	99%	712	398	712	417	712	416	712		713	706
	EP	718	412	717	418	717	417	719		723	713
D86 Distillation LV%	IBP	68									340
	5%	264									402
	10%	351									435
	30%	455									501
	50%	534									562
	70%	611									622
	90%	674									674
	95%	694									689
	EP	700									701

Subtask 2.5.8 Wax Fractionation

Experimental

The EECP Phase I site economic evaluation concluded that upgrading the 644K (700°F) plus F-T neat wax product to a high melting point food-grade wax specialty product could result in the production of a high market value product that would result in an economic EECP. The 644K (700°F) plus F-T neat wax product was distributed between the F-T light product and F-T heavy product streams from the LaPorte AFDU. As illustrated in the flow of work presented in **Schematic 2.5-1,** the water free F-T Light Product from Subtask 2.5.1.1 entitled **"**Water Separation of LaPorte Commingled Water and F-T Light Product Streams" and the F-T heavy product from Subtask 2.5.1.2 entitled "Catalyst/Wax Separation to 10 ppmw" were blended in a ratio-of-production blend in Subtask 2.5.1.3. The ratio-of-production blend was distilled in Subtask 2.5.2 entitled "Lab Batch Fractionation" to maximize the recoveries of a IBP-466K (380°F) neat F-T naphtha product, a 466K (380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T wax product meeting boiling range and quality specifications for the product evaluations.

Results and Discussion

The patent literature[1] cites the application of short path distillation technology in obtaining food-grade wax products with different melting points. Short path distillation technology was selected to mitigate the technical and economic risks of possible degradation from thermal cracking with conventional refining distillation technologies to both the yield and quality of the Subtask 2.5.4 finished food-grade wax product. The Phase II RD&T plan envisioned that a production run at steady state would be conducted under Subtask 2.5.4 as the basis-for-design operating conditions to generate a designated amount of 644K (700°F) plus food-grade wax product for distillation into low melting point and high melting point grades of wax products. However, there was an insufficient quantity of 644K (700°F) plus finished food-grade wax product generated from Subtask 2.5.4 entitled "Wax Finishing Pilot" to conduct the Subtask 2.5.8.

No short path distillation of the 644K (700°F) plus finished food-grade wax product into low- and high-melting point grades of waxes was conducted. The decision was made not to proceed with the short path distillation of the 644K (700°F) plus neat F-T wax product from Subtask 2.5.2 which is the wax feed component to Subtask 2.5.4 entitled "Wax Finishing Pilot." Characterization of the Subtask 2.5.4 wax feed component into different melting point wax grades with short patch distillation was deemed unnecessary in the absence of corresponding finished food-grade wax melting point grades for comparison.

Conclusions

Extensive testing was carried out for the EECP during the F-T Product Upgrading task in Phase II. The testing encompassed straight fractionation, hydrotreating, hydrocracking, wax finishing, diesel blending, ethylene cracking, and fuel cell reformer testing. The technical and economic risks to the proposed EECP were reduced by the Phase II testing. Wax Finishing testing determined the updated F-TPU design basis (Task 4.0 Topical Report). Ethylene cracking testing and fuel cell reformer testing showed the potential additional value created by F-T naphtha.

Key conclusion from F-T product testing during Phase II included:

1. The hydrocracker F-T diesel performed well as a test fuel and as a blend component in a test fuel prepared with hydrotreater F-T diesel in the product evaluations of Subtask 2.6.1 entitled "Lubricity Additive Testing," Subtask 2.6.2 entitled "Hot-Start Cycle Transient Engine Emission Test," and Subtask 2.6.3 entitled "Solvent Extraction."
2. The hydrocracker F-T naphtha product did not perform to expectations in Subtask 2.5.7.4 as a fuel cell reformer feed for the generation of hydrogen fuel.
3. A wax product meeting Saybolt Color and FDA UV Absorbance Part II food grade wax product specifications can be made from a soft wax/hard wax feed blend using a Nickel Alumina-based catalyst. The catalyst is very susceptible to temperature runaway.
4. It may be possible to Hy-Finish^{SM} the full range F-T Product and obtain the required separation in a vacuum column at a lower reboiler temperature. The estimated vacuum required is 1 mm Hg at 436K (325°F).
5. The two test fuels, the neat F-T diesel and the Hydrocracker F-T diesel, and all of their test fuel blends prepared with the Tier II CARB-like diesel fuel reference fuel performed very well during testing of cetane engine, pour point, cloud point, lubricity, viscosity, and storage stability.
6. The HT F-T naphtha is a good reformer feed for the production of hydrogen fuel. The HT F-T naphtha exhibits low levels of sulfur, aromatics, and olefins along with its high hydrogen to carbon ratio which all contribute to reduce ATR catalyst poisoning and carbon formation.

Bibliography

1. United States of America Patent Number 5,904,834 entitled “Synthetic Wax for Food Applications”, assigned to inventors Messrs. Joachim Ansorge, Arend Hoek, Willem Pieter Leenhouts, and Robert Anthony John Priston of the Shell Research Limited, May 18, 1999.

List of Acronyms and Abbreviations

Θ	time, sec
α	fractional disappearance of the feedstock
AFDU Unit	Alternativee Fuels Development
AGR	acid gas removal unit
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATR	autothermal reforming
bbl	barrel
BTX	benzene, toluene, xylene
C#	Compounds with Carbon Number of #
C	carbon
CARB	California Air Resources Board
CCR	California Code of Regulations
CFR	Code of Federal Regulations
CH_4	methane
cm	centimeters
CRU	Catalytic Reforming
cSt	centistokes
CO_2	Carbon Dioxide
CO	Carbon Monoxide
COV	Coefficients of Variation
CRU	Catalytic Reforming Unit
CTTV	ChevronTexaco Technology Ventures
davg	average gas density, lb/cu ft
DCRP	Delaware City Repowering Project
DER	Department of Emissions
DDC	Detroit Diesel Corporation
DOE	U.S. Department of Energy
EECP	Early Entry Coproduction Plant
EMA	Engine Manufactures' Association
EP	end point
EPA	Environmental Protection Agency
FTP	Federal Test Procedure
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
FDA	US Food and Drug Administration
Fe	iron
ft	feet
g	gram
G	total mass flow in coil per unit Time or fluid mass flow, lb/square foot/second
GC	gas chromatograph
GE	General Electric
H_2	hydrogen
H_2S	hydrogen sulfide
HC	Hydrocracker or Hydrocarbons
HT	Hydrotreater
HFRR	High Frequency Reciprocating Rig
Hg	mercury
HPS	high pressure separator
HRSG	heat recovery steam generator
IGCC	Integrated Gasification Combined Cycle
in	inch
IBP	initial boiling point
ICP	inductively coupled plasma
ILT	Integrated Laboratory Technologies
IP	The Institute of Petroleum
K	Kelvin
Kt	reaction rate constant, sec-1, at temperature t
KBR	Kellogg Brown & Root
Kg	kilogram
KOH	potassium hydroxide
kPa	kilo Pascals
L	coil length, ft
lbs	pounds
LHSV	Liquid Hourly Space Velocity
MDEA	Methyldiethanolamine
m^3	cubic meter
M	molecular weight of hydrocarbon and steam
mg	milligram
ml	milliliter
mm	millimeter
N_2	nitrogen
NAA	Neutron Activation Analysis

NH_3	ammonia
nm	nanometers
O_2	oxygen
NOx	Nitrogen Oxides
P/E	propylene/ethylene
PIANO	Paraffins, Iso-Paraffins, Aromatics, Naphthenes, and Olefins
Psia	pounds force per square inch Absolute
Psig	pounds force per square inch gauge
ppmw	parts per million (weight per volume)
R	universal gas constant
RD&T	Research, Development, and Testing
s	seconds
scf	standard cubic feet
SCFB	standard cubic feet per barrel
SLBOCLE	Scuffing Load Ball-on-Cylinder Lubricity Evaluator
SOF	Soluble Organic Fraction
SRU	Sulfur recovery unit
SO_2	sulfur dioxide
SO_4	Sulfate
SWS	sour water stripper
SwRI	Southwest Research Institute
t	absolute temperature
TAN	Total Acid Number
TEMA	Technology Marketing
TES	Texaco Energy Systems LLC.
TGTU	Tail gas recovery unit
P	total pressure
PM	Total Particulate Matter
UV	ultraviolet
Vc	volume of cracking coil
WTC	Westhollow Technology Center
wt%	weight percent

EARLY ENTRANCE COPRODUCTION PLANT PHASE II

Appendix A – Test Report

Subtask 2.5.2: LAB BATCH FRACTIONATION

Reporting Period:	January 2001 to June 2003
Contributors:	Fred D. Brent (ChevronTexaco) Lalit Shah (ChevronTexaco) Earl Berry (ChevronTexaco) Charles H. Schrader (ChevronTexaco) John Anderson (ChevronTexaco) Michael Henley (ChevronTexaco)
Date Issued:	September 19, 2003

Executive Summary

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are TES (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR) in addition to the U.S. Department of Energy (DOE). TES is providing gasification technology and Fischer-Tropsch (F-T) technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology, and KBR is providing engineering.

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was developed to mitigate the identified risks (Phase II RD&T Plan, October 2000). The risks to the EECP from Task 2.5 can be mitigated by demonstrating that the products derived from the upgrading of the F-T Synthesis total liquid product can meet or exceed current specifications associated with producing an acceptable naphtha feedstock component for a chemical plant steam cracker to produce ethylene and propylene or as a naphtha feedstock component for hydrogen fuel generation from a fuel cell reformer, finished diesel transportation fuels, and specialty food grade wax products. Subtask 2.5.2 entitled "Lab Batch Fractionation" will mitigate the potential risks to the EECP associated with maximizing the recovery and qualities of end use neat F-T naphtha, neat F-T diesel, and neat F-T wax products meeting boiling range specifications for the product evaluations of Task 2.5.

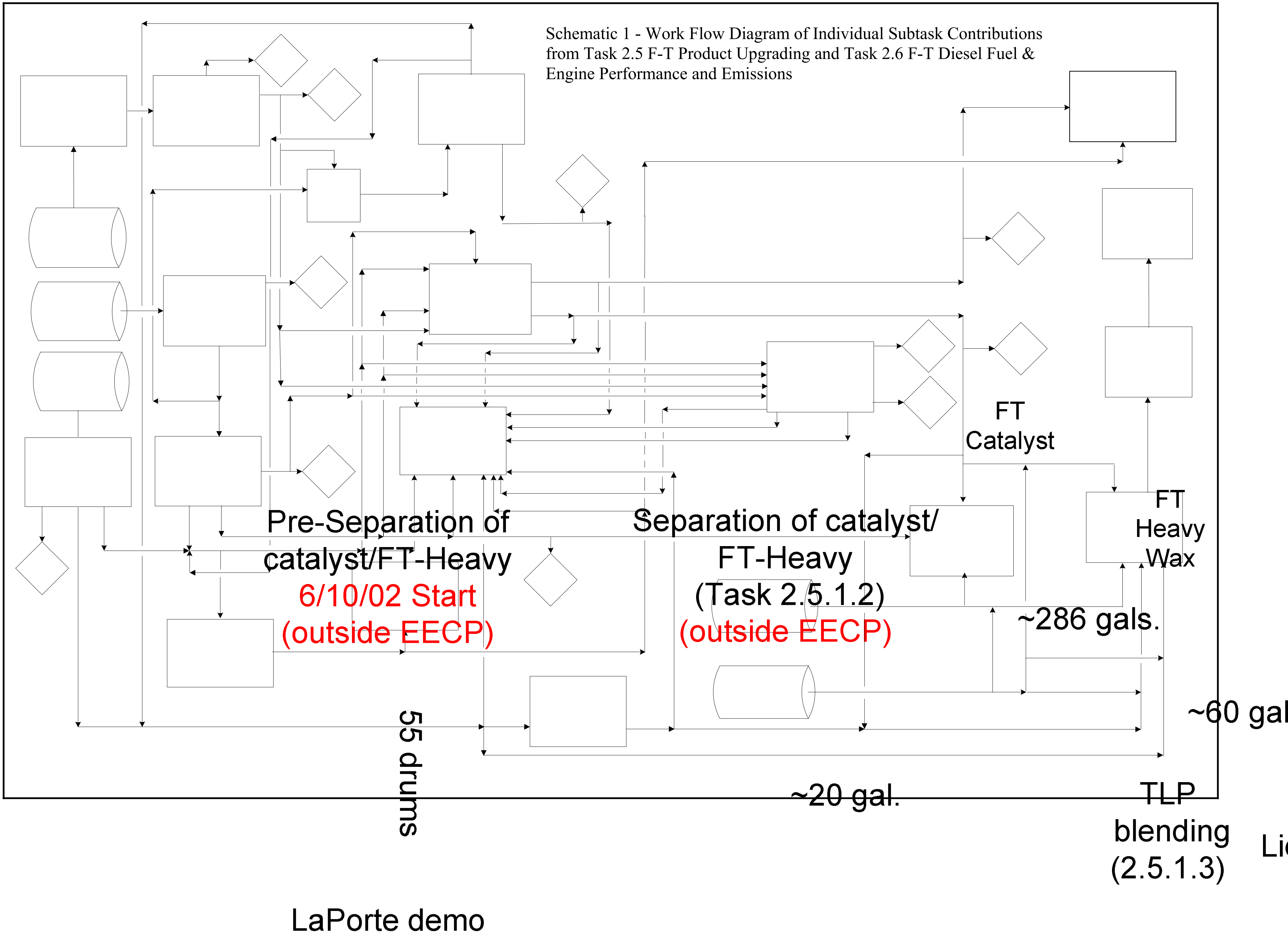
Subtask 2.5. 2 - Lab Batch Fractionation

The F-T Synthesis liquid products from the LaPorte AFDU demonstration were required to be distilled to the required fuel or specialty wax product boiling range specifications for feedstocks and materials to other Task 2.5 and Task 2.6 activities. There are technical and economic risks to the EECP if the F-T Synthesis products undergo degradation or liquid yield losses during the distillation process.[1] Subtask 2.5.2 technical risks are the degree of laboratory fractionation efficiency, recovery of products and possible contamination of distilled products. These technical and economic risks to the EECP will be mitigated if the distilled products achieve desired yield recoveries and qualities meeting fuel or specialty product boiling range specifications in order to satisfy the end use evaluation needs of the Subtasks illustrated in **Schematic 1** for Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emissions." The Subtask 2.5.2 Flow Work is illustrated in **Schematic 2**. Separate Task 2.5 and Task 2.6 Topical Reports were prepared for the DOE. Reports for each Subtask as part of the Phase II RD&T were also prepared and are appended to the respective Task 2.5 and Task 2.6 Topical reports.

Experimental

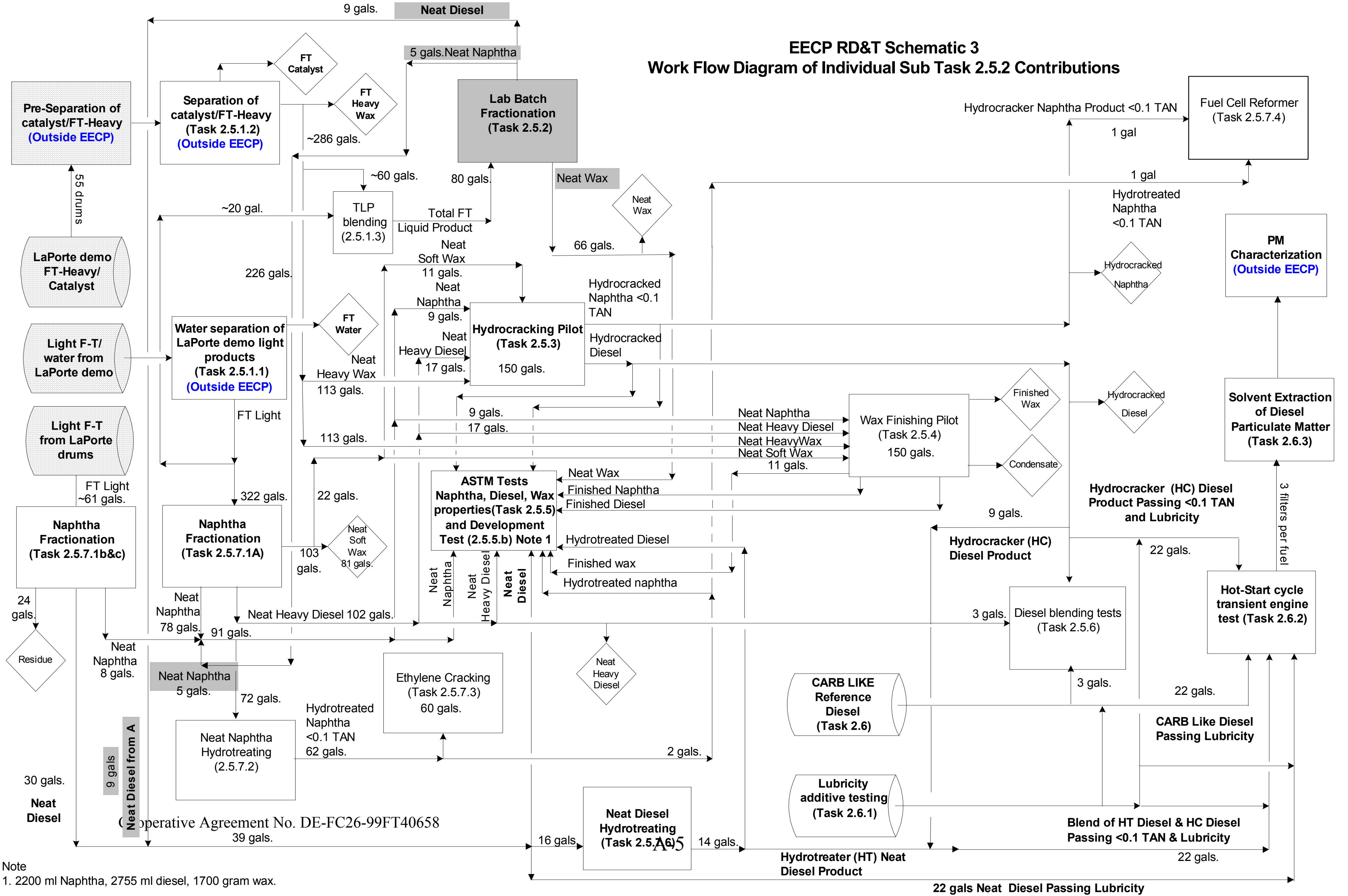
Feed Blend Components

The LaPorte AFDU demonstration F-T products will be used for all the Phase II RD&T Task 2.5 and Task 2.6 product upgrading. The LaPorte AFDU design did not allow for the separation of the F-T Light products and free water. To ensure accurate Phase II RD&T product upgrading results, free water was separated from 131 pounds (59.5 kg) of the F-T Light product by Subtask 2.5.1.1 entitled "Water Separation of LaPorte Commingled Water". The F-T synthesis technology for the EECP uses iron catalyst to produce a broad range of paraffin and olefins hydrocarbons with minor amounts of oxygenates and acids. The LaPorte AFDU demonstration used the primary filtration system developed by Rentech and Texaco. The F-T Heavy product contained more than 10 ppmw of the F-T synthesis catalyst and required addition filtration work from Subtask 2.5.1.2 entitled "Catalyst/Wax Separation to 10 ppmw" to obtain 472 pounds (214.5 kg) of F-T Heavy Product meeting a specification of 10 ppmw catalyst concentration in the F-T Heavy product. The EECP Team fractionated 603 pounds ((274 kg) of a ratio-of-production blend of the Fischer Tropsch Synthesis F-T Light and F-T Heavy product streams into sharp True Boiling Point (TBP) cuts of neat F-T naphtha (IBP-380F (466K)), neat F-T diesel (380°F (466K)-700°F (644K)) and neat F-T wax (700°F (644K +)) fractions employing batch distillation technology.



Schematic 1 - Work Flow Diagram of Individual Subtask Contributions from Task 2.5 F-T Product Upgrading and Task 2.6 F-T Diesel Fuel & Engine Performance and Emissions

Schematic 2-Chronological Flow of Work for Phase II RD&T Task 2.5 and Task 2.6



Note
1. 2200 ml Naphtha, 2755 ml diesel, 1700 gram wax.

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Updated: June 08 , 2003

Equipment

All equipment involved with Subtask 2.5.2 was thoroughly cleaned with new toluene then thoroughly rinsed new hexane and nitrogen dried. Aliquots of the new Toluene and new Hexane were submitted for sulfur, nitrogen, and aromatic analyses to establish a base line. Aliquots of the final rinse Hexane were submitted sulfur, nitrogen, and aromatic analyses confirming that all equipment employed for this project met the cleanliness specifications.

A weight of 131 pounds (59.5 kg) of the F-T Light Product from Subtask 2.5.1.1 entitled **“**Water Separation of LaPorte Commingled Water was blended in a ratio-of-production blend with a weight of 472 (214.5 kg) pounds of the F-T Heavy product from Subtask 2.5.1.2 entitled “Catalyst/Wax Separation to 10 ppmw.” This was accomplished in the designated 1000 #1 Reactor Kettle a Phaudler Glass-lined 1000 gallon (3785 liters) Reactor Kettle with an agitator and baffle, heated by hot water or steam to 325°F (436K) with a riser, condenser and 200 gallon (757 liters) glass-lined receiver vessel. The unit is operated at atmospheric and sub-atmospheric pressures (760 to 10 mm Hg).

The ratio-of-production blend was then fractionated into naphtha, diesel, and wax products in Pilot Plant 51 a 1000 gallon Stainless Steel Batch Distillation Column that is 24 feet tall by 14 inches inside diameter packed with 1 inch Stainless Steel Pall Rings. The column is equipped with a condenser, reflux divider and 2-200 gallon Stainless Steel receiver vessels. The column is operated at atmospheric and sub-atmospheric pressures (760 to 10 mm Hg) up to an atmospheric equivalent temperature of 616K (650°F). Mass balance closures of +/- 2 % are the desired target. Actual Subtask 2.5.2 handling and mass balance closures are noted and reported. The Pilot Plant 51 fractionation equipment efficiency will be measured as Gap and Overlap with the following specifications:

ASTM D-86 95 % Naphtha/5 % Diesel Gap = 30°F Min
ASTM D-86 95 % Diesel/5 % Wax Overlap = 30°F Max

The neat F-T naphtha and the neat F-T diesel distillation products from Subtask 2.5.2 have high Total Acid Numbers (TAN) and are corrosive to carbon steel containers. New polyethylene containers and new phenolic-lined 55-gallon ((208 liter) drums were used to safety store and handle these materials for the Task 2.5 and Task 2.6 product evaluations.

Results and Discussion

A summary is presented below of the important findings which mitigated potential risks to the EECP as result of the work conducted in Phase II RD&T Subtask 2.5.2 entitled “Lab Batch Fractionation.”and is appended to the Task 2.5 Topical Report entitled “F-T Product Upgrading” prepared for the DOE. Task 2.5 and Task 2.6 Topical reports were prepared for the DOE.

Subtask 2.5.2 entitled “Lab Batch Fractionation” mitigated the potential risks associated with maximizing the recovery and qualities of end use neat F-T naphtha, neat F-T diesel, and neat F-T wax products meeting boiling range specifications. The neat F-T naphtha was the end use product for Subtask 2.5.7.2 entitled “Neat Naphtha Hydrotreating.” The hydrotreated F-T naphtha product was the end use product for both Subtask 2.5.7.3 entitled “Ethylene Cracking” and Subtask 2.5.7.4 entitled “Fuel Cell Reformer.” The Subtask 2.5.2 neat F-T naphtha and neat F-T diesel products were also feed components in the feed slate to both the Subtask 2.5.3 entitled “Hydrocracking Pilot’ and the Subtask entitled “Wax Finishing Pilot.” The neat F-T wax product from Subtask 2.5.2 was the feed to Subtask 2.5.8 entitled “Wax Fractionation.” Work on Subtask 2.5.8 was not initiated for the reasons stated in the Task 2.5 Topical Report entitled “F-T Product Upgrading.”

An examination of the data presented in Table 1 show that a ratio-of-production blend was prepared which consisted of 78.3% by weight of the F-T Heavy Product and 21.7% by weight of the F-T Light Product. A total of 603 pounds of the ratio-of-production blend was prepared as feed to Subtask 2.5.2 entitled “Lab Batch Fractionation.” A laboratory batch fractionation operations was conducted to obtain an IBP-380^{o}F (466K) True Boiling Point (TBP) neat F-T naphtha product, 380^{o}F (466K)-700^{o}F (644K) TBP neat F-T diesel, and a 700^{o}F + (644K+) TBP neat F-T wax product. An examination of the data presented in Table 1 show that 4.2% by weight of neat F-T naphtha product was obtained from fractionation of the ratio-of-production feed blend. Inspection testing conducted on the neat F-T naphtha is presented in Table 2. The neat F-T diesel distillation product accounted for 10.1% by weight of the feed. Inspection testing conducted on the neat F-T diesel is presented in Table 3. The remaining 84.5% by weight of the feed consisted of the neat F-T wax product. As previously discussed the neat F-T wax product was designated as feed for Task 2.5.8 entitled “Wax Fractionation.” Work on Task 2.5.8 was not initiated. Therefore, limited inspection testing was carried out and is presented in Table 4 for information. An acceptable mass balance closure of 98.8 wt% was obtained for the Subtask 2.5.2 fractionation task. The distribution by boiling range of naphtha, diesel, and wax products is expected with the use of iron F-T synthesis catalyst processing low hydrogen to carbon monoxide syngas feed generated from the gasification of petroleum coke.

The Subtask 2.5.2 neat F-T naphtha product for Task 2.5 product evaluations will be tested and approved for blending with the neat F-T naphtha products from Subtask 2.5.7.1.a&b&c entitled “Naphtha Fractionation.” The separate Phase II RD&T Subtask 2.5.7.1 a&b&c Report entitled “Naphtha Fractionation” is appended to the Task 2.5 Topical Report entitled “F-T Product Upgrading” prepared for the DOE.

Subtask 2.5.7.1 fractionated the F-T Light Product after the risk of free water was successfully removed by Subtask 2.5.1.1. Subtask 2.5.7.1 performed the fractionation of three different size retains of F-T Light Product recovered from the LaPorte AFDU demonstration. Task 2.5.7.1.a fractionated approximately 322 gallons of F-T Light Product collected in a commercial ISOtainer vessel receiver to maximize the recovery of neat F-T naphtha, a neat F-T heavy diesel, and a neat F-T soft wax product. Task 2.5.7.1.b and Task 2.5.7.1.c each fractionated the contents of a partial filled 55-gallon drum receiver from the LaPorte AFDU demonstration to recover the neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products. Inspection testing found the neat F-T diesel product from Subtask 2.5.7.1.a to have some loss of front end boiling range components due to operating a continuous distillation column overhead product diesel receiver too hot resulting in the loss of diesel vapors from flashing. The Subtask 2.5.7.1.a neat F-T heavy diesel was not used as a feed component for Subtask 2.5.7.6 entitled “Neat Diesel Hydrotreating” and was not used directly in Task 2.6 product evaluations.

Inspection testing on the neat F-T naphtha products from Subtask 2.5.2 and Subtask 2.5.7.1 a&b&c are presented in Table 5. The individual product streams were approved for composite blending for hydrotreating in Subtask 2.5.7.2 entitled “Neat Naphtha Hydrotreating.” Inspection testing on the neat F-T diesel products from Subtask 2.5.2 and Subtask 2.5.7.1 b&c are presented in Table 6. The individual product streams were approved for composite blending for product evaluations reported in separate Task 2.5 and Task 2.6 Topical reports.

A designated amount of the composite blend will be upgraded in Subtask 2.5.7.6 entitled “Neat Diesel Hydrotreating.” The Subtask 2.5.7.6 hydrotreated diesel product will then undergo product evaluations in Task 2.6. A second designated quantity of the combined blend of Subtask 2.5.2 and Subtask 2.5.7.1.b&c neat F-T diesel overhead distillation products will go directly to product evaluation in Subtask 2.6.1 entitled “Lubricity Additive Testing” to measure the lubricity property of the neat F-T diesel and determine the need for treatment with a commercial additive to pass lubricity. A Subtask 2.6.1 neat F-T diesel product passing lubricity will qualify for product evaluation in Subtask 2.6.2 entitled “Hot-Start Cycle Transient Engine Test” and in Subtask 2.6.3 entitled “Solvent Extraction of Particulate Matter.”

Table 1 - Subtask 2.5.2

Mass Balance Closure
Around Subtask 2.5.2 Lab Batch Fractionation

Feed Analyses	**F-T Heavy Product**	**F-T Light Product**			
Weight, lbs (kg)	**472 (214.5)**	**131 (59.5)**			
Wt%	**78.3**	**21.7**			
Product Analyses	**Neat F-T Naphtha IBP-466°K IBP-380°F**	**Neat F-T Diesel 466°K-644°K 380°F-700°F**	**Neat F-T Wax 644°K+ 700°F+**	**Losses**	**Recovery**
Weight, lbs (kg)	**25.3 (11.5)**	**61 (27.7)**	**509.7 (231.7)**	**7 (3.2)**	
Wt%	**4.2**	**10.1**	**84.5**	**1.2**	**98.8**

Table 2 - Subtask 2.5.2

Neat F-T Naphtha Product Properties
From Subtask 2.5.2 Lab Batch Fractionation

(Blend Component with Subtask 2.5.7.1.b&c Neat F-T Naphtha)

ILT ID No.		2066772	
Gravity, °API		57.1	
Specific Gravity		0.7503	
Nitrogen	ppmw	2.5	
Sulfur	ppmw	<6	
		Temperature, (K)	(°F)
Simulated Distillation, V%			
	1%	334	141
	5%	360	188
	10%	369	204
	30%	422	300
	50%	432	319
	70%	447	345
	90%	466	379
	95%	468	383
	99%	470	387

Table 3 - Subtask 2.5.2			
Neat F-T Diesel Product Properties From Subtask 2.5.2 Lab Batch Fractionation (Blend Component with Subtask 2.5.7.1.b&c Neat F-T Diesel)			
ILT ID No.		**2066770**	
Gravity, °API		**43.5**	
Specific Gravity		**0.8086**	
Nitrogen	**ppmw**	**11**	
Sulfur	**ppmw**	**<6**	
		Temperature, (K)	**(°F)**
Simulated Distillation, V%			
	1%	**439**	**331**
	5%	**467**	**382**
	10%	**486**	**416**
	30%	**526**	**487**
	50%	**572**	**570**
	70%	**605**	**630**
	90%	**636**	**686**
	95%	**643**	**698**
	99%	**653**	**716**

Table 4 - Subtask 2.5.2

Neat F-T Wax Product Properties
From Subtask 2.5.2 Lab Batch Fractionation
Wax Testing Limited To Material Balance Closure on Subtask 2.5.2

(Wax Intended As End Use Product for Subtask 2.5.8 Wax Fractionation - Work Did Not Proceed on Subtask 2.5.8)

ILT ID No.		2066769	
Gravity, °API			
Specific Gravity			
		Temperature, (K)	(°F)
Simulated Distillation, V% (Difficult to dissolve wax in Carbon Disulfide Solvent)			
	1%	679	763
	5%	689	781
	10%	693	788
	30%	773	932
	50%	962	1273
	53%	>1008	>1355
	90%		
	95%		
	99%		

Table 5 - Subtask 2.5.2 Inspection Tests on Neat F-T Naphtha Products Task 2.5.2 and Subtask 2.5.7.1a&b&c Fractionation Products Blending for End Use Product for Task Sub 2.5.7.2 Neat F-T Naphtha Hydrotreating				
Subtask	**2.5.2**	**2.5.7.1.a**	**2.5.7.1.b**	**2.5.7.1.c**
Product Identification	**Naphtha IBP- 466K IBP-380°F**	**Naphtha IBP- 466K IBP-380°F**	**Naphtha IBP- 466K IBP-380°F**	**Naphtha IBP- 466K IBP-380°F**
Analyses				
Gravity, API	**57.1**	**55**	**55.2**	**54.7**
Specific Gravity	**0.7503**	**0.7587**	**0.7579**	**0.7599**
Sulfur, ppmw	**<6**	**2.1**	**0.6**	**0.3**
Nitrogen, ppmw	**2.5**	**1**	**1**	**0.6**

Table 6 - Subtask 2.5.2 Inspection Tests on Neat F-T Diesel Products Task 2.5.2 and Subtask 2.5.7.1a&b&c Fractionation Products Blending for End Use Product for Task Sub 2.5.7.6 Neat F-T Diesel Hydrotreating			
Subtask	**2.5.2**	**2.5.7.1.b**	**2.5.7.1.c**
Product Identification	**Diesel 466K-644K 380°F-700°F**	**Diesel 466K-644K 380°F-700°F**	**Diesel 466K-644K 380°F-700°F**
Analyses			
Gravity, API	**43.5**	**43.7**	**43.7**
Specific Gravity	**0.8086**	**0.8076**	**0. 8076**
Sulfur, ppmw	**<6**	**1.3**	**<1**
Nitrogen, ppmw	**11**	**2**	**2**

Conclusions

1. Lab batch fractionation maximized the yields and qualities of neat F-T naphtha, neat F-T diesel, and neat F-T wax from its feed slate while meeting fuel and specialty wax boiling range specifications.

2. The end use products generated from lab batch fractionation were used for feedstocks and materials in Task 2.5 and Task 2.6 product evaluations and contributed to the success of all Phase II RD&T.

Bibliography

1. United States of America Patent Number 5,904,834 entitled “Synthetic Wax for Food Applications”, assigned to inventors Messrs. Joachim Ansorge, Arend Hoek, Willem Pieter Leenhouts, and Robert Anthony John Priston of the Shell Research Limited, May 18, 1999.

List of Acronyms and Abbreviations

AGR – acid gas removal unit
ASTM - American Society for Testing and Materials
California Air Resources Board - CARB
California Code of Regulations – CCR
Carbon Dioxide – CO_2
Carbon Monoxide – CO
cm - centimeters
Code of Federal Regulations – CFR
Coefficients of Variation - COV
DCRP – Delaware City Repowering Project
Department of Emissions - DER
Detroit Diesel Corporation – DDC
EECP – Early Entry Coproduction Plant
Environmental Protection Agency- EPA
Federal Test Procedure – FTP
F-T -Fischer-Tropsch
ft – feet
g – gram
GC – gas chromatograph
HC - Hydrocracker
HT – Hydrotreater
H_2 – Hydrogen
Hydrocarbons – HC
IGCC – Integrated Gasification Combined Cycle
in – inch
kPa – kilo Pascals
kg - kilograms
mm – millimeter
O_2 – carbon dioxide
Oxides of Nitrogen - NO_x
Psia – pounds force per square inch absolute
ppm - parts per million (weight per volume)
Soluble Organic Fraction – SOF
SRU – Sulfur recovery unit
Sulfate – SO_4
SwRI – Southwest Research Institute
TGTU – Tail gas recovery unit
Total Particulate – PM
WTC – Westhollow Technology Center
wt% - weight percent

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix B - Test Report

Subtask 2.5.3: FISCHER-TROPSCH LIQUID HYDROCRACKING PILOT PLANT RUN

Reporting Period: January 2003 - May 2003

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Date Issued: June 21, 2003

Background

In the EECP concept, one of the product upgrading options is hydrocracking of the Fischer-Tropsch (F-T) hydrocarbon liquids to produce high quality (low sulfur and high cetane) diesel. As part of the RD&T Plan from Phase II of the EECP, F-T products from the La Porte demonstration run were blended to represent the whole F-T liquid product slate and hydrocracked with ChevronTexaco's ISOCRACKING technology.

Invented by ChevronTexaco, ISOCRACKING was the first modern hydrocracking technology, and today it is the premier hydrocracking technology in the world. Since its commercial introduction (1962), 50 ISOCRACKING units have been built and operated. 22 additional ISOCRACKING units are in various stages of engineering and construction.

ISOCRACKING® catalysts are dual-functional; the catalyst contains both a hydrogenation and a cracking function. The cracking sites promote cracking reactions, which reduce the size of the feed molecules to the molecular weight range desired for the products. The hydrogenation sites remove impurities from and saturate any double bonds in the feed or product molecules to produce clean, hydrogen-rich products.

ISOCRACKING technology is ideally suited to upgrading Fischer-Tropsch (F-T) products. The absence of any significant levels of sulfur or nitrogen means the ISOCRACKING® catalyst can operate in a clean environment, producing high yields of middle distillates. The paraffinic nature of F-T material means that the products from the ISOCRACKING unit will also be highly paraffinic, ideal for jet and diesel fuel.

ISOCRACKING technology embodies four process configurations together with more than 15 proprietary ISOCRACKING® catalysts. Design engineers select from among these process configurations and catalysts to match feedstock processing requirements with product manufacturing needs. For this program the commercially-proven single-stage recycle ISOCRACKING unit configuration was selected in combination with a commercially-proven, middle-distillate-selective ISOCRACKING® catalyst to maximize the yield of high quality diesel fuel obtained from F-T condensate and wax.

The products from the ISOCRACKING pilot plant run were fractionated into a naphtha range material and a diesel range material. The diesel range material was analyzed and engine tested to confirm its properties and performance as a high quality diesel fuel. The naphtha range material was analyzed and tested to confirm its suitability as a feedstock for ethylene cracking and fuel cell reforming.

Experimental

Process Description

ChevronTexaco Technology Marketing (TEMA) performed Pilot Plant Run 81-143 for the hydrocracking test of the Fischer-Tropsch product. Figure 2.5.3-1 shows the block flow diagram of the pilot plant setup for the hydrocracking test. This is the standard configuration for a hydrocracking pilot plant.

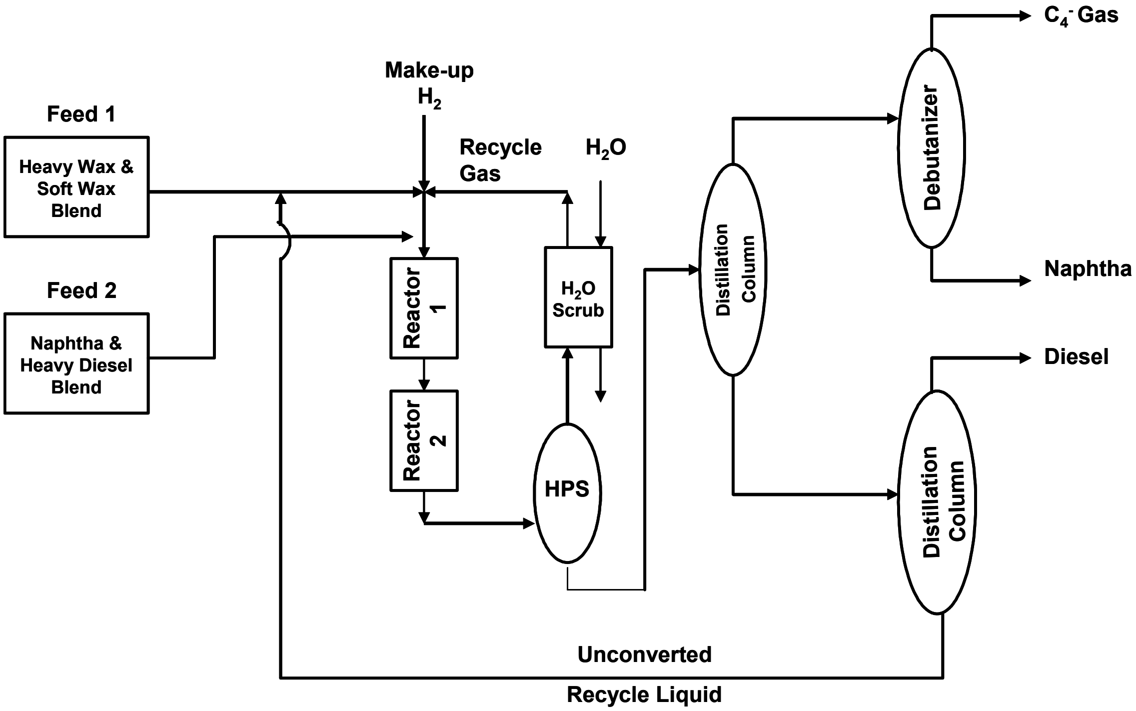


Figure 2.5.3-1 Hydrocracking Pilot Plant Block Flow Diagram

Feed 1 containing the Heavy Wax and Soft Wax Blend is mixed with the Unconverted Recycle Liquid. Then it combines with the Make-up Hydrogen and Recycle Gas before mixing with the Naphtha and Heavy Diesel Blend (Feed 2). The combined feeds are then fed to the hydrocracking reactors. There are two reactors in series. The reactors contain commercially proven middle-distillate-selective ISOCRACKING® catalyst. The reactor effluent then goes to a High Pressure Separator (HPS) where the liquid is separated from the vapor. The liquid is sent to distillation where it is separated into butane and lighter gases, naphtha (C5-466K, 380°F), diesel (466-644K, 380-700°F) and unconverted liquid to be recycled to the feed. The vapor from the HPS, composed mainly of hydrogen, is scrubbed with water to remove the trace amount of ammonia (NH_3) formed from the nitrogen in the feed. It is then recycled back to the reactors.

Feedstocks

The hydrocarbon products from the Fischer-Tropsch demonstration at the Alternative Fuels Demonstration Unit (AFDU) in La Porte, TX were used as the feed for the hydrocracking tests. ChevronTexaco Integrated Laboratory Technologies (ILT) performed much of the work in preparing a Fischer-Tropsch total hydrocarbon liquid feed for this task.

The pilot plant has two feed systems and two blends were made for the pilot plant test—the diesel & naphtha blend (Feed 2) and the heavy wax & soft wax blend (Feed 1). The diesel and naphtha blend (Feed 2) was prepared from the light hydrocarbon products from La Porte. The heavy wax was filtered to less than 10 ppm solids and blended with the soft wax for the heavy and soft wax blend (Feed 1). Table 2.5.3-1 gives the total volume and proportions of the blends. The ratio of each component in the blend in the feed was made to reflect the total liquid hydrocarbon product slate from the La Porte Demonstration.

Table 2.5.3-1 Hydrocracker Feed Blends

	Feed Component	Volume, m^3	Volume, Gallons	Volume % of Blend	% of Feed to Reactor	ID
Feed 2	Heavy Diesel	0.0594	15.7	66	15.9	WOW9258
	Neat Naphtha	0.0307	8.1	34		
Feed 1	Heavy Wax	0.437	115.5	91.5	84.1	WOW9257
	Soft Wax	0.0405	10.7	8.5		

Properties of these feed blends are given in Table 2.5.3-2. The boiling range target for the hydrocracked diesel product was 466-644 K (380-700ºF). The following lists the expected hydrocracked diesel product quality based on the target boiling range:

- Cloud Point/Cold Flow Plugging Point <-253K (10ºC)
- Flash Point >323 K (50ºC)
- Cetane Number/Cetane Index >70
- Viscosity @ 313 K (40ºC) >2.0 cSt
- TAN <0.05 mg KOH/g

The original goal was to produce 0.102 m^3 (27 gallons) of diesel product (466-644 K, 380-700ºF) at design, steady state conditions. This target was later modified to a minimum of 0.151 m^3 40 gallons to meet the fuel testing requirements (see Task 2.5.7.6).

Table 2.5.3-2

Feed Properties for Hydrocracking Pilot Plant

	Description		Heavy Wax / Soft Wax Blend		Diesel/Naphtha Blend	
	Sample ID		WOW9257		WOW9258	
	Gravity, °API		33.8		45.3	
	Specific Gravity		0.86		0.80	
	Nitrogen	wt, ppm	6.3		9.1	
	Sulfur	wt, ppm	3.2		2.2	
PONA	Aromatic	Vol %			pending	
	Olefin	Vol %			42.8	
	Paraffin/Naphthene	Vol%			37.2	
	Total N-paraffins	wt %	32.4			
	Oxygen by NAA	wt %	0.74		3.33	
	ASTM Color				0.3	
	Pour Point	K (°C)			257 (-16)	
	Cloud Point	K (°C)			302 (29)	
	Karl Fischer Water	ppm			0.25	
Simulated Distillation, LV%			Temperature, K	°F	Temperature, K	°F
		IBP			330	134
		0.5%			337	147
		5%			390	243
		10%			410	279
		30%			465	378
		50%			554	538
		70%			596	613
		90%			632	678
		95%			644	699
		99%			660	729
		EP			665	738
Simulated Distillation, WT%		IBP (1 %)	616	650		
		5%	681	767		
		10%	692	786		
		30%	754	898		
		50%	900	1160		
		61%	998	1338		
		EP (61.4%	1008	1355		

Results and Discussion

Hydrocracked Products and Yields

Diesel product properties were taken during yield periods. Table 2.5.3-3 documents the yields relative to feed as well as the product properties from the pilot plant test. The Cloud Point of the diesel was 257 K (-16°C). The average specific gravity was approximately 0.784 (49°API) and the Cetane Indexes were in the high 70's.

Table 2.5.3-3

Yields Relative to Feed and Product Properties

Run Number	81-143	
Run Hours	1214-1238	
Prod. Yields	WT. %	VOL. %
Total C4-	4.6	
C5-466 K (380°F)	35.6	43.1
466-644K (380°F-700°F)	59.9	64.6
Total C5+	95.5	107.7
H2 Consumption	sm^3/m^3	SCF/B
	169	951
Material Balance Closure, wt%	99	
Diesel Product Properties		
Specific Gravity	0.78	
Gravity, °API	49.1	
Cloud Pt, K (°C)	257 (-16)	
Flash Pt, K (°C)	342 (69)	
Cetane Index	78	
Simdist (D2887)		
Volume Percent	Temperature, K	°F
St	399	258
5	462	372
10	480	405
30	524	484
50	561	551
70	596	613
90	630	675
95	639	690
99.5	647	705

Diesel Production and Blended Product Qualities

A total of 0.151 m^3 (40 gallons) of on-spec hydrocracked diesel was produced during the hydrocracking operations. The first 0.123 m^3 (32.5 gallons) collected were labeled as WOW9298. 0.083 m^3 (22 gallons) of WOW9298 were sent to Southwest Research Institute (SWRI) for Hot-Start Cycle Transient Engine Test (Task 2.6.2) and Solvent

Extraction (Task 2.6.3). 0.0038 cubic meters (1 gallon) was retained for analysis. The remaining 0.036 m^3 (9.5 gallons) of WOW9298 along with 0.011 more cubic meters (3 gallons) of pilot plant diesel product produced late in the pilot plant run were blended with 0.0397 m^3 (10.5 gallons) of the hydrotreated diesel and labeled as WOW9306. The hydrocracked-hydrotreated diesel blend was made because there was not enough hydrotreated diesel for the Hot-Start Cycle Transient Engine Test and Solvent Extraction (See Task 2.5.7.6). Again, 0.0038 cubic meters (1 gallon) of the hydrotreated-hydrocracked diesel blend was retained for analysis and 0.0833 m^3 (22 gallons) were sent to Southwest Research Institute (SWRI) for Task 2.6.2 and Task 2.6.3. The final 0.015 m^3 (4 gallons) of pilot plant diesel produced at the end of the run were labeled as WOW9311. 0.0038 cubic meters (1 gallon) was retained for analysis and the other 0.011 m^3 (3 gallons) were sent to SWRI for Diesel Blending Tests (Task 2.5.6). The following Table 2.5.3-4 summarizes the diesel blends and its purpose. Table 2.5.3-5 gives the product properties for the various diesel blends.

Table 2.5.3-4 Hydrocracked Diesel Blends for Testing

ID	Description	Purpose
WOW9298	0.123 m^3 (32.5 gallons) produced Shipped 0.0833 m^3 (22 gallons); 0.0038 cubic meters (1 gallon) retained for analysis	Task 2.6.2 Hot Transit Engine Testing & Task 2.6.3 Solvent Extraction for hydrocracked diesel
WOW9306	0.036 m^3 (9.5 gal) WOW9298 + 0.011m^3 (3 gal) HCR Diesel 0.0397m^3 (10.5 gal) HDT Diesel Shipped 0.0833 m^3 (22 gallons); 0.0038 cubic meters (1 gallon) retained for analysis	Task 2.6.2 Hot Transit Engine Testing & Task 2.6.3 Solvent Extraction for hydrotreated diesel
WOW9311	0.011 m^3 (3 gal) produced at the end of the run	Task 2.5.6 Diesel Blending

The naphtha products from the pilot plant run were all blended together and labeled as PGQ1145. A sample was sent for fuel cell reformer testing (Task 2.5.7.4). The naphtha product qualities are given in Table 2.5.3-5. The naphtha product had a Total Acid Number (TAN) of less than 0.05 milligram KOH per gram. The Research Octane was low (as expected)—less than 40.

Table 2.5.3-5
Hydrocracked Product Properties

Description		Naphtha		Diesel		Diesel Blend		Diesel	
						55% HCR'd Diesel		End of Test	
ID		PGQ1145		WOW9298		WOW 9306		WOW9311	
Specific Gravity		0.71		0.78		0.79		0.79	
Gravity, °API		67.1		48.9		48.6		48.7	
Nitrogen	wt ppm	< 0.1		< 0.1		< 0.15			
Sulfur	wt ppm	2.1		< 1		< 1			
AED Analyses									
Oxygen	wt %	not available							
Alcohol	wt %	not available							
Olefins	wt %	not available							
ASTM Color				0.0		0			
Pour Point	K (°C)			245 (-28)		263 (-10)			
Cloud Point	K (°C)			257 (-16)		272 (-1)			
Cold Filter Plugging Point	K (°C)			258 (-16)		270 (-3)			
Karl Fischer Water	ppm	< 10							
Aromatics	wt %			pending		pending			
Ramsbottom Carbon	wt %			0.05		0.05			
TAN	mg KOH / g	< 0.05		< 0.05		< 0.05			
Viscosity at 40 °C	cSt			3.0		3.0			
Flash Pt	K (°C)			349 (76)		354 (81)			
Ash Oxide, D482	wt %			< 0.005		< 0.005			
Research Octane		<40							
Cetane Number				73.6					
Cetane Index				74.9					
		Temperature							
		K	°F	K	°F	K	°F	K	°F
Simulated Distillation, LV%	IBP	294	70	360	188	360	189	340	152
	0.5%	296	74	390	242	397	256	370	207
	5%	329	132	462	373	467	382	457	363
	10%	333	140	481	407	487	417	482	409
	30%	369	204	525	486	526	487	535	503
	50%	397	256	560	549	560	549	567	562
	70%	424	303	594	609	595	612	599	618
	90%	454	358	627	669	629	672	629	673
	95%	461	370	635	683	637	688	636	686
	99%	471	388	642	697	647	706	644	699
	99.5%	474	394	645	701	651	713	645	702
D86 Distillation, LV%	IBP			439	330	444	340		
	5%			474	394	479	402		
	10%			495	431	497	435		
	30%			534	502	534	501		
	50%			570	566	567	562		
	70%			601	623	601	622		
	90%			631	676	630	674		
	95%			639	691	638	689		
	EP			640	692	645	701		

The hydrocracked diesel blend (WOW9298) met all of the product quality targets as listed below.

	Expected Product Spec's	**Actual (WOW9298)**
Cold Flow Plugging Point	< 263 K (-10°C)	257 K (-16°C)
Flash Point	> 323 K (50°C)	349 K (76°C)
Cetane Number/ Cetane Index	>70	73.6/74.9
Viscosity @ 40°C	> 2.0 cSt	3.0 cSt
TAN	<0.05 mg KOH/g	<0.05 mg KOH/g

The hydrocracked diesel had a cloud point of 257 K (-16ºC). The hydrotreated diesel had a cloud point of 280 K (7ºC). The blend of hydrocracked and hydrotreated diesel resulted in a cloud point of 272K (-1ºC).

Conclusions

Approximately 0.35 m^3 (93 gallons) of Fischer-Tropsch hydrocarbon liquids were hydrocracked using ChevronTexaco Technology Marketing's (TEMA's) pilot plant. The run produced 0.10 m^3 (27 gallons) of naphtha range material and approximately 0.15 m^3 (40 gallons) of on-spec diesel material. The diesel range material met or exceeded all of the product quality targets.

List of Acronyms and Abbreviations

°API	degree(s) API
°C	degrees Celsius
°F	degrees Fahrenheit
AFDU	Alternative Fuels Demonstration Unit
API	American Petroleum Institute
ASTM	American Society of Testing and Materials
C#	hydrocarbons with # number of carbons
C#-	hydrocarbons with less than # number of carbons
C#+	hydrocarbons with more than # number of carbons
cSt	centistoke(s)
EECP	Early Entrance Co-Production
EP	End Point
Fe	Iron
F-T	Fischer-Tropsch
g	gram
gal	gallons
H_2	Hydrogen
H_2O	Water
HPS	High Pressure Separator
IBP	Initial Boiling Point
ID	Identification
ILT	ChevronTexaco Integrated Laboratory Technologies
K	kelvin(s)
KOH	potassium hydroxide
LV%	liquid volume percent
m^3	cubic meter(s)
mg	milligram(s)
NAA	Neutron Activation Analysis
NH_3	Ammonia
N-paraffins	normal paraffins
ppm	parts per million
Prod.	Product
Pt	point
RD&T	Research, Development and Testing
SWRI	Southwest Research Institute
TAN	Total Acid Number
TEMA	ChevronTexaco Technology Marketing
TX	Texas
vol%	volume percent
wt	Weight
wt%	Weight percent

Early Entrance Coproduction Plant
Bechtel Wax Hy Finishing^{SM}
Appendix C – Test Report

Subtask 2.5.4: Wax Finishing

Reporting Period:	December 2002 - May 2003
Contributors:	Marjan J. Roos
Date Issued:	May 2003

EXECUTIVE SUMMARY

The purpose of this study is to perform pilot testing to confirm the required operating conditions for upgrading of a Fischer-Tropsch (FT) Product, utilizing Bechtel Wax Hy-Finishing^{SM} technology.

The Hy-Finishing^{SM} Unit would treat the feed from an upstream Fischer-Tropsch Synthesis Unit covering a full boiling range of liquid products. The goal is to process the full boiling range of feeds simultaneously in the Hy-Finishing^{SM} unit, producing stabilized naphtha, low sulfur diesel and finished food grade waxes. An alternative would be to Hy-Finish^{SM} the wax only, producing finished food grade waxes.

The Early Entrance Coproduction Plant (EECP) FT Product Upgrading Pilot Testing Program consists of the following Tasks

Task A: Blending and Analysis of the Feedstock
Task C: Design Basis Confirmation

The catalyst used for the Design Basis Confirmation is a nickel catalyst (alumina-based).

If the wax is treated separately from the naphtha/diesel fraction, an on-spec food grade wax can be obtained. However, it is not possible to process the full boiling range of liquid Fischer Tropsch products simultaneously. In the pilot unit, the temperature required to separate the naphtha/diesel from the wax in an atmospheric column downstream of the reactor results in discoloration of the wax product.

The selected reactor operating conditions from the pilot units are as follows

- Reactor Temperature - 603 K (625 °F)
- Reactor Pressure - 13891 kPa (2000 psig)
- Hydrogen Treatgas Rate - 674 Nm^3/m^3 (4000 scf/bbl) Hydrogen (H_2)/oil
- Liquid Hourly Space Velocity (LHSV) – 0.5

It should be noted that the temperature in the reactor is unstable and numerous episodes of runaway temperatures occurred during the pilot testing program.

If any further pilot testing with the Nickel catalyst is performed, it is recommended to use a jacketed reactor with a heat transfer fluid to take away the heat of reaction. Furthermore, a vacuum tower should be used for the separation of the naphtha/diesel fraction from the wax fraction. This allows lower reboiler temperatures which will prevent discoloration of the wax.

BACKGROUND

Texaco Energy Systems LLC was selected by the U.S. Department of Energy (DOE) to lead a team that will design the EECP for the production of electricity and high-quality diesel fuel using a combination of ChevronTexaco's proprietary gasification and Rentech's FT technologies.

The team will carry out a research, development and testing program, which will culminate with the creation of the preliminary engineering design for commercial implementation of a multi-product plant.

ChevronTexaco's initial focus will be to commercialize the EECP concept using low-value hydrocarbons, such as refinery by-products, as the fuel source.

The ChevronTexaco gasification technology, a process that converts solid, liquid or gaseous hydrocarbon feedstocks into synthesis gas, will be used to generate the feed source for the Rentech Fischer-Tropsch technology.

Petroleum coke was selected as the gasification feedstock because, when compared to coal, it is a lower cost feedstock option and a highly probable feedstock for the first application of the co-production concept. The feasibility study was based on an actual Gulf Coast refinery with existing petroleum coke production. Maximum utilization of existing infrastructure allows for capital investment to be minimized thereby improving the economics of the first application of the concept.

In Phase I of the EECP Project, the Motiva Port Arthur Refinery was chosen as the site for a conceptual process design, capital and operating cost estimates, and economic analyses.

Bechtel Hy-Finishing^{SM} was selected for finishing of the FT product. The objective is to treat the full range FT Product in one Hy-Finishing^{SM} unit in order to minimize capital cost. The initial scope of the pilot testing programs consisted of 5 tasks:

Task A: Blending and Analysis of the Feedstock
Task B: Catalyst Screening (Outside of the EECP Project)
Task C: Design Basis Confirmation
Task D: Production Run
Task E: Fractionation of Hy-Finished^{SM} FT Distillate and Wax

As a consequence of the merger of Chevron and Texaco, Texaco's ownership share of the Motiva Port Arthur refinery was sold and is no longer a candidate to site for the EECP Project. Task D, intended to produce 70 gallons of food grade wax, and Task E were specifically designed to support this particular EECP location, and are no longer required as result of the site reevaluation assessment.

EXPERIMENTAL

Introduction

The EECP FT Product Pilot Testing Program scope consists of 2 Tasks

Task A:	Blending and Analysis of the Feedstock
Task C:	Design Basis Confirmation

Task A: Blending and Analysis of the Feedstock

A.1 Introduction

The purpose of this task is to prepare for Hy-Finishing^{SM} pilot testing of a FT product. This task consists of the following steps:

1. Blending of the feed
2. Analytical testing of individual feed components and blended feedstock

The feedstock was shipped in four different fractions:

- FT Naphtha Initial Boiling Point (IBP)-466 K (IBP-380 °F)
- FT Heavy Diesel 505-644 K (450-700 °F)
- FT Soft Wax 644 K+ (700 °F+)
- FT Heavy Wax 644 K+ (700 °F+)

In addition to the above four feedstocks, a separate drum containing cleaned FT Heavy Wax ("Drum 44") and a separate container of FT Soft Wax was provided for start-up of the pilot unit.

A.2 Blending of the Feed

Containers and equipment used in the blending and transfer procedure were rinsed with Isopar solvent and tested to meet the sulfur specification (<0.5 parts per million-weight [ppmw]), nitrogen specification (<0.5 ppmw), and aromatics specification (<0.5 vol.%).

The naphtha and diesel will be fed separately from the waxes. The wax will have to be heated up to 408 K (275 °F), which would result in the loss of naphtha if all feeds were mixed.

Blended feed was prepared using the following blending ratio:

Feed Component Feed Code	Naphtha+Diesel, wt%, 1190	Wax, wt%, 1191
FT Naphtha	4.84	
FT Diesel	10.12	
FT Soft Wax		7.04
FT Heavy Wax		78.00

Separate blends were prepared for each task.

A.3 Analytical Testing

Analytical testing of the two blends (naphtha/diesel and soft wax/hard wax) is performed on the feed stocks per the protocol noted below in Table I.

The feedstock provided by ChevronTexaco contains a quantity of a start-up oil (Durasyn) from the pilot plant used to provide the feedstock**.** Analytical testing of the blended feedstock will confirm the quantity and distribution of Durasyn among the feed components.

Table I. Feedstock Inspection Testing

Section 3i Testing Protocol - Feedstock Inspection Testing			
Analytical Tests	**Test Method**	**FT Naphtha & FT Diesel**	**FT 664 K (700 °F)+ Soft & Hard Waxes**
FT Naphtha	Blend Component , wt%	4.84	
FT Diesel	Blend Component, wt%	10.12	
FT 664 K (700 °F)+ Soft Wax	Blend Component, wt%		7.04
FT 664 K (700 °F)+ Heavy Wax	Blend Component, wt%		78
Durasyn Content, wt.%	(American Society for Testing and Materials [ASTM] D-5442 Modified)		See attchment 3
Gravity, American Petrolum Institute (API)	(ASTM D-1298)	46.0	32.5
Gravity, Specific	(Calculated)	0.7972	0.8628
Distillation by Gas Chromatograph (GC)		ASTM D-2887, K (°F)	ASTM D-2887 Modified High Temp, K (°F)
	IBP	356 (181)	See attachment 1
	5%	397 (255)	
	10%	423 (301)	
	20%	449 (349)	
	30%	489 (420)	
	40%	532 (498)	
	50%	560 (548)	
	60%	585 (594)	
	70%	604 (628)	
	80%	624 (663)	
	90%	643 (697)	
	95%	654 (718)	
	FBP	690 (783)	
Acid Number, mg KOH/g	(ASTM D-664)	4.79	0.86

Section 3i Testing Protocol - Feedstock Inspection Testing

Analytical Tests	Test Method	FT Naphtha & FT Diesel	FT 664 K (700 °F)+ Soft & Hard Waxes
Hydrogen Content, wt%	(ASTM D-4808)		14.3
Flash Point, K (°C)	(ASTM D-92)		522 (249)
	(ASTM D-93)	302 (29)	
Viscosity, cSt	(ASTM D-445)		
@ 313 K (40°C)		1.979	
@ 373 K (100°C)		0.924	not determined
@ 394 K (121.2°C)			23.48
Pour Point, K (ºC)	(ASTM D-97)	283 (10)	
Melting Point, K (ºC)	(ASTM D-87)		379 (106)
Congealing Point, K (ºC)	(ASTM D-938)		371 (98)
Oil Content, weight percent (Wt%) (<15% Oil)	(ASTM D-721)		not determined
Solvent Extractable, Wt% (>15% Oil)	(ASTM D-3235)		not determined
U.S. Food and Drug Administration (FDA) Ultra Violet (UV) Absorbance	(21CFR 172.886 see AST Inc. Lab)		
	Part One		
	280-289 nm		1.106 (fail)
	290-299 nm		0.921 (fail)
	300-359 nm		0.741 (fail)
	360-400 nm		0.262 (fail)
	Part Two		
	280-289 nm		0.236 (fail)
	290-299 nm		0.183 (fail)
	300-359 nm		0.134 (fail)
	360-400 nm		0.024 (fail)
Color, ASTM	(ASTM D-1500)	0.5	7.5
Color, Saybolt	(ASTM D-156)		Out of range
Sulfur, wppm	(ASTM D-2622 if >30 wppm)	N/A	N/A

A.4 Results and Discussion

Wax viscosity at 373 K (100 °C) is not determined; wax is solid at this temperature. Instead, viscosity at 394 K (121.2°C) was reported.

Aromatics content of naphtha diesel blend is reported as 19.1%. This is likely to be wrong. This test may not be suited for this material and maybe classifying other components as aromatics.

ASTM D2887 Modified for wax blend: it was reported previously that 40% of this material boils above 978 K (1300 °F), although the end-point according to the analytical test is 881 K (1127 °F).

ASTM D-721 for oil contents of less than 15% and ASTM D-3235 for Solvent Extractables in Wax of greater than 15% were not determined. The wax shows a lack of solubility in the solvent specified in the ASTM test procedures and further test method development would be required to attain a meaningful result.

The wax blend has not been analyzed for Saybolt color since the ASTM D1500 color is 7.5 The Saybolt color range starts at ASTM D1500 <2.

Task C Design Basis Confirmation For Hy-Finishing^{SM} Of Fischer Tropsch Wax

C.1 Introduction

The purpose of this task is to confirm the operating conditions for the selected catalyst for Hy-Finishing^{SM} pilot testing of a FT wax. This task consists of the following steps

1. Blend the feed into a naphtha/diesel blend and a soft wax/hard wax blend
2. Test the blended FT feed stocks across the Hy-Finishing^{SM} pilot unit P88. Fractionate the stabilized total Hy-Finished^{SM} HF Product, into distillate and wax, to enable the analytical testing required for the design basis confirmation.
3. Test the soft wax/hard wax blend across the Hy-Finishing^{SM} pilot unit at one set of conditions based on the design basis confirmation runs
4. Analytical Testing of the products of Task C

Fixed bed catalytic hydroprocessing pilot plant P88, modified for dual feed, will be used for the design basis confirmation. This pilot unit is dedicated to processing only clean oil feedstocks. A 260cc catalyst bed volume will be used.

C. 2 Pilot Plant Description

Refer to Figure 1. The naphtha/diesel feed and the wax feed are separately charged into bulk feed tanks, then routed to a Feed Weigh Tube. The weight is logged. The feeds are pumped into the preheater using a metering pump, followed by a high pressure booster pump. The wax blend is heated to 422 K (300 °F), while the naphtha/diesel blend is at ambient temperature.

During the catalyst screening task, once-though hydrogen is used. The amount of makeup gas is controlled by a flow meter in the hydrogen make-up line. The gas is compressed to the required pressure by a recycle gas compressor and combined with the liquid feeds.

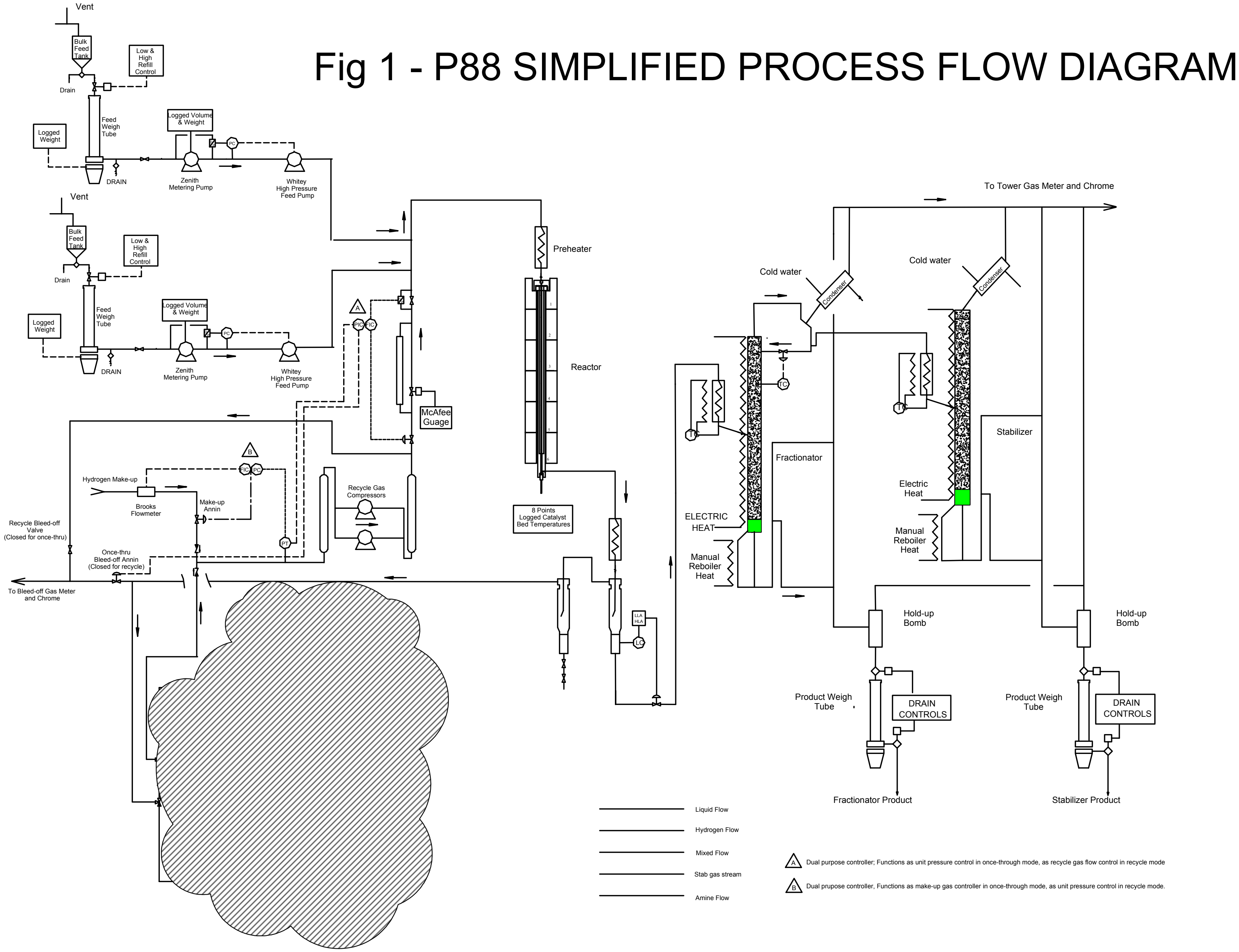
The combined gas/liquid mixture is heated up in the preheater to the required reactor temperature. The reactor is an isothermal fixed-bed reactor with 6 heater blocks and 8 thermocouples to log catalyst bed temperatures. Maximum single reactor catalyst bed capacity is 434 cc with a maximum feed rate of about 800 cc/hr and a maximum temperature of 811K (1000 °F). For the catalyst screening runs a 260 cc catalyst bed is used, and the feed rate is 130 – 260 cc/hr (0.5-1 LHSV).

The reactor bottoms is cooled and routed to a separator, where the separation of reactor product gas and liquid takes place. The bleed–off gas flow is logged and analyzed. The liquid reactor product continues to the fractionator. The fractionator is an atmospheric tower where the naphtha/diesel is separated from the wax. The fractionator bottoms are collected in a holdup bomb and the amount of product is weighted.

The fractionator overhead flows to the Stabilizer Tower, the liquid product is collected in a holdup bomb and the amount of product is weighted.

The off-gas from the fractionator and stabilizer are combined, the flow rate is logged and the gas is analyzed.

Fig 1 - P88 SIMPLIFIED PROCESS FLOW DIAGRAM



C.3 Reactor cleaning

1. Clean the reactors by alternately toluene soaking and wire brushing until the toluene comes out water-white.

2. Flush all part of the unit that are to be in service with toluene.

    - Boil toluene in the tower(s) to clean the packing, condenser and reflux system.
    - Periodically drain low spots and dead-end lines.
    - Continue until the effluent liquids are near water-white.

3. Replace toluene with Isopar.

    - Continue to drain low spots and dead-end lines.
    - When the composite effluent is the same color as the feed, analyze for sulfur.
    - If the product contains sulfur, sample at various points (separator, tower bottoms, etc), and analyze for sulfur to determine the source of contamination.
    - If necessary, remove the tower packing, burn off carbon deposits, clean and reinstall tower.
    - Likewise, if necessary, remove product tube(s) and clean in the same manner as the reactor.
    - Continue flushing until the composite product meets the sulfur specification (<0.5 ppmw), nitrogen specification (<0.5 ppmw), and aromatics specification (<0.5 vol.%).

C.4 Design Basis Confirmation – wax blend

Table I. Design Basis Confirmation Operating Conditions – wax blend feed

Run	**P88-60-**					
Catalyst	Nickel catalyst (alumina based)					
Feed/Code	Blended FT Start-Up Wax					
ASTM D1500 color	7.5					
Run no. P88-60-	**1**	**2**	**3**	**4**	**5**	
LHSV	0.5	0.5	0.5	0.5	0.5	
Pressure, kPa (psig)	13891 (2000)	13891 (2000)	13891 (2000)	13891 (2000)	10443 (1500)	
Temperature, K (°F)	561 (550)	589 (600)	603 (625)	616 (650) (*)	603 (625)	
H2 circulation, Nm^3/m^3 (scf/bbl) Once thru	674 (4000)	674 (4000)	674 (4000)	674 (4000)	674 (4000)	
ASTM D1500 color	2.5	0.5	0.0	-	1.0	

Noticeable improvement in wax color with increased reactor temperature. Run P88-60-4 took too long to line out, and the run was aborted. Lower pressure run P88-60-5 results in darker product color. Run P88-60-3 meets the UV Adsorption and the Saybolt color spec (+30).

C.5 Design Basis Confirmation – Full Range Feedstock

For continuation of the design basis confirmation task with full range feedstock, the stabilized total liquid Hy-Finished^{SM} product will have to be fractionated in a distillate (664 K/700 °F minus) and a wax (664 K /700 °F plus) fraction. This separation will take place in the fractionator. The fractionator reboiler temperature is set at 603 K (625 °F). Instead of once through hydrogen, the gas will be recycled.

Listed below are the scheduled operating conditions. A decision tree method based on results of each previous run will be used to select the operating conditions for the following run. The first run will be a repeat of run P88-60-3, but with full range feed and recycle gas instead of once through.

Table II. Design Basis Confirmation Operating Conditions – full range feed

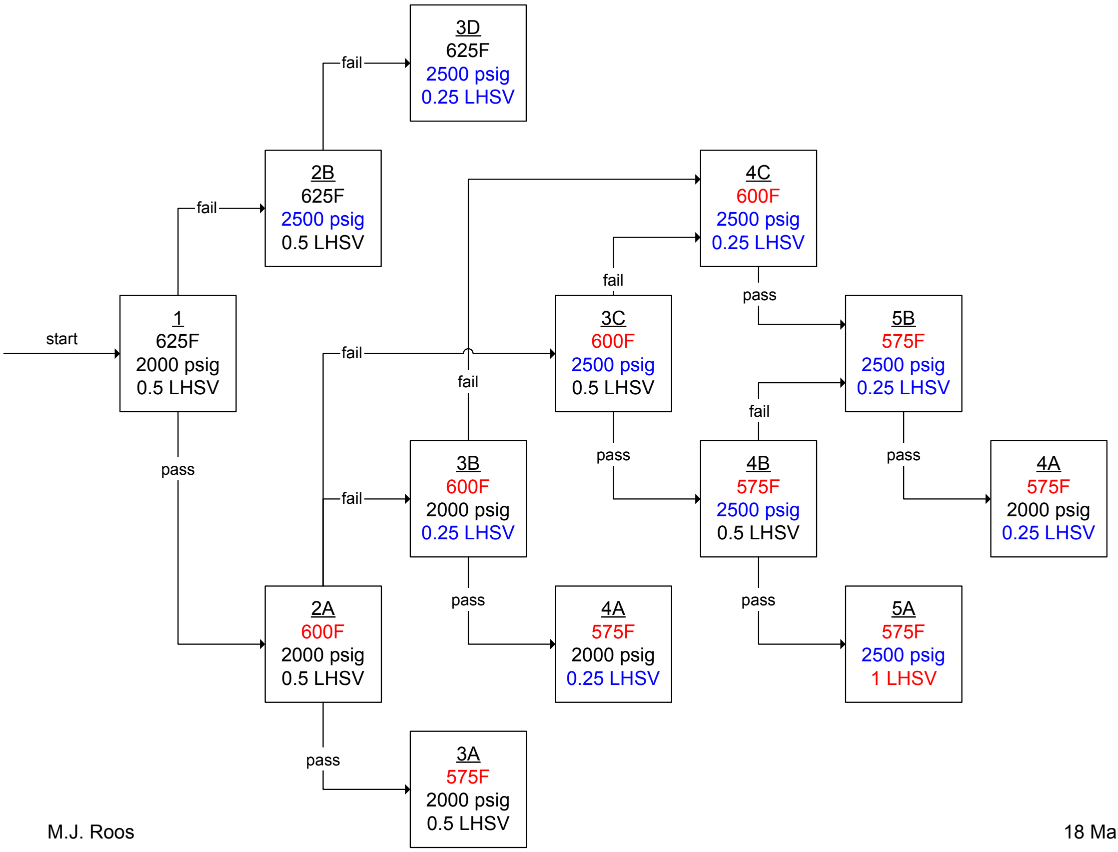
Pilot Unit	**P88-62-**					
Catalyst	Nickel catalyst (alumina based)					
Feed	FT Naphtha/Diesel blend , FT Wax Blend					
Run no. P88-62-	**1**	**2A**	**2B**	**3A**	**3B**	**3C**
Temperature, K (°F)	603 (625)	589 (600)	603 (625)	575 (575)	589 (600)	589 (600)
Pressure, kPa (psig)	13891 (2000)	13891 (2000)	2500	13891 (2000)	13891 (2000)	2500
LHSV	0.5	0.5	0.5	0.5	0.25	0.5
H2 circulation, Nm^3/m^3 (scf/bbl) Recycle mode	674 (4000)	674 (4000)	674 (4000)	674 (4000)	674 (4000)	674 (4000)

Pilot Unit	**P88-62-**					
Catalyst	Nickel catalyst (alumina based)					
Feed	FT Nap/Dsl blend, FT Wax Blend					
Run no. P88-62-	**3D**	**4A**	**4B**	**4C**	**5A**	**5B**
Temperature, K (°F)	603 (625)	575 (575)	575 (575)	589 (600)	575 (575)	575 (575)
Pressure, kPa (psig)	2500	13891 (2000)	2500	2500	2500	2500
LHSV	0.25	0.25	0.5	0.25	1	0.25
H2 circulation, Nm^3/m^3 (scf/bbl) Recycle mode	674 (4000)	674 (4000)	674 (4000)	674 (4000)	674 (4000)	674 (4000)

See decision tree for the path to follow.

Fig. 2 Design Basis Confirmation Operating Conditions Decision Tree

ChevronTexaco EECP FT Pilot Testing - Task C Design Basis Confirmation



M.J. Roos

18 Mar 03

Methane starts building up in the recycle gas even when heating up on Isopar feed. Appearently, methane groups are broken off from the Isopar. Upon reaching 561 K (550 °F) run feed is introduced, starting with the wax blend. Upon introduction of the naphtha/diesel blend, an exotherm occurred passing through the entire bed in about 5 minutes. After cool down and reintroduction of the feeds another exothem occurred. The methane content of the recycle gas increased to over 75 %wt, indicating that major cracking occurred. After cooling down, the unit was further heated up with product of a previous run in order to try to avoid new runaway reactions. Upon reaching 578K (580 °F), the feed was changed to wax blend. During further heating some minor exotherms occurred, until the pressure in the reactor started building up. The unit had to be shut down, and the catalyst bed had collapsed. The wax product from the fractionator bottom was brown during all this time.

After these experiences, it was decided to load the reactor with diluted catalyst, i.e. half of the catalyst was mixed with inert material on a 50/50 basis, and the bottom of the reactor was loaded with the remaining undiluted catalyst. Also, it was decided to add two runs to age the catalyst before starting with run 1. The first run was to be done with wax feed only, and once-thru hydrogen. The second run was to be done with wax feed only, and with recycle hydrogen.

Table III. Design Basis Confirmation Operating Conditions – diluted catalyst

Pilot Unit	**P88-63-**					
Catalyst	Nickel catalyst (alumina based)					
Feed	FT Wax Blend					
Run no. P88-63-	1	2				
Temperature, K (°F)	603 (625)	603 (625)				
Pressure, kPa (psig)	13891 (2000)	13891 (2000)				
LHSV	0.5	0.5				
H2 circulation, Nm^3/m^3 (scf/bbl)	674 (4000) Once thru	674 (4000) Recycle				

No exotherms were experienced during heating up of the unit. The wax product from the fractionator bottom was still brown. A major exotherm occurred while the unit was operating at 603K (625 °F), followed by two minor exotherms. The exotherms all began in the bottom of the bed (in the undiluted catalyst) and worked their way up in the diluted portion of the bed. It was decided to abort the experiments after the last exotherm in order not to compromise safety issues.

C.6 Design Basis Confirmation – Heavy Feedstock

One design basis confirmation run was scheduled to be done with heavy feedstock at the operating conditions selected based on the results of the runs above. It was decided to use the results from run P88-60-3 for this confirmation run, and not to perform any further testing.

C.7 Analytical Testing

Since no distillate cut material was produced, extended analytical testing was only performed on the wax product from run P88-60-3. It should be noted that this material has not been stabilized.

Table IV. Design Basis Confirmation Analytical Testing Requirements – Wax product

Section 3.iii Testing Protocol Basis for Design - Product Testing for Feed Composed of FT Heavy Product Liquid			
Analytical Tests	Test Method	Food Grade Wax Cut Specification Tests	Measured Results
Melting Point, K (°C/°F)	(ASTM D-87)	>326 (54.4°C/130°F)	376 (103/217)
Oil Content, wt. %	(ASTM D-721) If >15wt% Oil see D-3235	0.5 Max	28.48
Solvent Extractables, wt%	(ASTM D-3235)	Report if D-721 >15 wt%	32.75
Color, Saybolt	(ASTM D-156)		
Initial		Plus 30 Min	+30

Section 3.iii Testing Protocol
Basis for Design - Product Testing for Feed Composed of FT Heavy Product Liquid

Analytical Tests	Test Method	Food Grade Wax Cut	Measured Results
30 Days Storage		Plus 30 Min	+30
FDA UV Absorbance	(21CFR 172.886) see AST Inc. Lab*		
	Part One	Pass	Fail
	Part Two,		
	280-289 nm	0.150 Max	0.123 (pass)
	290-299 nm	0.120 Max	0.089 (pass)
	300-359 nm	0.080 Max	0.058 (pass)
	360-400 nm	0.020 Max	0.012 (pass)
Metals, Iron, wppm	(Texaco to Specify see Shell WTC Lab)*	1 Max	<4.0
Yield, wt% FF	Mass Balance Closure ± 2%	Report	97.5
Yield, vol% FF	Mass Balance Closure ± 2%	Report	-
Gravity, API	(ASTM D-1298)	Report	37.8
Gravity, Specific	(Calculated)	Report	0.8358
Distillation	(ASTM D-2887 or D-2887M High Temp)	Report	See attchment 2
Durasyn By-Products	(ASTM D-5542 Modified)		
Yield, wt% FF	GC Carbon Number Distribution-Extended	Report	See attchment 4
		Characterization Tests	
Congealing Point, K (ºC)	(ASTM D-938)	Report	366 (93)
Penetration @ 350 K (77 ºC), mm	(ASTM D-1321)	Report	73
Viscosity, cSt @ 373 K (100°C)	(ASTM D-445)	Report	Solid
Viscosity, cSt @ 394 K (121.2°C)	(ASTM D-445)	Report	11.35
Sulfur, wppm	(ASTM D-2622 if >30 wppm)	Report if > 30 wppm	<30
Sulfur, wppm	(ASTM D-5430 if <30 wppm)	Report if <30 wppm	0.3
Nitrogen, wppm	(ASTM D-4629)	Report	4.4

C.8 Conclusion

The wax meets the food grade specification tests, except for oil content and FDA UV Absorbance Part One, although it passes Part Two.

Since the wax has not been stabilized, it is not surprising that the oil content exceeds the limit. The light ends may be removed by vacuum distillation.

It is obvious that the catalyst is very active, and uncontrollable cracking reactions occur at the reactor temperatures required for on-spec product. If a commercial unit is built, designed to use Nickel catalyst, it should be designed with quenching options or with a jacketed reactor to be able to take away the heat of reaction.

RESULTS AND DISCUSSION

1. Effect of Fractionator Reboiler Temperature on color of Wax Product

After a full range FT Product is being processed in the Hy-Finishing^{SM} reactor , the product has to be separated into a naphtha/diesel fraction and a wax fraction. This separation takes place in the Fractionator downstream of the Reactor. In order to make a 644K (700 °F) split, stripping nitrogen in combination with a reboiler is used. The fractionator bottom temperature is set at 603 K (625 °F).

If wax only is being processed, no separation has to take place in the Fractionator. In that case the bottom temperature is set at a low temperature, just high enough to ensure that the wax stays fluid, 436 K (325 °F).

It was observed that the color of the fractionator bottom product is sensitive to the reboiler temperature.

Comparison of runs 60-3 / 63-1 shows the impact of fractionator reboiler temperature on the ASTM D1500 color of the wax product. All other operating conditions are identical.

Table V. Impact of Fractionator Reboiler Temperature on ASTM D1500 Color of Wax Product

Run	60-3	63-1
Reboiler temperature, K (°F)	436 (325)	603 (625)
Catalyst	Ni-Alumina-based	Ni-Alumina-based
Feed type	soft+hard wax	soft+hard wax
ASTM D1500 color	0	4

This demonstrates that it is not possible to process the naphtha/diesel feed combined with the wax feed and subsequently separate the products in an atmospheric column because the temperature required for the separation discolors the wax product.

It may be possible to separate the products in a vacuum column provided that the vacuum is deep enough to enable separation at approximately 436 K (325 °F). A preliminary estimate was made showing vacuum required to be 1 mmHg.

2. Temperature excursions with Ni catalyst

Nickel catalysts have shown to be very susceptible to temperature runaways. Exotherms occurred during every series of runs starting at 561 K (550 °F), and reaching temperatures above 811 K (1000 °F). The exotherms could be controlled by either quenching or depressuring the unit. The catalyst did not seem to lose activity as a consequence of these exotherms, although the catalyst collapsed when subjected to temperatures above 922K (1200 °F)

Despite these temperature runaways, the Nickel Alumina-based catalyst was selected as the preferred catalyst for the FT Product Upgrading.

Per client instructions, the design basis confirmation Task C was terminated after two subsequent attempts with the full range FT Product to reproduce the results obtained during the catalyst screening. Both attempts resulted in severe exotherms, while the fractionator product color was off-spec.
It was later discovered that the wax discoloration was caused by thermal degradation in the Fractionator, because the reboiler temperature was set at 603 K (625 °F) for the naphtha/diesel separation.

If any further pilot testing is performed with a Nickel catalyst, it is recommended to use a jacketed reactor with a heat transfer fluid to take away the heat of reaction.

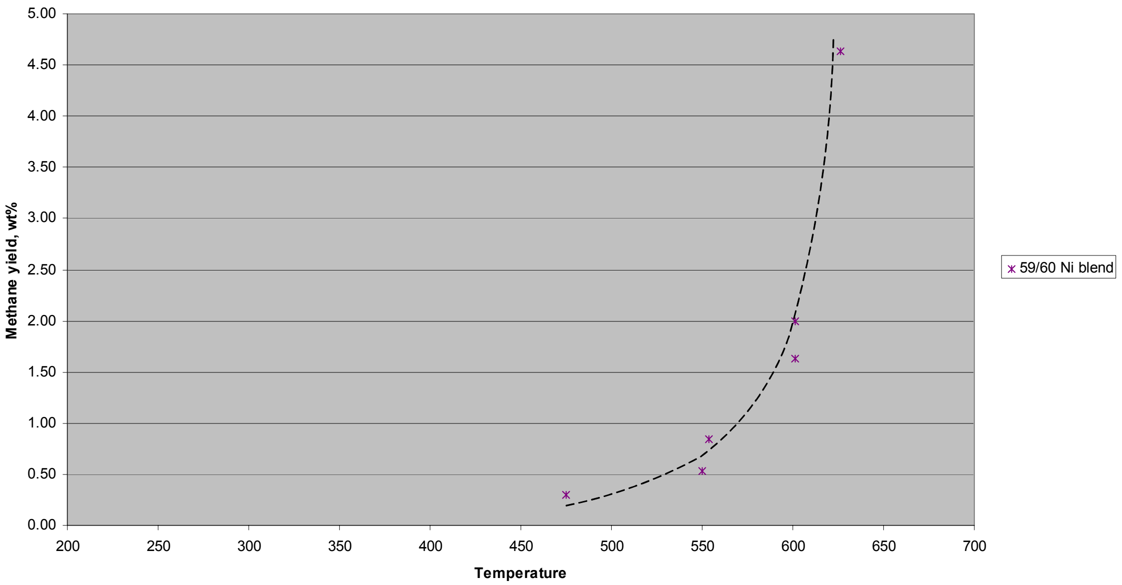
A commercial scale unit, designed to operate with a nickel catalyst, would modt probably be based on inter-bed quenching to control the reactor temperature.

3. Hydrocarbon Yields

3.1 Methane

Figure 2 shows the methane production as function of the reactor temperature. The methane production increases exponentially when the reactor temperature exceeds 561 K (550 °F). This is the pilot unit reactor temperature at which the temperature excursions usually start.

Fig. 3 Methane production as function of Temperature



3.2 Ethane

The amount of ethane produced increases with reactor temperature. The ethane yield is very low so the accuracy of the data may be limited.

3.3 C3, C4, C5, C6+

No obvious yield temperature correlation was found for C3 thru C5. The C6+ yields are scattered over the temperature range, there does not seem to be a relation between C6+ yield with temperature.

4. Hydrogen consumption

There is no obvious trend between H_2 consumption and wax color. The H_2 consumption seems to increase with increased methane production, but the data is very scattered. This may be attributed to erratic gas flow readings.

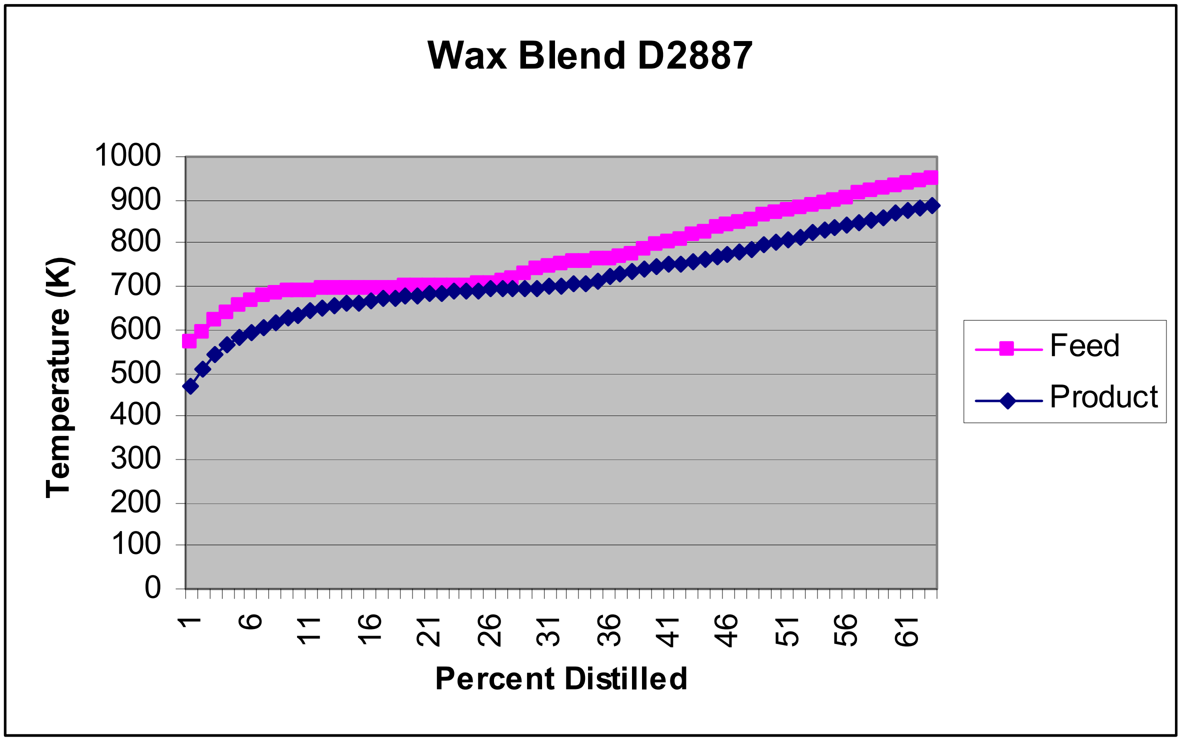
5. Water production

The water draws are not very consistent, a big difference was reported between the amount of water collected per shift during identical operating conditions. This was attributed to hold up in the pilot unit.

There is a general increase in water production with decrease in ASTM D1500 color. This may be an indication that oxygenates are converted.

6. ASTM D2887 Distillation

Shown below is the results of the D2887 boiling point distribution for the feed and the product. The product has gotten lighter as result of cracking.



CONCLUSIONS

1. On-spec wax product from a soft wax/hard wax feed blend can be made using Ni Alumina-based catalyst at the following reactor conditions:

    - Reactor Temperature - 603 K (625 °F)
    - Reactor Pressure - 13891 kPa (2000 psig)
    - Hydrogen Treatgas Rate - 674 Nm^3/m^3 (4000 scf/bbl) H_2/oil
    - LHSV – 0.5

    The catalyst is very susceptible to temperature runaway.

2. It has not been proven that the full range FT Product can be Hy-Finished^{SM} in one reactor. Attempts to treat the full range FT Product at conditions required for on-spec wax resulted in unstable reactor temperatures and temperature excursions.

3. It is not possible to Hy-Finish^{SM} the full range FT Product and separate the reactor products using an atmospheric fractionator. The required reboiler temperature discolors the wax.

4. It may be possible to Hy-Finish^{SM} the full range FT Product and obtain the required separation in a vacuum column at a lower reboiler temperature. The estimated vacuum required is 1 mm Hg at 436 K (325 °F).

LIST OF ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
bbl	barrel
°C	Degree Celsius
C3	hydrocarbons with 3 carbon atoms
C4	hydrocarbons with 4 carbon atoms
C5	hydrocarbons with 5 carbon atoms
C6+	hydrocarbons with 6 or more carbon atoms
cc	cubic centimeter
cc	cubic centimeter
cSt	Centi Stokes
DOE	Department of Energy
Dsl	Diesel
EECP	Early Entrance Co-Production Plant
°F	Degree Fahrenheit
FBP	Final Boiling Point
FDA	Food and Drug Administration
FT	Fischer Tropsch
G	gram
GCD	Gas Chromatography
H2	Hydrogen
Hr	Hour
IBP	Initial Boiling Point
K	Degree Kelvin
KOH	Potasium Hydroxide
KPa	kilo Pascal
LHSV	Liquid Hourly Space Velocity
M^3	cubic meter
mg	milligram
mm	millimeter
mm Hg	milli meters Mercury
N/A	not applicable
Nap	Naphtha
Ni	Nickel
Nm	nano meter
Nm^3	Normal cubic meter (273 K, 101.3 kPa)
ppmw	Parts per Million Weight
psig	Pounds per Square Inch gauge
scf	standard cubic foot (60 °F, 0 psig)
Temp	Temperature
US	United States
UV	Ultra Violet
Vol	Volume
wppm	Parts per Million Weight
Wt%	Weight percent

ATTACHMENT 1 - WAX BLEND FEED ASTM D-2887 MODIFIED HIGH TEMP

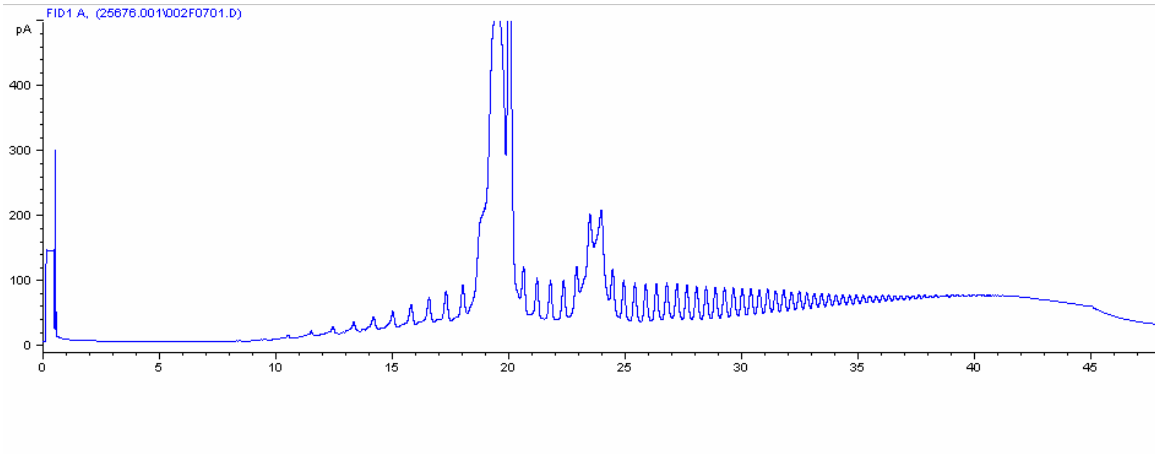
WAX BLEND FEED ASTM D-2887 MODIFIED HIGH TEMP						
% OFF	BP(K)	BP(°F)		% OFF	BP(K)	BP(°F)
IBP	571	(568.4)		32%	755	(898.7)
1%	593	(608.2)		33%	758	(903.9)
2%	620	(656.1)		34%	760	(909)
3%	641	(693.3)		35%	763	(913.6)
4%	653	(715.7)		36%	768	(923.6)
5%	664	(735.4)		37%	776	(936.3)
6%	676	(756.4)		38%	785	(954.1)
7%	684	(772.1)		39%	794	(969.5)
8%	687	(777.1)		40%	802	(984.1)
9%	689	(780.9)		41%	810	(999.1)
10%	691	(784.2)		42%	818	(1012.5)
11%	692	(786.5)		43%	827	(1028.5)
12%	693	(788.2)		44%	834	(1042.1)
13%	694	(789.8)		45%	842	(1055.5)
14%	695	(791.3)		46%	849	(1068)
15%	696	(792.7)		47%	855	(1080)
16%	696	(793.9)		48%	862	(1092.8)
17%	697	(795.2)		49%	869	(1104.1)
18%	698	(796.6)		50%	875	(1115.8)
19%	699	(798.3)		51%	882	(1127.9)
20%	700	(800.1)		52%	888	(1139)
21%	701	(802.5)		53%	895	(1150.7)
22%	702	(804.4)		54%	901	(1161.9)
23%	703	(805.8)		55%	907	(1172.4)
24%	704	(807.1)		56%	913	(1183.1)
25%	705	(809.6)		57%	919	(1193.8)
26%	711	(819.8)		58%	924	(1204.1)
27%	719	(835.3)		59%	930	(1213.5)
28%	729	(853.1)		60%	936	(1224.4)
29%	739	(870.1)		61%	942	(1235.9)
30%	747	(884.1)		62%	948	(1246)
31%	752	(893.2)				

ATTACHMENT 2 - WAX BLEND PRODUCT P88-60-3 ASTM D-2887 MODIFIED HIGH TEMP

WAX BLEND PRODUCT P88-60-3 ASTM D-2887 MODIFIED HIGH TEMP						
% OFF	BP(K)	BP(°F)		% OFF	BP(K)	BP(°F)
IBP	470	(386)		36%	729	(851.9)
1%	506	(452)		37%	734	(861.9)
2%	543	(517.3)		38%	740	(872.3)
3%	565	(557.9)		39%	746	(882.7)
4%	582	(587.5)		40%	749	(888.7)
5%	595	(611.8)		41%	754	(896.9)
6%	607	(632.3)		42%	757	(902.5)
7%	616	(649.4)		43%	761	(910.6)
8%	628	(671.2)		44%	767	(920.8)
9%	635	(684.1)		45%	774	(932.9)
10%	643	(697.4)		46%	781	(945.3)
11%	649	(708.5)		47%	788	(958.1)
12%	654	(716.8)		48%	795	(970.9)
13%	658	(725.4)		49%	802	(983.3)
14%	663	(733.9)		50%	809	(997)
15%	666	(739)		51%	816	(1009.3)
16%	671	(747.6)		52%	823	(1020.9)
17%	675	(754.5)		53%	830	(1034.1)
18%	677	(758.3)		54%	837	(1046.6)
19%	680	(764.1)		55%	843	(1056.9)
20%	683	(769.9)		56%	849	(1068.7)
21%	686	(774.3)		57%	855	(1079.6)
22%	687	(776.7)		58%	861	(1090.9)
23%	688	(779.3)		59%	868	(1102)
24%	690	(782.8)		60%	874	(1113.5)
25%	692	(786.2)		61%	880	(1125.2)
26%	694	(789)		62%	887	(1137.1)
27%	695	(791.3)		63%	894	(1149.8)
28%	696	(793.2)		64%	901	(1162.2)
29%	697	(795.7)		65%	908	(1174.2)
30%	699	(799.4)		66%	915	(1186.7)
31%	702	(803.6)		67%	922	(1199.6)
32%	704	(806.7)		68%	928	(1211.5)
33%	707	(813.5)		69%	936	(1224.9)
34%	713	(824.4)		70%	944	(1239.4)
35%	722	(839.4)				

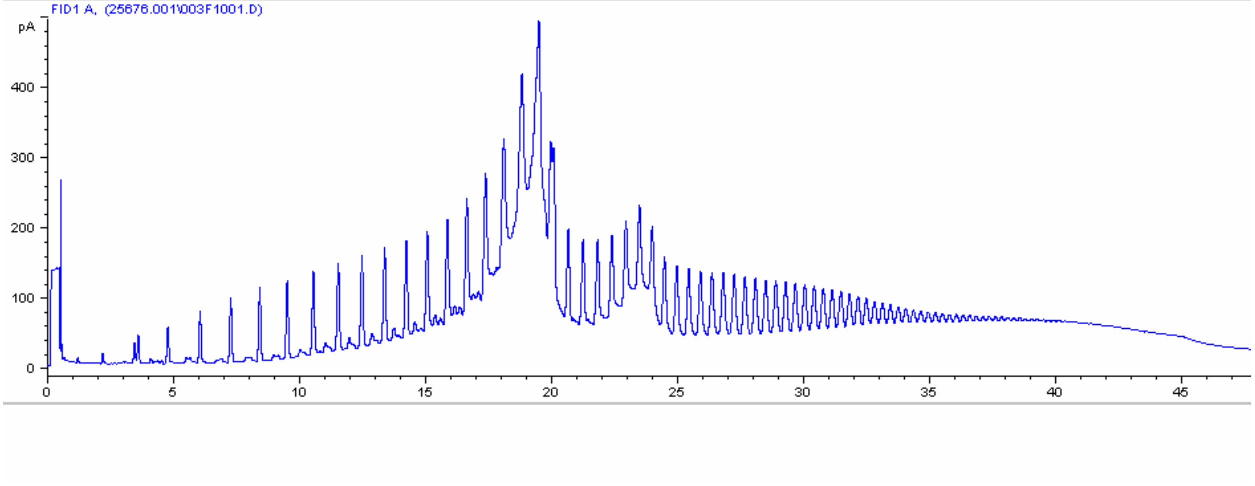
ATTACHMENT 3

GC Carbon Number Distribution-Extended – Blended Wax Feed



ATTACHMENT 4

GC Carbon Number Distribution-Extended – Blended Wax Product



EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix D - Test Report

Subtask 2.5.5.5b: OXYGEN TEST DEVELOPMENT

Reporting Period: June 2001 - February 2003

Contributors: Mike Dammann (Southwest Research Institute)
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Date Issued: March 18, 2003

SwRI-04786/01

Final Report for

Task 2.5.5b Hydrocarbons Characterization and Tests - Iron & Oxygenates

Oxygen Concentration Determination for F-T Naphtha and Diesel Boiling Range Fractions

Contract SwRI131729E
SwRI Project 01-04786

Prepared By

Mike Dammann
Jimell Erwin, Ph.D.

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March 18, 2003

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March 18, 2003

APPROVED:

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Vice President
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I. Executive Summary

In EECP Task 2.5.5b Hydrocarbons Characterization and Tests - Iron & Oxygenates, Texaco Energy Systems foresaw the need for oxygen and iron analyses during the course of the EECP work. The concentrations of iron and oxygen are important indicators of how the F-T liquids, as feedstocks to upgrading processes, might affect process catalysts.

Oxygen concentration measurement in hydrocarbon samples is usually made by an indirect technique such as by difference considering carbon, hydrogen, and other heteroatom concentrations or by inert pyrolysis followed by detection of oxygen-containing CO or CO_2 . The total oxygen measurements recounted in the report are by pyrolysis.

Measurement of the individual, oxygen-containing species in the F-T samples was attempted by gas chromatography coupled with a nondispersive infrared (NDIR) detector. Good chromatographic separation was achieved, but it was decided that further investigation of the IR technique was nonproductive as the probability of achieving the needed selectivity for oxygen by way of the NDIR could likely not be achieved within the limited scope of the project.

The second experimental approach attempted involved the interfacing of a GC to an inductively coupled plasma mass spectrometer (ICP-MS). The direct detection of oxygen by the MS detector eliminated the need for the pyrolysis step previously used. It was determined that this detection limit was still too high to meet the desired project objectives. Ultimately it was decided to rely upon total oxygen concentration, and no further work was performed upon measuring the distribution of oxygenates. No iron analyses were requested.

II. Background

In EECP Task 2.5.5b Hydrocarbons Characterization and Tests - Iron & Oxygenates, Texaco Energy Systems foresaw the need for oxygen and iron analyses during the course of the EECP work. The concentrations of iron and oxygen are important indicators of how the F-T liquids, as feedstocks to upgrading processes, might affect process catalysts. The type, concentrations, and distribution of oxygenates reflects the nature of the F-T feedstock and the efficiency of hydrogenation in subsequent processing. The work described here measured the total concentration of oxygen in various upgraded samples. Also described is the preparations for measuring the distribution of oxygenates in liquid samples. No iron analyses have yet been requested.

Oxygen concentration measurement in hydrocarbon samples is usually made by an indirect technique such as by difference considering carbon, hydrogen, and other heteroatom concentrations or by inert pyrolysis followed by detection of oxygen-containing CO or CO_2 . The total oxygen measurements recounted here are by pyrolysis. For measuring the distribution of oxygen-containing compounds, not only is separation of compounds required, but also an ability to exclusively detect oxygen in the presence of abundant other material in the separated peaks. This high degree of discrimination is the key to such speciation.

A. Experimental

The oxygen measurement techniques used during this investigation were based upon the method described by Robert Culmo.[1*] The technique involved pyrolyzing the sample in an inert environment at 1000°C, with the pyrolysis products passing in turn over platinized carbon, platinum gauze, and platinized carbon again to convert any pyrolyzed oxygen containing products to carbon monoxide. The gas products were then passed over a scrubber to remove any acid gasses, such as hydrogen chloride and hydrogen sulfide, formed during the pyrolysis step. The scrubbed gas containing the carbon monoxide is converted to carbon dioxide by passing over copper oxide at 700°C. The carbon dioxide thus produced is measured in the gas stream by measuring the difference in the thermal conductivity of the gas before and after a carbon dioxide scrubber. The magnitude of the differential signal is proportional to the oxygen content of the sample. Comparing the signal of a sample to that of samples of known oxygen content allows quantitative measurement of the oxygen content. Considering the many steps of this technique, the usual precision as practiced in standard methods is a few hundred ppm of oxygen by weight. Applying special care, this limit can be frequently lowered to about 100 ppm. To achieve lower limits, adaptations of the standard method must be employed as described below.

Total oxygen measurement -- The method for measuring low levels of total oxygen concentration involved setting up an elemental analyzer exactly as described by Culmo. This setup did not allow speciation of the individual oxygen containing compounds, but gave a total oxygen content of each sample. An "oxygen scrubber" cartridge was used to prepare the carrier gas used by the analyzer that absorbed any oxygen present. By using a large sample aliquot and

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[*] Underlined, superscripted numbers in the text refer to entries in the bibliography

careful technique, it was determined that this method could detect oxygen at the 10-20 µG/G range with a 10% relative uncertainty (1µG/G = 1 ppm). This was the technique used to analyze all samples sent to SwRI for oxygen determination.

Six samples were received at SwRI for total oxygen analysis in four separate shipments. The samples were logged into SwRI's laboratory information system (LIMS) and given unique ID numbers to allow tracking in the lab. Each shipment of samples was also assigned a work order number to allow tracking of samples by shipment. Table 1 lists the sample ID's, SwRI system ID assigned, the work order number assigned, and the date the samples were received.

Table 1 - Samples received for analysis in Task 2.5.5

TESI ID	SwRI System ID	Work Order Number	Date Received
PP 34-91@30-54 C2B	219144	23689	01/21/03
PP 34-91@54-78 C2B	219145	23689	01/21/03
PP 34-91@85-85 C2B	219146	23689	01/21/03
PP 34-91 102-102 C2B	219195	23694	01/22/03
PP 34-91 114-126 C2B	219358	23707	01/23/03
PP 34-91 126-150 C2B	219396	23712	01/24/03

Oxygenate measurement by IR -- The first experimental approach for oxygenate speciation attempted to obtain the oxygenate measurements involved interfacing a gas chromatograph (GC) to an oxygen detection system (ODS) consisting of a pyrolysis/scrubber/oxidation setup as described above in this report with the exception that a nondispersive infrared (NDIR) detector that was specific to carbon dioxide was used for the detector. The GC was also equipped with a non-destructive thermal conductivity detector (TCD) in series with, and immediately before, the oxygen detection system to allow detection of any compounds eluting from the GC even if they did not contain oxygen. The chromatographic conditions of the GC were setup to allow the separation of organic compounds from each other for a range of compounds containing two carbon atoms through organic about twenty carbon atoms with an elution time of about 15 minutes. A test solution containing small amounts of methanol and octanol in hexane was used for instrument setup.

Oxygenate measurement by MS -- The second experimental design attempted involved the interfacing of a GC to an inductively coupled plasma mass spectrometer (ICP-MS). ICP-MS is known as a very selective technique with extremely good sensitivity. In a typical ICP-MS application, samples are run from an aqueous solution. The solution is pumped to a pneumatic nebulizer which atomizes a portion of the sample. The small atomized droplets are sprayed into flowing argon and passed via an inert, high temperature-tolerant injection tube into a torch, which is inductively heated to approximately 10,000°C. At this temperature, the gas and almost everything in it is atomized and ionized, forming a plasma, which provides a rich source of both excited and ionized atoms. In ICP-MS, positive ions in the plasma are focused down a quadrapole mass spectrometer. By acquiring the mass spectrum of the plasma, data can be obtained for any ionized species or element. The mass spectrometer only detects and quantitates ions that have the mass to charge ratio (m/z) selected for data acquisition. This means that the mass 16 channel will only detect ions that have a m/z of 16, examples of such ions are 16O+, 12C1H4+, 16O2++, or 32S++. Due to the extremely high temperature of the plasma, most compounds are immediately decomposed into their individual atoms, which are then ionized in the electron-deficient plasma to their positive ions that are detected and quantitated in the mass spectrometer, this eliminates or greatly reduces any contribution to a given m/z signal from potential polyatomic (more than one atom) ions.

B. Results and Discussion

Total oxygen results -- Each sample was run in at least duplicate and the resulting average oxygen content is presented in Table 2. Please note that sample PP 34-91@85-85 C2B, system ID 219146, was determined to be aqueous and not organic in nature. This was confirmed by a Karl Fischer water content of 98.0 wt%. The other two samples received 01/21/03, PP 34-91@30-54 C2B, system ID 219144, and PP 34-91@54-78 C2B, system ID 219145, had water contents of less than 10 µG/mL.

Table 2- Total Oxygen results in Task 2.5.5

TESI ID	SwRI System ID	Oxygen content
		Weight %
PP 34-91@30-54 C2B	219144	1.053
PP 34-91@54-78 C2B	219145	0.900
PP 34-91@85-85 C2B	219146	n/a **
PP 34-91 102-102 C2B	219195	0.738
PP 34-91 114-126 C2B	219358	0.781
PP 34-91 126-150 C2B	219396	0.806

** Sample not organic in nature

To verify the oxygen numbers obtained via this technique, two samples PP 34-91 114-126 C2B, system ID 219358, and PP 34-91 126-150 C2B, system ID 219396 were run for carbon and hydrogen content and presented as Table 3. Oxygen is often reported from the difference of the carbon and hydrogen content and 100%, this number is included in Table 3. Please note that the uncertainty of the carbon and hydrogen results are in the 0.2% relative range. This gives an uncertainty of the oxygen by difference number of 0.2 wt% - 0.4 wt% absolute. The oxygen by difference numbers agree within normal errors with the measured oxygen results.

Table 3 - Carbon and Hydrogen Results for Task 2.5.5

TESI ID	SwRI System ID	Carbon Content	Hydrogen Content	Oxygen By Difference
PP 34-91 114-126 C2B	219358	84.26%	15.40%	0.34%
PP 34-91 126-150 C2B	219396	84.19%	15.12%	0.69%

Oxygenate measurement by IR Result -- A test solution containing small amounts of methanol and octanol in hexane was used for instrument setup. It became apparent during the optimization of this technique, that although the ODS was very sensitive to the oxygen compounds, it was also somewhat sensitive to non-oxygen containing compounds, as some of the cracked products formed during the pyrolysis step were also detected by the NDIR detector. The ODS gave a selectivity to oxygen versus carbon of about 1000, i.e. the signal for 1000 µg of carbon gave the same signal as 1 µG of oxygen. This was determined to be insufficient to allow the detection of oxygen in the 1 μG/G to 100 μg/gm range (1μG/G = 1 ppm) as desired by the client. To achieve the desired sensitivity of oxygen in carbon compounds, a selectivity of 10,000 to 1,000,000 would be needed. It was decided that further investigation of the IR technique was nonproductive as the probability of achieving the needed selectivity for oxygen could likely not be achieved within the limited scope of this project.

Oxygenate measurement by MS Results -- In this experiment, the liquid sample introduction system was bypassed and the gas outlet of the GC was connected directly to the sample injection tube via a heated transfer line with a connection to add additional make up gas to add to the total flow of the gas allowing the residence time of the sample in the plasma to be adjusted. The direct detection of oxygen by the MS detector eliminated the need for the pyrolysis step previously used. Ions monitored during these GC-ICP-MS runs were m/z 16 (16O+), m/z 18 (18O+) and m/z 13 (13C+). The ion m/z 12 (12C+) was not monitored due to the extremely high sensitivity of the ICP-MS that caused the signal for m/z 12 to exceed the safe limit for the detector at very low detection levels. The ion m/z 13, corresponding to 13C, which is naturally distributed in all carbon compounds as 1.1% of the carbon atoms, was more than sensitive enough to allow detection of any carbon compounds in this experiment. Initial experiments with this setup were very promising as the ICP-MS was extremely selective for oxygen.

The major problem encountered was the very high background in the m/z 16 channel. It was hypothesized that the background was due to small amounts of oxygen in the argon used for plasma support and as the carrier gas in the GC. To reduce or eliminate any contribution from the argon gas, a gas scrubber was installed that reduced any oxygen to less than 1 ppmv. This seemed to lower the m/z 16 background slightly, but the signal was still very large. The high background limited the ability to detect small amounts of oxygen coming from the sample.

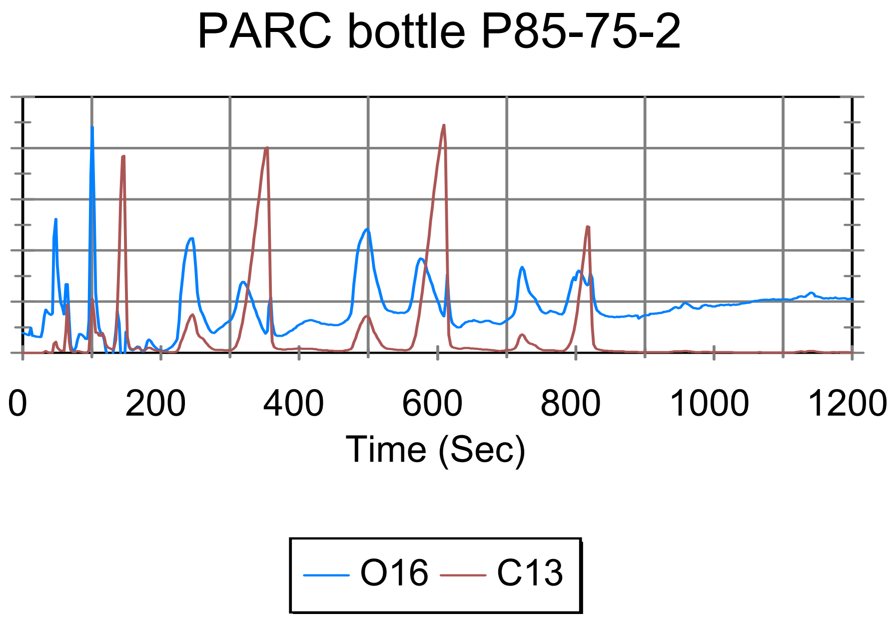

Figure 1. F-T heavy naphtha chromatogram of O^{16} and C^{13} peaks

After careful optimization of operating conditions such as forward plasma power, makeup gas flow rates, and mass spectrometer tuning, it was estimated that the system was able to detect oxygen in a sample at approximately 20 - 50 μG/G per compound or chromatographic peak. An example chromatogram of the sample provided by PARC is given in Figure 1. A table listing the injections made during setup of experimental design two is presented as Table 4. It was determined that this detection limit was still too high to meet the desired project objectives. Ultimately it was decided to rely upon total oxygen concentration, and no further work was performed upon measuring the distribution of oxygenates.

Table 4 GC-ICP-MS Injection Log

Injection #	Date	Time
001	10/22/02	05:32:52 PM
002	10/22/02	05:34:20 PM
003	10/22/02	05:35:22 PM
004	10/22/02	05:45:17 PM
005	10/22/02	05:52:32 PM
006	10/22/02	06:00:29 PM
007	10/22/02	06:09:38 PM
008	10/22/02	06:14:25 PM
009	10/22/02	06:19:30 PM
010	10/22/02	06:26:22 PM
011	10/22/02	06:30:38 PM
012	10/22/02	06:35:57 PM
013	10/22/02	06:41:38 PM
014	10/22/02	06:48:10 PM
015	10/22/02	06:55:04 PM
016	10/22/02	06:59:52 PM
017	10/22/02	07:02:52 PM
018	10/22/02	07:05:59 PM
019	10/22/02	07:11:09 PM
020	10/23/02	04:44:20 PM
021	10/23/02	04:48:39 PM
022	10/23/02	04:51:58 PM
023	10/23/02	04:57:24 PM
024	10/23/02	05:03:42 PM
025	10/23/02	05:09:14 PM
026	10/23/02	05:14:40 PM
027	10/23/02	05:20:03 PM
028	10/23/02	05:23:50 PM
029	10/23/02	05:29:11 PM
030	10/23/02	05:35:06 PM
031	10/23/02	05:40:03 PM
032	10/23/02	05:47:10 PM
033	10/23/02	05:49:43 PM
034	10/23/02	05:59:47 PM
035	10/23/02	06:13:16 PM
036	10/23/02	06:21:59 PM
037	10/23/02	06:27:31 PM
038	10/23/02	06:32:25 PM

Table 4 cont - GC-ICP-MS Injection Log

Injection #	Date	Time
039	10/23/02	06:37:46 PM
040	10/23/02	06:43:18 PM
041	10/23/02	06:47:48 PM
042	10/24/02	05:30:12 PM
043	10/24/02	05:32:47 PM
044	10/24/02	05:33:39 PM
045	10/24/02	05:41:06 PM
046	10/24/02	05:46:24 PM
047	10/24/02	05:52:03 PM
048	10/24/02	05:59:29 PM
049	10/24/02	06:07:28 PM
050	10/24/02	06:14:44 PM
051	10/24/02	06:22:57 PM
052	10/24/02	06:26:40 PM
053	10/24/02	06:29:47 PM
054	10/24/02	06:33:49 PM
055	11/04/02	04:32:45 PM
056	11/04/02	04:33:24 PM
057	11/04/02	04:43:12 PM
058	11/04/02	04:50:10 PM
059	11/04/02	04:52:47 PM
060	11/04/02	05:00:22 PM
061	11/04/02	05:08:00 PM
062	11/04/02	05:14:57 PM
063	11/04/02	05:22:44 PM
064	11/04/02	05:30:09 PM
065	11/04/02	05:36:27 PM
066	11/04/02	05:43:51 PM
067	11/04/02	05:51:29 PM
068	11/04/02	05:57:30 PM
069	11/04/02	06:05:00 PM
070	11/04/02	06:15:05 PM
071	11/04/02	06:26:18 PM
072	11/04/02	06:31:42 PM
073	11/04/02	06:37:40 PM
074	11/04/02	06:39:53 PM
075	11/04/02	06:46:06 PM
076	11/06/02	10:51:13 AM

Table 4 GC-ICP-MS Injection Log

Injection #	Date	Time
077	11/06/02	10:59:21 AM
078	11/06/02	11:02:45 AM
079	11/06/02	11:09:19 AM
080	11/06/02	11:15:37 AM
081	11/06/02	11:21:00 AM
082	11/06/02	11:33:23 AM
083	11/06/02	12:07:00 PM
084	11/06/02	12:07:36 PM
085	11/06/02	12:14:42 PM
086	11/06/02	12:21:14 PM
087	11/06/02	12:24:56 PM
088	11/06/02	12:28:26 PM
089	11/06/02	12:52:17 PM
090	11/06/02	12:57:07 PM
091	11/06/02	01:03:18 PM
092	11/06/02	01:08:02 PM
093	11/06/02	01:12:43 PM
094	11/06/02	01:34:04 PM
095	11/06/02	01:40:57 PM
096	11/06/02	01:41:38 PM
097	11/06/02	01:44:11 PM
098	11/06/02	01:53:13 PM
099	11/06/02	02:07:23 PM
100	11/06/02	02:12:54 PM
101	11/06/02	02:18:35 PM
102	11/06/02	02:27:17 PM
103	11/06/02	02:50:03 PM
104	11/06/02	02:53:44 PM
105	11/06/02	03:00:15 PM
106	11/06/02	03:27:00 PM
107	11/06/02	03:27:54 PM
108	11/06/02	03:58:46 PM
109	11/06/02	04:29:16 PM
110	11/06/02	04:37:21 PM
111	11/06/02	04:44:47 PM
112	11/06/02	04:55:58 PM
113	11/06/02	05:09:23 PM
114	11/06/02	05:10:12 PM
115	11/06/02	05:12:36 PM
116	11/06/02	05:28:46 PM
117	11/06/02	05:36:35 PM
118	11/06/02	05:57:55 PM
119	11/06/02	06:06:03 PM

Table 4 cont - GC-ICP-MS Injection Log

Injection #	Date	Time
120	11/12/02	05:47:40 PM
121	11/12/02	05:50:08 PM
122	11/12/02	05:52:45 PM
123	11/12/02	05:58:39 PM
124	11/12/02	06:08:56 PM
125	11/12/02	06:14:36 PM
126	11/12/02	06:17:11 PM
127	11/12/02	06:18:11 PM
128	11/12/02	06:28:11 PM
129	11/12/02	06:28:59 PM
130	11/12/02	06:38:32 PM
131	11/12/02	06:39:49 PM
132	11/12/02	06:42:53 PM
133	11/12/02	06:43:35 PM
134	11/12/02	06:46:07 PM
135	11/21/02	01:13:36 PM
136	11/21/02	01:14:58 PM
137	11/21/02	01:19:39 PM
138	11/21/02	01:23:20 PM
139	11/21/02	01:27:23 PM
140	11/21/02	01:31:07 PM
141	11/21/02	01:33:23 PM
142	11/21/02	01:36:08 PM
143	11/21/02	01:43:45 PM
144	11/21/02	01:48:37 PM
145	11/21/02	01:52:22 PM
146	11/21/02	01:53:29 PM
147	11/21/02	01:59:03 PM
148	11/21/02	01:59:49 PM
149	11/21/02	02:00:47 PM
150	11/21/02	02:09:27 PM
151	11/21/02	02:14:37 PM
152	11/21/02	02:15:17 PM
153	11/21/02	02:15:40 PM
154	11/21/02	02:16:52 PM
155	11/21/02	02:18:04 PM
156	11/21/02	02:19:21 PM
157	11/21/02	02:19:52 PM
158	11/21/02	02:31:53 PM
159	11/21/02	02:33:13 PM
160	11/21/02	02:37:18 PM
161	11/21/02	02:42:07 PM
162	11/21/02	02:42:50 PM

Table 4 GC-ICP-MS Injection Log

Injection #	Date	Time
163	11/21/02	03:26:05 PM
164	11/21/02	03:28:26 PM
165	11/21/02	03:30:20 PM
166	11/21/02	03:40:29 PM
167	11/21/02	03:40:48 PM
168	11/21/02	03:44:58 PM
169	11/21/02	03:49:20 PM
170	11/21/02	03:59:00 PM
171	11/21/02	04:00:17 PM
172	11/21/02	04:01:06 PM
173	11/21/02	04:03:49 PM
174	11/21/02	04:04:34 PM

Table 4 cont - GC-ICP-MS Injection Log

Injection #	Date	Time
175	11/21/02	04:10:49 PM
176	11/21/02	04:45:10 PM
177	11/21/02	05:00:29 PM
178	11/21/02	05:28:47 PM
179	11/21/02	05:31:46 PM
180	11/21/02	05:44:56 PM
181	11/21/02	06:05:22 PM
182	11/21/02	06:05:58 PM
183	11/21/02	06:07:33 PM
184	11/21/02	06:44:03 PM

III. Conclusions

Six samples were received at SwRI for total oxygen analysis. The measurement technique involved pyrolyzing the sample in an inert environment at 1000°C and measuring the reaction products. By using a large sample aliquot and careful technique, it was determined that this method could detect oxygen at the 10-20 μG/G range with a 10% relative uncertainty (1μG/G = 1 ppm). This was the technique used to analyze all samples sent to SwRI for total oxygen determination.

The first experimental approach attempted for oxygenate measurement involved interfacing a gas chromatograph (GC) to an oxygen detection system (ODS) consisting of a pyrolysis/scrubber/oxidation setup as described in the background section of this report with the exception that a nondispersive infrared (NDIR). It became apparent during the optimization of this technique, that although the ODS was very sensitive to the oxygen compounds, it was also somewhat sensitive to non-oxygen containing compounds, as some of the cracked products formed during the pyrolysis step were also detected by the NDIR detector. It was decided that further investigation of the IR technique was nonproductive as the probability of achieving the needed selectivity for oxygen could likely not be achieved within the limited scope of this project.

The second experimental design attempted involved the interfacing of a GC to an inductively coupled plasma mass spectrometer (ICP-MS). The direct detection of oxygen by the MS detector eliminated the need for the pyrolysis step previously used. It was determined that this detection limit was still too high to meet the desired project objectives. Ultimately it was decided to rely upon total oxygen concentration, and no further work was performed upon measuring the distribution of oxygenates.

Considering the value in identifying both the profile of oxygen-containing compounds produced during F-T synthesis and the remaining “refractory” compounds after processing of a given severity, the completion of the oxygen speciation effort has great appeal. It should be noted that several avenues of improvement remained when it became apparent that success would not be obtained within the current project’s scope. Although the approach was regarded as exploratory when proposed, the completed experiments showed that good separation was obtained from the methods that used a column even though the separation had not yet been fully optimized. The detection with the greatest sensitivity, mass spectroscopy had great response to the oxygen, but unfortunately was showing too high a signal-to-noise ratio for low level measurement of individual compounds. When the opportunity next occurs, there could be much to be expected of the speciation of oxygenates in F-t liquids.

IV. Bibliography

1. Culmo, Robert, “Microdetermination of Oxygen in Organic Compounds with an Automatic Elemental Analyzer”, Mikrochimica Acta [Wien] pp811-815, 1968.

V. List of Acronyms and Abbreviations

F-T	Fischer-Tropsch
G	Gram(s)
GC	Gas chromatograph
ICP-MS	Inductively coupled plasma – mass spectrograph
ID	Identification number
L	Liter
LIMS	Laboratory information system
m/z	Mass to charge ratio
NDIR	Nondispersive infrared
ppm	Parts per million (weight per volume)
TCD	Thermal conductivity detector

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix E - Test Report

Subtask 2.5.7.6: FISCHER-TROPSCH DIESEL BLENDING TESTS

Reporting Period: December 2003 - May 2003

Contributors: Jimell Erwin, Ph.D. (Southwest Research Institute)

Date Issued: June 5, 2003

SwRI-04786/04

Final Report for

Task 2.5.6 Diesel Blending Tests

Key Diesel Fuel Performance Properties of Neat F-T Diesel, Hydrocracker Product, and Neat FT or Hydrocracker F-T Diesel Products in Blends with an Advanced Petroleum Diesel Fuel

Contract SwRI131729E
SwRI Project 01-04786

Prepared By

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I. Executive Summary

In EECP Task 2.5.6, Diesel Blending Tests, the diesel fuel boiling range products were examined for key properties of concern for diesel fuel use. Fischer-Tropsch liquids in the diesel fuel boiling range are of particular interest because of their highly desirable performance and emissions properties compared to similar boiling point range petroleum-derived stocks, which have received a typical degree of refinery processing. Performance equivalent to or better than a commercial reference fuel having low sulfur content and low aromatics concentration was expected. It was not feasible to prepare test diesel fuels meeting commercial specifications for product inspection; however, the behavior of mixtures at 25/75, 50/50, and 75/25volume percents of the straight run products from distillation and hydrocracking in the petroleum reference fuel were tested.

The fuels tested were Neat F-T Diesel Product, Hydrocracker (HC) F-T Diesel Product, and a petroleum reference fuel with low sulfur and aromatics concentrations (Chevron Phillips Chemical Company Diesel 2004 Tier 2). Tests included cetane number, pour point, cloud point, viscosity, storage stability, and lubricity.

The results indicated that the cold flow properties as inferred from viscosity, pour point, and cloud point would be acceptable for operation within the contiguous 48 states.

Lubricity as measured by Scuffing Load Ball on Cylinder testing was acceptable for both F-T materials. Measurement on the High Frequency Reciprocating Rig showed acceptable performance for unadditized, Neat F-T diesel product, while the Hydrocracker (HC) F-T diesel product and its blends as well as the petroleum-derived reference fuel could not meet the suggested minimum guideline for this test.

Accelerated stability of the neat F-T diesel product, Hydrocracker (HC) F-T diesel product and the petroleum-derived reference fuel was deemed acceptable compared to the maximum limit proposed for adoption in New Zealand where a numerical limit is poised for imminent adoption.

II. Background

The F-T diesel fuel boiling range products were examined because of their highly desirable performance and emissions properties as diesel fuels and their high value as a superior blending component. F-T process liquids were used to produce diesel fuel from the inception of the process in Germany decades ago.[1*] Even considering the early days of this usage, various problems can attend F-T liquids when used as diesel fuel.[2] Many of the utilization issues come from the high wax content, which is important at low temperatures, and the reactive components (oxygenates and olefins), which can negatively impact product stability in the diesel pool.[3]

Many opportunities for commercialization of F-T diesel fuels are emerging. In October, 2002 DOE held a workshop[4] to receive input on possibility of designating Fischer-Tropsch diesel fuel as an Alternative Transportation Fuel under the Energy Policy Act (EPACT) of 1992. EPACT promotes both alternative fuels and "replacement fuels", which are defined as nonpetroleum fuels used in conventional vehicles including lower level blends. Under the act, an alternative fuel must have nonpetroleum components used in high percentages and may have special vehicle requirements. F-T liquids, if designated, would be first alternative fuel for use in conventional vehicles, excluding biodiesel, which has a special provision, and is not an EPACT-designated alternative fuel.

The main impetus in the current market for utilizing F-T components in diesel fuel has been the emergence of "ultraclean diesel fuels."[5] Generally, the definition of ultraclean diesel fuel includes low sulfur content (10 parts per million or less) and low aromatics (10 volume percent or less). Petroleum diesel fuel sources (mostly crude oils) require considerable desulfurization, dearomatization, and associated hydrogen production to succeed. F-T diesel possesses these properties as an inherent result of its normal production process.

Performance of F-T diesel equivalent to or better than a commercial reference fuel is expected,[6] and several key tests were needed to demonstrate whether this superior performance had been achieved by the current materials. It was not feasible during this limited part of the project to prepare test diesel fuels meeting all of the commercial specifications for product inspection, usually those listed as part of ASTM D 975; however, the behavior of the straight run products from distillation and hydrocracking were tested for the values of several properties that were expected to be most affected by the hydrocarbon makeup of the F-T diesel boiling point range products. The tests used blends of the F-T components with the commercial, petroleum-derived reference fuel used elsewhere in the project.

Two F-T project materials and a reference fuel meeting California diesel fuel requirements were examined for cetane number (D 613), pour point (D 97), cloud point (D 2500), viscosity at 40°C (D 445), storage stability (D 2274), and lubricity (D 6078 and D 6079). To see the response of these properties toward blending, mixtures at 25/75, 50/50, and 75/25 volume percents were made with the reference fuel. This produced six blends and 3 neat fuel samples for testing. The results of the blending and laboratory tests are given below in this report

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[*] Underlined numbers superscripted in the text refer to the bibliographic citations in the appendix.

A. Experimental

After the blends were made, they were logged as project samples, subsampled, and delivered to the various laboratory stations for inspection. The measurement results were collected, plotted and discussed below.

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Preparation of Blends -- Due to the corrosive properties of the neat, F-T 480F-700°F (522°K-644°K)diesel, material handling procedures and blends used new glass or plastic containers with polymer-lined caps. Carbon steel containers (drums or sample cans) were not used for the F-T liquid samples due to safety concerns of corrosion and experimental concern for contamination. Similarly, recycled containers were not used.

All containers & vessels, blending equipment, fractionation equipment, and pilot plant test equipment that come in contact with F-T material were cleaned to reduce background contamination levels of heteroatoms (S, N, O, or metals) or foreign hydrocarbons (aromatics) below the detection level of the analytical means being employed.

The test fuel blendstocks were:

FL-2783/6, Neat F-T Diesel (Fl-2783 from the 55-gal drum, Fl-2786 from the 5-gal can)

Fl-2784, (WOW 9298) Task 2.5.3 Hydrocracker (HC) F-T Diesel Product

FL-2782, Chevron Phillips Chemical Company Diesel 2004 Tier 2 fuel #2.

The test matrix was completed with the above diesel blendstock components.

The three compositions produced were chosen to evenly span the concentration range between the neat F-T liquids and the reference fuel: 25 volume percent reference fuel, 50 volume percent reference fuel, and 75 volume percent reference fuel. The matrix of test blends and samples is presented in Table 1.

Table 1. Task 2.5.6 Diesel Blend Compositions

Blendstock	Work Plan	1	3	4	6	7	9
	ID No	LN^{-}1315	LN-1316	LN^{-}1317	LN1318	LN-1319	LN^{-}1320
FL-2782 Reference	Blend Proportions, Volume%	25	25	50	50	75	75
FL-2786 Neat F-T		75		50		25	
FL-2784 HC F-T Diesel			75		50		25

Property Measurements -- Quantities of the neat and processed Fischer-Tropsch diesel fuels of about 2 gallons were provided for the diesel blending tests. The concerns for F-T or any highly paraffinic diesel fuel are the properties most influenced by the waxy paraffin content, including cetane number, pour point, cloud point, and viscosity. Similarly, the concern for the unavoidable reactive compounds containing oxygen that occur in F-T product liquid is that they might affect properties influenced by the reactivity or the polar nature of a fuel, such as storage stability or lubricity. These properties were chosen as key representatives of the larger set of properties of interest for diesel fuel designated in ASTM D 975 "Standard Specification for Diesel Fuel Oils". The selected properties with required volumes and specification requirements are in Table 2.

Table 2. Properties for Task 2.5.6 Diesel Blending Tests

Measurement	ASTM Method	Volume Required	ASTM D 975 D-2 Requirement
Cetane Number	D 613	1000 m1	40 min
Pour Point	D 97	100ml	Regional*
Cloud Point	D 2500	100ml	Regional*
Viscosity at 40EC	D 445	125ml	1.9 – 4.1 cSt
* For example, coldest 90th percentile continental US temperature = -34ºC (coldest 90th percentile Alaska, US temperature = -49ºC)			
Nonofficial, usually acceptable values			
Storage Stability	D 2274	700ml	max 2.5 mG/100mL
Lubricity, BOCLE	D 6078	100ml	>2000 G, Ap X.3.3 >3100G EMA FQP-1A
Lubricity, HFRR	D 6079	10ml	<450 US (460 Europe)

B. Results and Discussion

Test Fuel Blends -- The test fuel blends described above were prepared volumetrically in ASTM Class A glassware. 2400 mL of each blend were prepared and subdivided according to Table for the various laboratory tests. Adequate material was available for each test including the cetane number determination, which normally requires a gallon.

The blends made clear solutions that showed no signs of compatibility problems, haze, precipitation, or phase separation. The original blends and subsamples were kept in clean glassware bottles and vials with polymer-lined lids. These materials were all consumed in the course of the initial testing and handling so that no materials remain for storage observations or testing.

Property Measurements -- The test blends and blendstocks described above were analyzed according to Table 2. The results appear below in Table 3. In the sections that follow, each property and its results are discussed in turn.

Table 3. Property Measurement Results for Task 2.5.6

Method	Property	units	Base Fuel	Neat F-T	HC F-T	Blend 1	Blend 3	Blend 4	Blend 6	Blend 7	Blend 9
			FL-2782	Fl-2783/6	FL-2784	LN-1315	LN-1316	LN-1317	LN-1318	LN-1319	LN-1320
	PPRD Lab #		29854	29856	29855	29138	29139	29140	29141	29142	29143
D2274	Accelerated Stability	mG/100mL	0.8	1	0.9	1.42	0.6	1.9	0.8	0.2	0.1
D2500	Cloud Point	Deg C	-26	-2	-17	-5	-19	-8	-23	-22	-28
D445	Viscosity, 40c	cSt	2.3	3.14	3.73	3.321	2.908	2.938	2.709	2.629	2.516
D6078	Scuffing Load BOCLE	grams	2850	5250	2350	4950	2000	5800	2150	4750	1950
D6079	Major Axis	mM	0.62	0.35	0.59	0.36	0.62	0.36	0.60	0.40	0.60
	Minor Axes	mM	0.59	0.3	0.58	0.32	0.60	0.32	0.58	0.35	0.58
	Wear Scar	mM	0.605	0.23	0.585	0.340	0.610	0.340	0.590	0.375	0.590
	Description	.	not recorded	evenly worn oval	circular; heavily abraded	evenly worn oval	circular; heavily abraded	evenly worn oval	circular; heavily abraded with brown deposits	evenly worn oval	circular; heavily abraded
	Fuel Temp	degC	60	60	60	60	60	60	60	60	60
D613	Cetane Number		51	76	74.5	76	74	71.5	66.4	60.1	55.6
D97	Pour Point	deg C	-24	-3	-24	-9	-27	-15	-30	-24	-30

Cetane Number -- D 613-03a "Standard Test Method for Cetane Number of Diesel Fuel Oil" Cetane number is a standardized, arbitrary measure of fuel ignition quality. It is influenced by the time interval between the beginning of injection and autoignition of the fuel in the piston cylinder of a designated engine: the shorter the delay time interval, the higher the cetane number. The cetane number scale ranges from zero to 100, but typical values lie in the range of 30 to 65 cetane number. Fuels having low cetane number cause engine noise and detonation, poor starting, irregular power, and black exhaust smoke. For instance, engines will not start without "motoring" (being externally turned) and usually will not run on fuel with less than ~17 cetane number. Diesel engines operate better on fuels with high cetane numbers. Values above 50 begin to produce noticeably better operation than fuels which merely meet the minimum specification. Furthermore, higher cetane number produces lower hydrocarbon emissions while allowing engine settings that have smaller increases of nitrogen oxides than would be obtained with average fuels[7]. All of the F-T test fuel blends exhibited excellent ignition quality as measured by the cetane number.

Cetane number increases as the paraffin content of the fuel increases or with the addition of combustion ignition improvement additives. Among the paraffins, those with a higher distillation range and specific gravity have higher cetane number; hence, F-T products make excellent, high cetane number blendstocks.

The results of blending the two F-T stocks with the reference diesel fuel are shown in Figure 1. The reference fuel was a low aromatic product having an initial high cetane number. It is possibly for this reason that the unusual cetane number blending response evident in the figure was exhibited. Normally, when mixing diesel blendstocks with dissimilar cetane numbers, the blends exhibit cetane numbers more like the low cetane number component. An example of this characteristic is shown in the example of Figure 2, which shows blends of a typical petroleum-derived D-2 with neat and caustic-washed SRC-II diesel[8]. This example emphasizes the effect of aromatic compounds from the SRC-II liquid. There is a view that the ignition quality of diesel fuel arises mostly from paraffin compounds and that the aromatic or other nonparaffinic constituents merely represent diluents that diminish the paraffins' cetane number. At odds with this view are the facts that aromatic compounds provide a marked increase of the energy content of the diesel fuel and exert a distinct effect on the exhaust emissions.

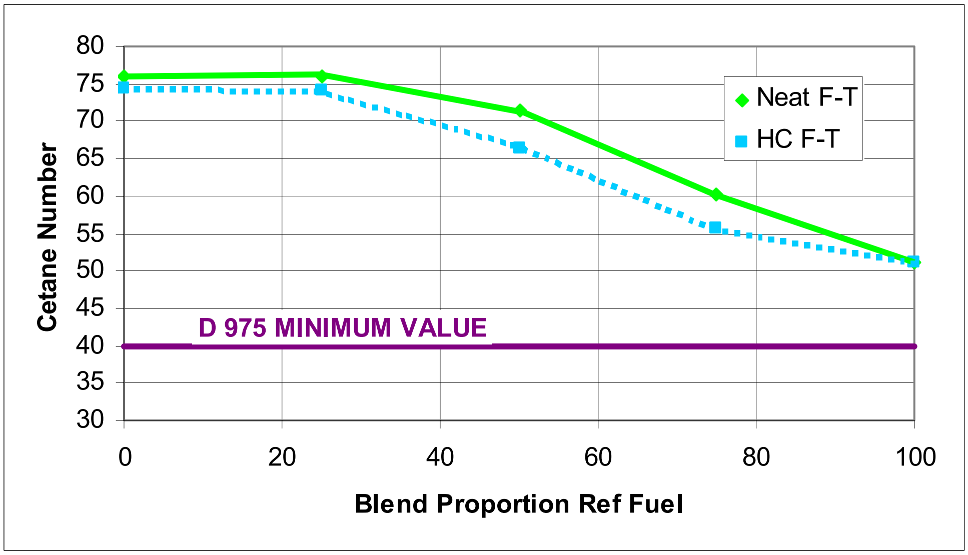

Figure 1. Cetane Number of Blends of Neat or Hydrocracker (HC) F-T Diesel

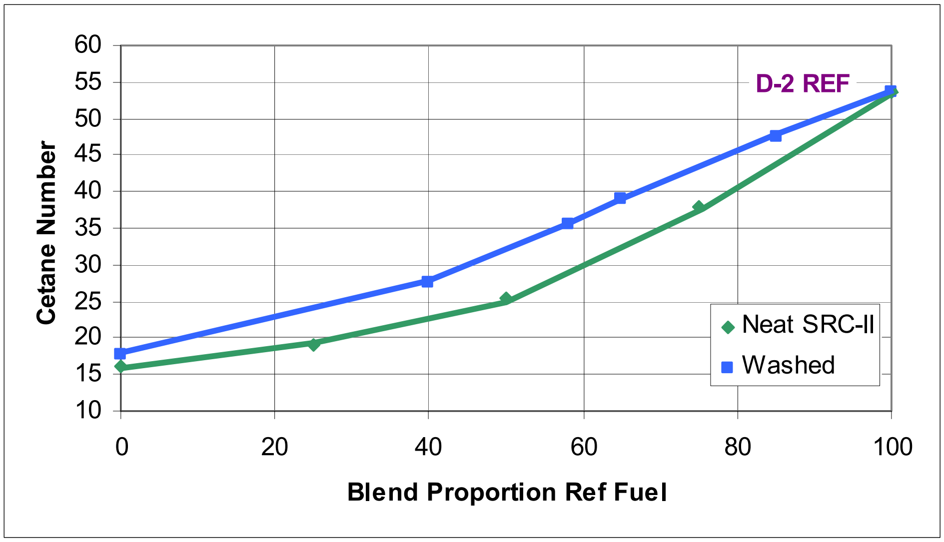

Figure 2. Example of Cetane Number Blending Response

As ever more stringent emissions regulations force petroleum-derived diesel fuels to more closely resemble the reference fuel in the current work, the remarkable upward-curving cetane number response may be obtained when F-T stocks are blended. This effect might not be seen when the nonF-T components are more aromatic. The upward curve is so unusual that further study may be warranted.

Pour Point -- D 97-02 “Standard Test Method for Pour Point of Petroleum Products” This test method is intended for use on any petroleum product and is suitable for diesel fuels. The results of the pour point measurements test blends are in Table 3. This cold flow property gives an indication of how well a fuel will perform at low temperatures in the fuel system as it flows. The test provides the low temperature near which a hydrocarbon product will not flow. Cold flow properties, particularly pour point temperature, are of concern for diesel fuel containing F-T blendstocks. The waxy paraffins are the most susceptible to aggregating at low temperatures leading to a thickened or gelled product.

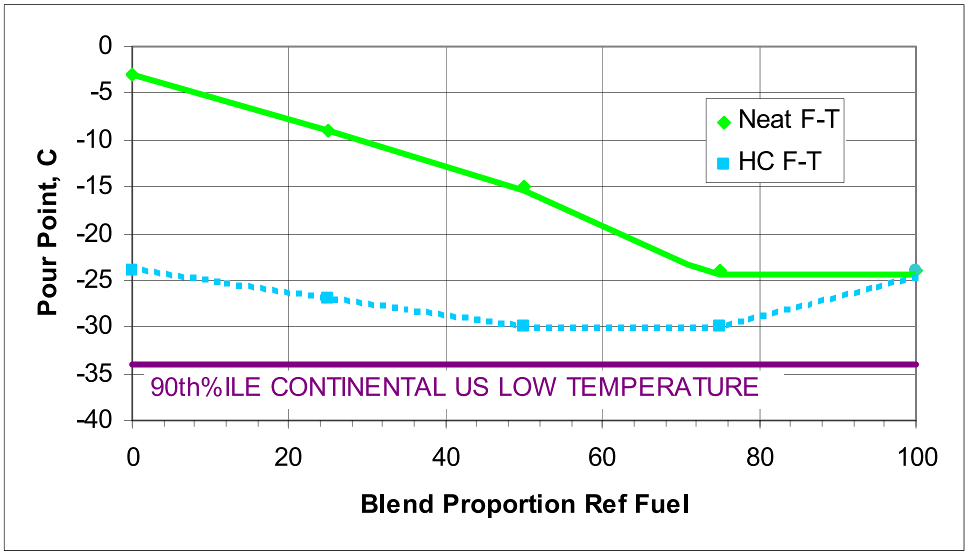

Figure 3. Pour Points of Blends of Neat or Hydrocracker (HC) F-T Diesels

There is no single ASTM D 975 specification value for pour point because of the wide variability of prevailing low temperatures across the continent and outlying areas. D 975 includes an appendix of 90th percentile low temperatures by month for the contiguous US states and Alaska. While the lowest winter temperature in Alaska is –49ºC, the lowest temperature in the 48 contiguous states is –34ºC in Wisconsin in January. This temperature was plotted with the pour point results for the two F-T blends in Figure 3. As shown, the values for the test fuels are all above this value. In fact the neat F-T materials have pour points equal to or greater than the petroleum reference fuel. The pour point depression of the 50 and 75V% Hydrocracker (HC) blends is very unusual and may reflect a subtle hydrocarbon type incompatibility of the Hydrocracker (HC) stock and the reference fuel.

Cloud Point -- D 2500-02 “Standard Test Method for Cloud Point of Petroleum Products” This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C and may not apply to samples with ASTM color higher than 3.5. The cloud point is the temperature at which wax is first seen coming out of solution. The wax crystals thus formed revert to the liquid state as the temperature rises. This property of hydrocarbon fuels helps to assess low temperature operability. There is no generally accepted correlation in the market place between cloud point, pour point or freezing temperature because the use of pour point depressant additives to lower the pour point affect the relationship for finished fuels. Like viscosity, cloud point may predict the temperature that would give high pressure drop across filters on start-up. Cloud point does not have an assigned ASTM D 975 value and, like pour point, is agreed upon regionally between buyer and seller.

To show the effect of cloud point, the values for the two sets of test fuels were plotted with the 90th percentile low temperature for the 48 contiguous states. Figure 4 presents the plots with the low temperature line. The blends all performed very well against this limit as did the reference fuel. For both materials, there was an unexpected "dip" in the curve for the 75V% reference fuel/25V% test fuel blends.

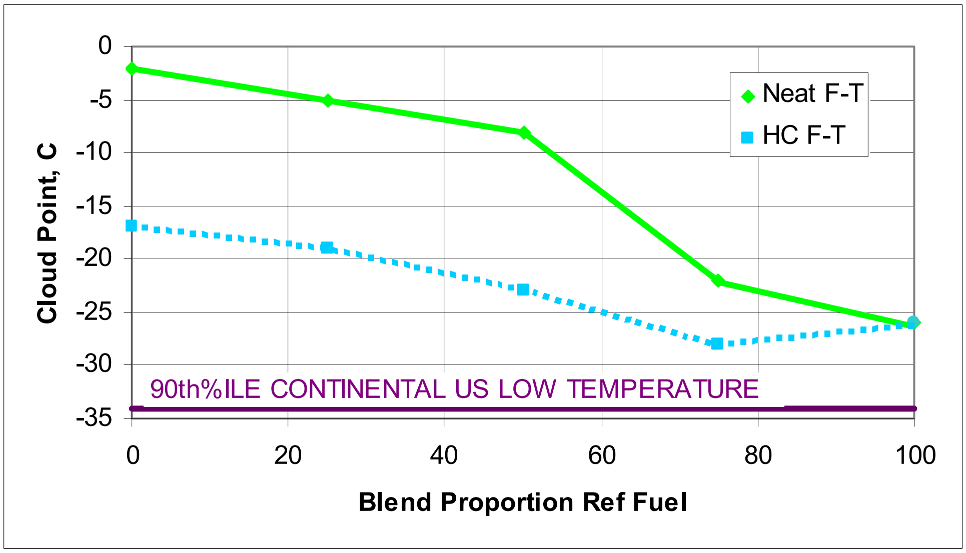

Figure 4. Cloud Points of Blends of Neat or Hydrocracker (HC) F-T Diesels

Viscosity at 40°C -- D 445-03 "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)" This test method defines the standard procedure for the determination of the kinematic viscosity, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a rated glass capillary viscometer. The property of viscosity reflects the inner (intrinsic) resistance of a liquid to applied pressure that would result in flow. The viscosity of the test blends for each F-T stock made smooth curves that were nearly linear. The range of values remained within the high and low limits prescribed in ASTM D 975 as seen in Figure 5.

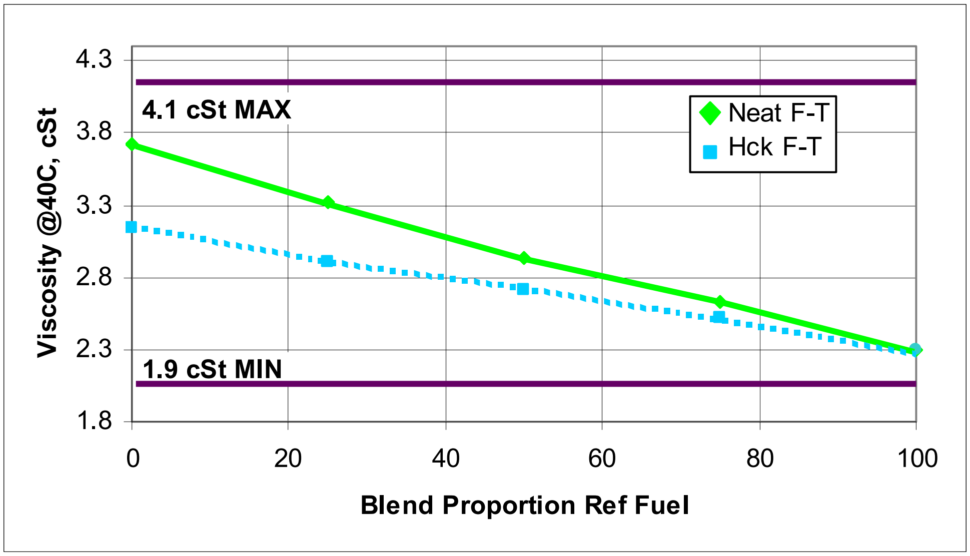

Figure 5. Viscosity at 40°C of Blends of Neat or Hydrocracker (HC) F-T Diesels

Viscosity affects the lubrication of fuel-wetted parts and the delivery of fuel to the combustion chamber by flow in the fuel lines. Proper viscosity is needed to prevent early injector wear and poor fuel atomization. Fuels with low viscosity may result in leakage or increased wear, while high viscosity may cause poor starting and fuel delivery.

High viscosity diesel fuels may form larger droplets during fuel injection into the combustion chamber making for poor fuel atomization that will affect combustion and cause increased exhaust smoke and emissions. F-T liquids are particularly inclined to high viscosity because of the paraffinic nature of the hydrocarbons present. Furthermore, their unique composition may respond differently to viscosity adjustment additives than more conventional stocks. Viscosity is therefore an important property for F-T diesel fuels.

Storage Stability -- ASTM D 2274 “Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)” is used internationally to monitor the tolerance of a fuel to its storage conditions. In the test, the fuel sample is exposed to oxygen for 16 hours under specified conditions; afterward the oxidation products are separated by filter and measured. Reactive compounds such as the possible ethers and other oxygenates that might be present in a F-T liquid are likely to combine with the dissolved oxygen of ASTM D 2274 much as they would combine with oxygen of the air during storage. Following activation by molecular oxygen, the reactive compounds begin to further combine with olefins and branched paraffins in the fuel to form heavier compounds. Though only a small fraction of the total, these heavy components grow heavy enough to precipitate from the fuel during storage. Further, these polymeric impurities are susceptible to condensation reactions on hot surfaces leading to varnishes and plug-causing solids.

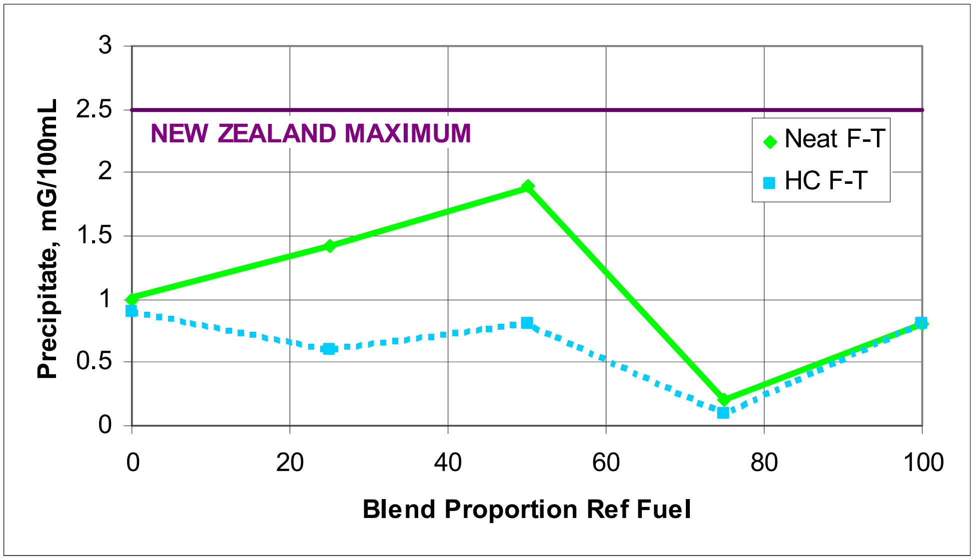

Figure 6. Accelerated Storage Stability of Blends of Neat or Hydrocracker (HC) F-T Diesel

There is no ASTM D 975 acceptable value; but for instance, New Zealand is considering 25 G/m^3 (2.5 mG/100mL) as a specification limit.[9] Fuels that present unacceptably high values under D 2274 may require more severe or alternate processing. In some cases, low concentrations of antifoulant additives chosen to interfere with the reactions of instability may be sufficient to produce an acceptable stable diesel product.

The results of the blending study and subsequent accelerated stability measurements are plotted in Figure 6 along with the D 2274 values of the neat materials. Also in the plot is the proposed stability limit for New Zealand. The claimed D 2274 test reproducibility at the 1.0 mg/100 mL total insolubles level is ± 1.06.

Lubricity, BOCLE -- D 6078-99 “Standard Test Method for Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)” This test method evaluates the lubricity (load carrying ability) of diesel fuels using a scuffling load ball-on-cylinder lubricity evaluator (SLBOCLE). This test method is applicable to middle distillate fuels, such as Grades Low Sulfur No. 1 D, and No. 2 D diesel fuels, in accordance with Specification D 975; and other similar petroleum-based fuels which can be used in diesel engines. The test applies a variable weight to the holder of a captive ball bearing as it bears upon a turning cylinder bathed in the test fluid at controlled temperature. Weight is added in 100-gram increments until a scar appears on the cylinder.

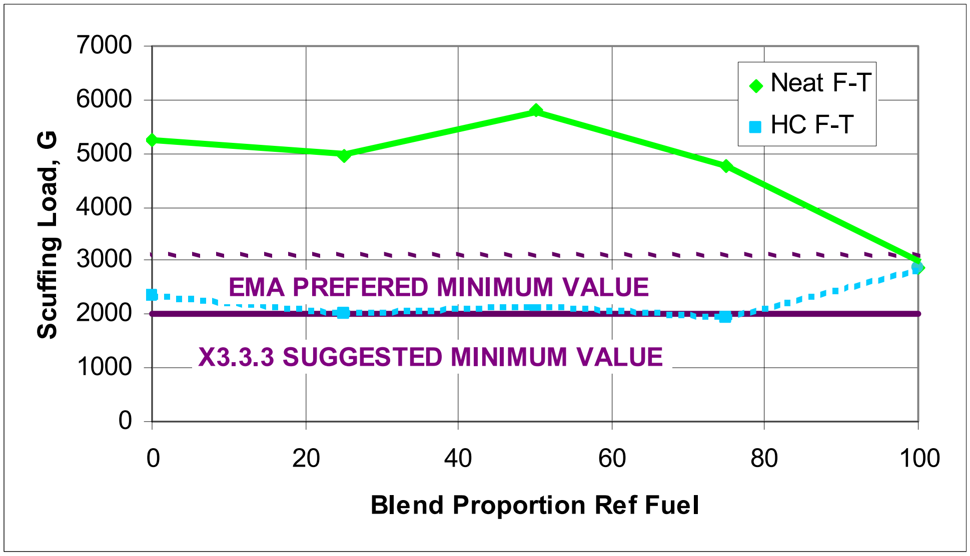

Figure 7. Lubricity by SLBOCLE of Blends of Neat or Hydrocracker (HC) F-T Diesel

The lubricity of interacting surfaces is a standardized parameter related to the inherent coefficient of friction between the materials making up the surfaces and including the media between the surfaces.[10] Lubricity of a liquid fuel describes its ability to minimize friction between, and damage to, fuel system surfaces in relative motion under loaded conditions. Diesel fuel injectors rely on the lubricating properties of the fuel for acceptable operation and service life. ASTM D 975 does not directly address this property, but its appendix X3.3.3 cites guidelines for acceptable service from liquids whose minimum scuffing load is 2000 – 2800 grams.[12]

The lubricity results from the scuffing load testing appear in Figure 7. All fuels and blends fall within or very nearly fall within the least stringent standard, 2000 grams; however, only the neat, F-T containing diesel blends meet the more rigorous requirement of 2800 grams.

The Engine Manufacturers’ Association (EMA) has adopted a more rigorous guideline.[11] Under this recommendation, a scuffing load weight of 3100 grams is needed. By this measure, the neat, F-T containing diesel blends meet the threshold, but not the petroleum-derived reference fuel and none of the Hydrocracker (HC) F-T materials.

Lubricity, HFRR -- D 6079-02 "Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)" This test method covers the evaluation of the lubricity of diesel fuels using a mechanical tester developed in Europe. This test relies upon measurement of the width of a wear scar produced by a pin moving back and forth across a test block immersed in the liquid of interest.

As a relatively new test, it is not known whether this test method will predict the lubricating performance of all fuel compositions or fuel/additive combinations. Of particular interest to fuel development is the widespread adoption of the HFRR test and the repeatability of its results. Relying upon a pin-on-surface, the method requires relatively less metal to be prepared to a standard condition compared to the BOCLEM, which relies upon the rolling ball moving on the turning cylinder. The greater similarity of the BOCLEM to fuel system components is counterbalanced by the reproducibility of the HFRR, but they both depend upon the repeatability of preparation of the metal coupons.

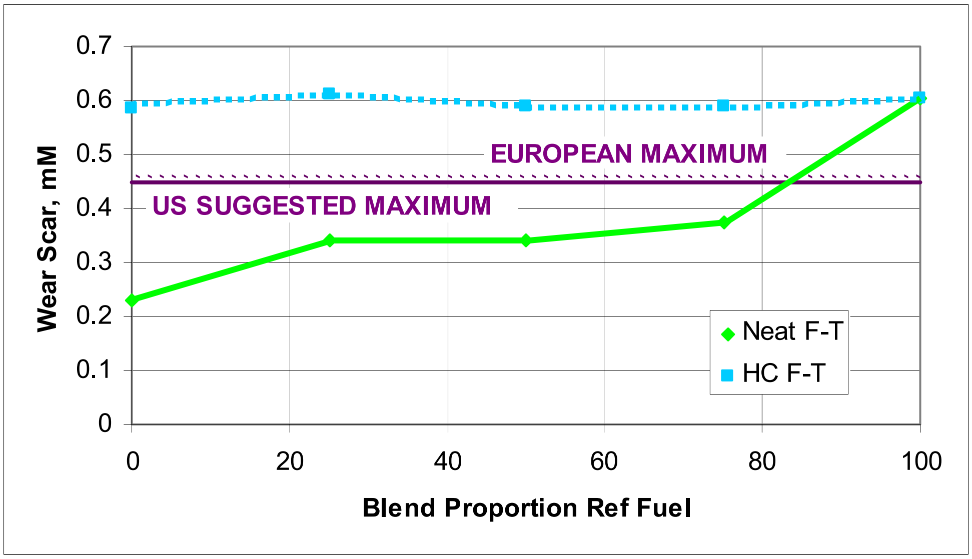

Figure 8. Lubricity by HFRR of Blends of Neat or Hydrocracker (HC) F-T Diesel F-T Diesel

ASTM D 975 does not prescribe a set limit for acceptable HFRR wear scar, but its appendix X3.33 mentions the findings of the ISO interlaboratory study[13] that nominate a wear scar no larger than 450 microns as adequate to protect all fuel injection equipment. The European specification for diesel fuel includes a maximum wear scar dimension of 460 micron as acceptable. All of the Neat F-T diesel blends but none of the F-T Hydrocracker (HC) blends nor the petroleum reference diesel fuel met the HFRR lubricity standards of the US and Europe. These results are shown in Figure 8.

III. Conclusions

The two test fuels, Neat F-T Diesel and Hydrocracker (HC) diesel, and all off their blends with ultraclean petroleum reference fuel performed very well during testing for cetane number, pour point, cloud point, viscosity, storage stability, and lubricity.

Cetane numbers of the neat materials and blends were all higher than the reference fuel and higher than the minimum ASTM D 975 specified value. The response of cetane number to blending resulted in a non-linear response that favored the higher cetane number.

Pour point blends had values that varied between the values of the neat materials except for a "dip" in the value at 75V% reference fuel in both sets of fuels. The pour points were all above the lowest wintertime temperature occurring in the 48 contiguous states 90% of the time.

Cloud point was also acceptably high and exhibited the same "dip" at 75V% reference fuel content of the blends.

The viscosity of the test blends for each F-T stock made smooth curves that were nearly linear. The range of values remained within the high and low limits prescribed in ASTM D 975.

Storage stability was acceptable for all three neat materials and their blends. The curves of precipitate weight versus reference fuel content possessed an unusual "dip" at 75V% reference fuel content.

Lubricity measured by the ball on cylinder lubricity evaluation machine was acceptable for all neat materials and blends according to the most liberal guideline; however, there is a range of guideline threshold values of 2000 to 3100 grams. The blends containing the Hydrocracker (HC) F-T diesel fall below the higher limits.

The lubricity of The Neat F-T Diesel as measured by HFRR did not require additive to produce a wear scar less than either the working US or European thresholds. Lubricity additive would be required for the Hydrocracker (HC) F-T Diesel Fuel – just as it would for the petroleum reference fuel, which produced a 605 micron wear scar, clearly above the threshold. This petroleum-derived reference fuel's lubricity serves as a comparison for the F-T fuels and emphasizes that the lubricating quality of a fuel is not uniquely linked to its source, but depends heavily upon the processing history.

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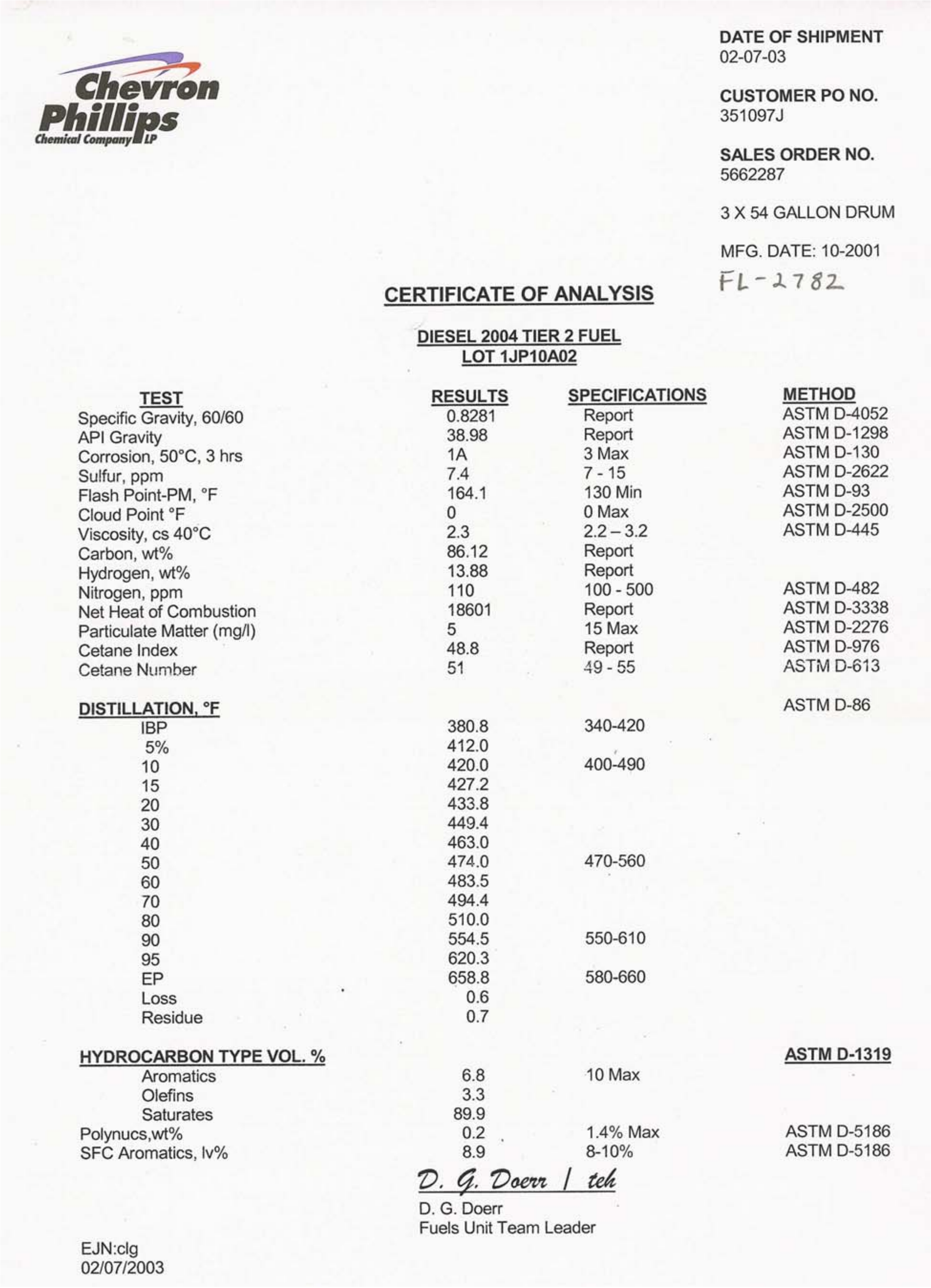
V. List of Acronyms and Abbreviations

Ap X.3.3	Appendix X3.3 in ASTM method D 6078-99 "Standard Test Method for Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)"
ASTM	American Society for Testing and Materials
cSt	CentiStokes
F-T	Fischer-Tropsch
G	Gram(s)
HC	Hydrocracker
HFRR	High Frequency Reciprocating Rig
mM	Millimeter
ppm	Parts per million (weight per volume)
SLBOCLE	Scuffng Load Ball on Cylinder Lubrication Evaluation Machine
EMA	The Engine Manufacturers' Association
EPACT	Energy Policy Act of 1992
S	Sulfur
N	Nitrogen
O	Oxygen



Chevron
Phillips
Chemical Company LP

DATE OF SHIPMENT
02-07-03

CUSTOMER PO NO.
351097J

SALES ORDER NO.
5662287

3 X 54 GALLON DRUM

MFG. DATE: 10-2001

FL-2782

CERTIFICATE OF ANALYSIS

DIESEL 2004 TIER 2 FUEL
LOT 1JP10A02

TEST	RESULTS	SPECIFICATIONS	METHOD
Specific Gravity, 60/60	0.8281	Report	ASTM D-4052
API Gravity	38.98	Report	ASTM D-1298
Corrosion, 50°C, 3 hrs	1A	3 Max	ASTM D-130
Sulfur, ppm	7.4	7 - 15	ASTM D-2622
Flash Point-PM, °F	164.1	130 Min	ASTM D-93
Cloud Point °F	0	0 Max	ASTM D-2500
Viscosity, cs 40°C	2.3	2.2 – 3.2	ASTM D-445
Carbon, wt%	86.12	Report	
Hydrogen, wt%	13.88	Report	
Nitrogen, ppm	110	100 - 500	ASTM D-482
Net Heat of Combustion	18601	Report	ASTM D-3338
Particulate Matter (mg/l)	5	15 Max	ASTM D-2276
Cetane Index	48.8	Report	ASTM D-976
Cetane Number	51	49 - 55	ASTM D-613
DISTILLATION, °F			ASTM D-86
IBP	380.8	340-420	
5%	412.0		
10	420.0	400-490	
15	427.2		
20	433.8		
30	449.4		
40	463.0		
50	474.0	470-560	
60	483.5		
70	494.4		
80	510.0		
90	554.5	550-610	
95	620.3		
EP	658.8	580-660	
Loss	0.6		
Residue	0.7		
HYDROCARBON TYPE VOL. %			**ASTM D-1319**
Aromatics	6.8	10 Max	
Olefins	3.3		
Saturates	89.9		
Polynucs,wt%	0.2	1.4% Max	ASTM D-5186
SFC Aromatics, lv%	8.9	8-10%	ASTM D-5186

D. G. Doerr / teh

D. G. Doerr
Fuels Unit Team Leader

EJN:clg
02/07/2003

EARLY ENTRANCE COPRODUCTION PLANT
PHASE II

Appendix F - Test Report

Subtask 2.5.7.1.a&b&c: NAPHTHA FRACTIONATION

Reporting Period: January 2001 to June 2003

Contributors:
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Date Issued: September 16, 2003

Executive Summary

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are TES (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR) in addition to the U.S. Department of Energy (DOE). TES is providing gasification technology and Fischer-Tropsch (F-T) technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology, and KBR is providing engineering.

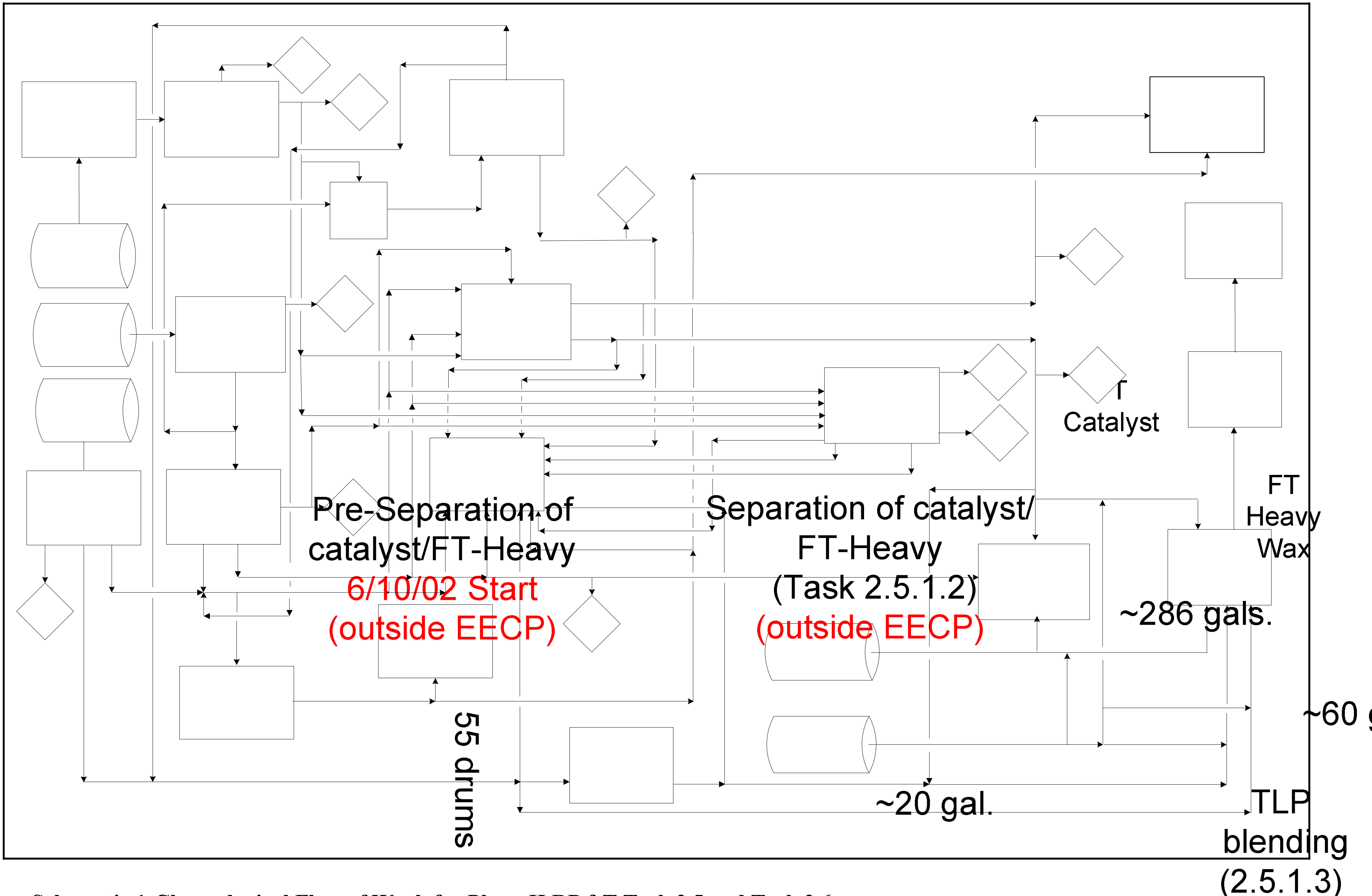
Each of the EECP subsystems was assessed for technical risks and barriers. A plan was developed to mitigate the identified risks (Phase II RD&T Plan, October 2000). The risks to the EECP from Task 2.5 can be mitigated by demonstrating that the products derived from the upgrading of the F-T Synthesis total liquid product can meet or exceed current specifications associated with producing an acceptable naphtha feedstock component for a chemical plant steam cracker to produce ethylene and propylene or as a naphtha feedstock component for hydrogen fuel generation from a fuel cell reformer, finished diesel transportation fuels, and specialty food grade wax products. Subtask 2.5.7.1.a&b&c entitled "Naphtha Fractionation" will mitigate the potential risks to the EECP associated with maximizing the recovery and qualities of end use neat F-T naphtha, neat F-T diesel, and neat F-T wax products meeting boiling range specifications for the product evaluations of Task 2.5.

Subtask 2.5. 7.1. a&b&c –Naphtha Fractionation

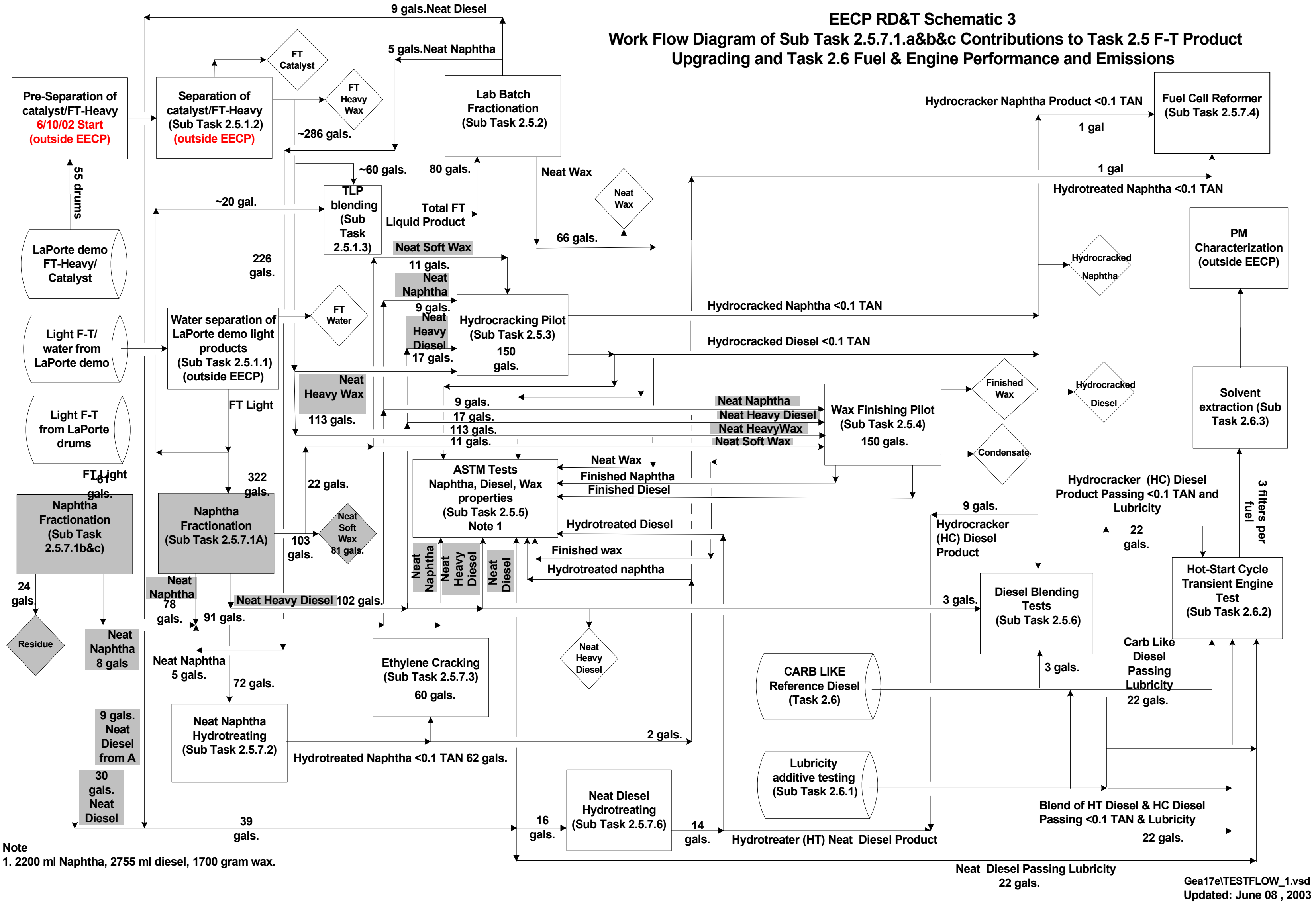
The F-T Synthesis liquid products from the LaPorte AFDU demonstration must be distilled to the required fuel or specialty wax product boiling range specifications. There are technical and economic risks to the EECP if the F-T Synthesis products undergo degradation or liquid yield losses during the distillation process.[1] Subtask 2.5.7.1.a&b&c technical risks are the degree of laboratory fractionation efficiency, recovery of products and possible contamination of distilled products. These technical and economic risks to the EECP are mitigated if the distilled products achieve desired yield recoveries and qualities meeting fuel or specialty product boiling range specifications in order to satisfy the end use evaluation needs of the Subtasks illustrated in **Schematic 1** for Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emissions." The Subtask 2.5.7.1a&b&c Flow of Work is illustrated in **Schematic 2**. Separate Task 2.5 and Task 2.6 Topical reports were prepared for the DOE. Topical reports for each Subtask funded by the DOE as part of the Phase II RD&T were also prepared and are appended to the respective Task 2.5 and Task 2.6 Topical reports. Only the results for the Subtask 2.5.7.1.a&b&c Topical report entitled "Naphtha Fractionation" are reported herein.

The Phase II RD&T Subtask 2.5.7.1.a&b&c Topical Report entitled "Naphtha Fractionation" is appended to the separate EECP DOE Topical Report Task 2.5 entitled "F-T Product Upgrading." The risks to be mitigated by Subtask 2.5.7.1.a&b&c fractionations were the maximum recoveries of neat F-T diesel, neat F-T naphtha, and neat F-T soft wax products meeting both fuel and specialty wax product boiling range specifications with the minimal introduction of background contaminants from upgrading equipment and sample handling. Subtask 2.5.7.1a&b&c fractionated the F-T Light Product from the LaPorte AFDU demonstration after the risk of free water was successfully removed. Subtask 2.5.7.1a&b&c performed the fractionation of three different size retains of F-T Light Product recovered from the LaPorte AFDU demonstration. Task 2.5.7.1.a fractionated approximately 1219 liters (322 gals) of F-T Light Product collected in a commercial ISOtainer vessel receiver to maximize the recoveries of neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products. Task 2.5.7.1.b and Task 2.5.7.1.c each fractionated the contents of two partial filled 208 liter (L) (55 gallon(gal)) drums from the drains of an overhead product receiver on the LaPorte AFDU demonstration unit in order to maximize the recovery of neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products.

Inspection testing was done on each of the distillation products obtained from Subtask 2.5.7.1.a, 2.5.7.1.b, and 2.5.7.1.c before composite blending was done to maximize end use products for Task 2.5 and Task 2.6. The results of Subtask 2.5.7.1.a&b&c are presented in this Topical Report appended to Task 2.5 prepared for the DOE. In order to maximize the recovery of neat F-T naphtha for Task 2.5 product evaluations the Subtask 2.5.7.1.a&b&c neat F-T naphtha products were tested and approved for blending with the Subtask 2.5.2 entitled "Lab Batch Fractionation" neat F-T naphtha product. Subtask 2.5.2 distillation and product quality results are reported in a separate Subtask 2.5.2 Topical Report appended to the Task 2.5 Topical Report prepared for the DOE. The neat F-T naphtha was a feed component in the preparation of a ratio-of-production feed blend representing the LaPorte AFDU demonstration F-T Light and F-T Heavy Product streams. This ratio-of-production feed blend is composed of the neat F-T



Schematic 1-Chronological Flow of Work for Phase II RD&T Task 2.5 and Task 2.6



Schematic 2-Work Flow of Subtask 2.5.7.1a&b&c Contributions to Task 2.5 and Task 2.6

naphtha, neat F-T heavy diesel, neat F-T soft wax and neat F-T hard wax products. This ratio-of-production feed blend is the feed slate to both the Subtask 2.5.3 entitled "Hydrocracking Pilot" and the Subtask 2.5.4 entitled "Wax Finishing Pilot." The combined blend of Subtask 2.5.7.1.a&b&c and Subtask 2.5.2 neat F-T naphtha overhead distillation products is also the end use product for Subtask 2.5.7.2 entitled "Neat Naphtha Hydrotreating." The hydrotreated F-T naphtha product is the end use product for both Subtask 2.5.7.3 entitled "Ethylene Cracking" and Subtask 2.5.7.4 entitled "Fuel Cell Reformer."

Inspection testing was done on each of the distillation products obtained from Subtask 2.5.7.1.a, 2.5.7.1.b, and 2.5.7.1.c before composite blending was done to maximize end use products for Task 2.5 and Task 2.6. In order to maximize the recovery of neat F-T diesel for Task 2.5 product evaluations the Subtask 2.5.7.1.a&b&c neat F-T diesel products were tested and approved prior to any blending with the Subtask 2.5.2 entitled "Lab Batch Fractionation" neat F-T diesel product. Inspection testing found the desired 466K (380°F) to 644K (700°F) boiling range specification for the neat F-T diesel product from Subtask 2.5.7.1.a was not achieved due to the lost of its (466K (380°F) to 505K (450°F)) front end boiling range components from operating a Subtask 2.5.7.1.a continuous distillation column overhead product diesel receiver at too hot a temperature resulting in the flashing and loss of diesel vapors into the vacuum system. The 505K (450°F) to 644K (700°F) neat F-T heavy diesel was not used directly in product evaluations for Task 2.6 entitled "Fuel/Engine Performance and Emissions." The 505K (450°F) to 644K (700°F) neat F-T heavy diesel was considered a satisfactory end use product for Task 2.5 product evaluations. The neat F-T heavy diesel was a feed component in the preparation of a ratio-of-production feed blend representing the LaPorte AFDU demonstration F-T Light and F-T Heavy Product streams. This ratio-of-production feed blend is composed of the neat F-T naphtha, neat F-T heavy diesel, neat F-T soft wax and neat F-T hard wax products. This ratio-of-production feed blend is the feed slate to both the Subtask 2.5.3 entitled "Hydrocracking Pilot" and the Subtask 2.5.4 entitled "Wax Finishing Pilot." The primary upgrading objective of Subtask 2.5.3 is the Hydrocracking of the 644K (700°F) plus neat F-T wax to 644K (700°F) minus distillates. The primary upgrading objective of Subtask 2.5.4 is the conversion of the 644K (700°F) plus neat F-T wax to a high melting point food grade wax product. The 505°K (450°F) to 644K (700°F) neat F-T heavy diesel was considered a satisfactory end use product for Subtask 2.5.6 entitled "Diesel Blending Tests." The primary objective of Subtask 2.5.6 is to mitigate the technical and economical risks associated with the direct blending of an F-T neat diesel into the transportation diesel pool.

The 466K (380°F) to 644K (700°F) neat F-T diesel product from Subtask 2.5.7.1.b&c is the designated end use diesel product for the Task 2.6 product evaluations. The Subtask 2.5.7.1.b&c neat F-T diesel products for Task 2.6 product evaluations were tested and approved for blending with the 466K (380°F) to 644K (700°F) neat F-T diesel product from Subtask 2.5.2 entitled "Lab Batch Fractionation." The combined blend of Subtask 2.5.2 and Subtask 2.5.7.1.b&c neat F-T diesel overhead distillation products will take two routes for Task 2.6 product evaluations. A designated quantity of the combined blend of Subtask 2.5.2 and Subtask 2.5.7.1.b&c 466K (380°F) to 644K (700°F) neat F-T diesel overhead distillation products will go directly to product evaluation in Subtask 2.6.1 entitled "Lubricity Additive Testing" to measure the lubricity property of the neat F-T diesel and determine the need for treatment with a commercial additive to pass lubricity. A Subtask 2.6.1 neat F-T diesel product passing lubricity will qualify for product evaluation in Subtask 2.6.2 entitled “Hot-Start Cycle Transient Engine Test” and in Subtask 2.6.3 entitled “Solvent Extraction of Particulate Matter.” A second designated quantity of the combined blend of Subtask 2.5.2 and Subtask 2.5.7.1.b&c 466K (380°F) to 644K (700°F) neat F-T diesel overhead distillation products will under go product evaluation in Subtask 2.5.7.6 entitled “Neat Diesel Hydrotreating.”

Inspection testing was done on each of the distillation products obtained from Subtask 2.5.7.1.a, 2.5.7.1.b, and 2.5.7.1.c before composite blending was done to maximize end use products for Task 2.5 and Task 2.6. In order to maximize the recovery of 644K (700°F) plus neat F-T soft wax for Task 2.5 product evaluations the Subtask 2.5.7.1.a&b&c neat F-T soft wax products were tested and approved prior to any blending. Inspection testing found the 644K (700°F) plus neat soft wax product from Subtask 2.5.7.1.b and Subtask 2.5.7.1.c to be contaminated with high concentration of iron solids (>2000 ppmw). These two neat 644K (700°F) plus soft wax product retains found to be contaminated were discarded. The 644K (700°F) plus neat F-T soft wax product from Subtask 2.5.7.1.a entitled “Naphtha Fractionation” is the designated end use product for Task 2.5 product evaluations.

The Subtask 2.5.7.1.a 644K (700°F) plus neat F-T soft wax product was a feed component in the preparation of a ratio-of-production feed blend representing the LaPorte AFDU demonstration F-T Light and F-T Heavy Product streams. This ratio-of-production feed blend is composed of the neat F-T naphtha, neat F-T heavy diesel, neat F-T soft wax and neat F-T hard wax products. This ratio-of-production feed blend is the feed slate to both the Subtask 2.5.3 entitled “Hydrocracking Pilot” and the Subtask 2.5.4 entitled “Wax Finishing Pilot.” The primary upgrading objective of Subtask 2.5.3 is the Hydrocracking of the 644K (700°F) plus neat F-T wax to 644K (700°F) minus distillates. The primary upgrading objective of Subtask 2.5.4 is the conversion of the 644K (700°F) plus neat F-T wax to a high melting point food grade wax product.

Experimental

Feed Blend Components

Subtask 2.5.7.1.a Naphtha Fractionation –LaPorte AFDU ISOtainer

A commercial “ISOtainer” product receiver vessel was purchased and set up to collect the F-T Light Product at the LaPorte AFDU demonstration. The LaPorte AFDU demonstration design did not allow for the separation of the F-T Light products and free water. To ensure accurate Phase II RD&T Task 2.5 entitled “F-T Product Upgrading” and Task 2.6 entitled “Fuel/Engine Performance and Emission Testing” product upgrading results, free water was separated from the F-T Light Product by Subtask 2.5.1.1 entitled “Water Separation of LaPorte Commingled Water and F-T Light Product.” Subtask 2.5.1.1 was performed by the Southwest Research Institute (SwRI) at their San Antonio, Texas laboratory facilities and was completed outside DOE funding for Phase II RD&T. After the initial separation of free water, the F-T Light Product was transferred into eight 208 liter (55-gal) poly ethylene lined drums. These eight drums were shipped to the ChevronTexaco Energy and Technology Company Integrated Laboratory Technology Company at Richmond, California for end use in Task 2.5 product evaluations.

The objective of fractionating the contents of the composite blend of eight drums of the F-T Light Product from the LaPorte AFDU demonstration ISOtainer is to maximize the recoveries of an IBP-466K (380°F) True Boiling Point (TBP) Neat F-T Naphtha product and a 466K (380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax product for end use in Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emission Testing." Inspection testing found the 644K+ (700°F+) plus neat soft wax product from Subtask 2.5.7.1.b and Subtask 2.5.7.1.c to be contaminated with high concentration of iron solids. The two neat soft wax product retains found to be contaminated were discarded. The neat F-T soft wax product from Subtask 2.5.7.1.a entitled "Naphtha Fractionation" is the designated end use product for Task 2.5 product evaluations.

Subtask 2.5.7.1.b Naphtha Fractionation-LaPorte AFDU Drum No. 1

Two 208 liter (55-gal) poly ethylene lined drums containing F-T Light Product from the LaPorte AFDU demonstration were received at the ChevronTexaco Energy and Technology Company Integrated Laboratory Technology Company at Richmond, California. The two drums were designated as Drum Number One and Drum Number Two. These two drums of F-T Light Product were recovered from an overhead product receiver on the LaPorte AFDU demonstration unit whereas the majority of the F-T Light Product from the LaPorte AFDU demonstration was collected directly in a purchased commercial "ISOtainer" designated as a receiver for the F-T Light Product liquids. Drum One and Drum Two were handled and distilled individually out of concern of potential contamination residing with the contents of each drum. The objective for distilling the contents of each drum is to maximize the recoveries of an IBP to 466K (380°F) True Boiling Point (TBP) Neat F-T Naphtha product and a 466K (380°F) to 644K (700°F) neat F-T diesel product for end use in Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emission Testing." Inspection testing found the 644K (700°F) plus neat soft wax product from Subtask 2.5.7.1.b (Drum Two) and Subtask 2.5.7.1.c (Drum Two) to be contaminated with high concentration of iron solids (>2000 ppmw iron solids). The two neat soft wax product retains found to be contaminated with iron solids were discarded. The neat F-T soft wax product from Subtask 2.5.7.1.a (eight drums of F-T Light Product from ISOtainer) is the designated end use neat F-T soft wax product for Task 2.5 product evaluations. The LaPorte AFDU F-T Light Product contents of Drum Number One under went upgrading in Subtask 2.5.7.1.b entitled "Naphtha Fractionation."

Subtask 2.5.7.1.c Naphtha Fractionation – LaPorte AFDU Drum No. 2

Two 208 liter (55-gal) poly ethylene lined drums containing F-T Light Product from the LaPorte AFDU demonstration were received at the ChevronTexaco Energy and Technology Company Integrated Laboratory Technology Company at Richmond, California. The two 208 liter (55-gal) drums were designated as Drum Number One and Drum Number Two. These two drums of F-T Light Product were recovered from an overhead product receiver on the LaPorte AFDU demonstration unit whereas the majority of the F-T Light Product from the LaPorte AFDU demonstration was collected directly in an ISOtainer designated for F-T Light product liquids. Drum One and Drum Two were handled and distillated individually out of concern of potential contamination residing with the contents of each drum. The objective for distilling the contents of each drum is to maximize the recoveries of an IBP to 466K (380°F) True Boiling Point (TBP) neat F-T Naphtha product and a 466K (380°F) to 644K (700°F) neat F-T diesel product for end use in Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emission Testing." Inspection testing found the 644K (700°F) plus neat soft wax product from Subtask 2.5.7.1.b and Subtask 2.5.7.1.c to be contaminated with high concentration of iron solids (>2000 ppmw). The two neat soft wax product retains found to be contaminated with iron solids were discarded. The neat F-T soft wax product from Subtask 2.5.7.1.a entitled "Naphtha Fractionation" is the designated end use product for Task 2.5 product evaluations. The LaPorte AFDU F-T Light Product contents of Drum Number Two under went upgrading in Subtask 2.5.7.1.b entitled "Naphtha Fractionation."

Scope of Work

Approximately 1219 liters (322 gals) of F-T Light Product transferred from the LaPorte AFDU demonstration ISOtainer product receiver into eight 208 liter (55-gal) polyethylene lined drums after carrying out a free water removal processing step were fractionated under Subtask 2.5.7.1.a into a neat F-T naphtha product with an IBP-466K (380°F) True Boiling Point (TBP) boiling range, a neat F-T diesel product with a 466K (380°F) to 644K (700°F) TBP boiling range, and a 644K (700°F) plus neat F-T soft wax product employing both batch and continuous distillation technology. Approximately 231 liters (61 gal) of F-T Light Product distributed between two 208 liter (55-gal) drum containers designated Drum Number One for Subtask 2.5.7.1.b and Drum Number Two for Subtask 2.5.7.1.c containing LaPorte AFDU F-T Light Product were fractionated into a neat F-T naphtha product with an IBP-466K (380°F) True Boiling Point (TBP) boiling range, a neat F-T diesel product with a 466K (380°F) to 644K (700°F) TBP boiling range, and a 644°K (700°F) plus neat F-T soft wax product employing batch distillation technology.

A common scope of work exists for Subtask 2.5.7.1.a (batch and continuous distillation of 1211 liters (320 gals) of F-T Light Product in eight 208 liter (55-gal) drums originally from the ISOtainer), Subtask 2.5.7.1.b (batch distillation of F-T Light Product in a 208 liter (55-gal) drum designated as Drum One) and Subtask 2.5.7.1.c (batch distillation of F-T Light Product in a 208 liter (55-gal) drum designated as Drum Two). The scope of work (SOW) consists of the following work procedures:

(1) Verify cleanliness of all distillation equipment. Decant off the separate water phase present in the Drum.
(2) Use a hydrophilic filter to reduce the dissolved water content of the remaining hydrocarbons in the Drum to an acceptable level to avoid foaming in the batch and/or continuous distillation still equipment.
(3) Determine the dissolved water content of the hydrocarbon phase remaining after step 2.
(4) Perform a small laboratory distillation on the hydrocarbon phase obtained from step (2) with the known Karl-Fischer dissolved water content from step (3). Define the acceptance criteria for maximum dissolve water content, wt% (Karl-Fischer dissolved water content by ASTM test method) to be met on the hydrocarbon phase of the Drum contents prior to conducting the batch

and/or continuous distillation(s). The objective is to avoid foaming and poor separation between product cuts during batch distillation.

(5) Conduct an ASTM D-2887 simulated distillation on the hydrocarbon phase of the drum to define the yields of IBP-466K (380°F) neat F-T naphtha product, a 466K (380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax product for use in determining the product yields desired from the batch fractionation.

(6) An additional filtration sample preparation step was added to reduce the iron solids content of the hydrocarbon phase remaining in the Drum beyond whatever is removed in the course of the filtration for water removal in step (2). The EECP team proposes that the iron solids that remain in the hydrocarbon phase be charged to the batch and/or continuous distillation still(s) as part of the hydrocarbon feed.

(7.a) On the batch and/or continuous distillation equipment distill the entire hydrocarbon contents of the Drum to collect an IBP to 466K (380°F) TBP neat F-T naphtha product, a 466K (380°F) to 644K (700°F) TBP neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax product. It may be necessary due to still pot size limitations for batch distillation to conduct multiple runs to fractionate the drum contents.

(7.b) It was recommended to take a couple of narrow cuts prior to and up to the target endpoint of both the naphtha and diesel overhead cuts. Small test blends and D 2887 simulated distillations could be performed to insure that both the naphtha and diesel cut endpoints are not over shot during batch and/or continuous distillation operations.

(8) Perform background contamination level check testing of the batch and/or continuous distillation equipment. The objective of the testing is to document that contaminant levels greater than 0.5-ppmw sulfur per ASTM D 5453, 0.5- ppmw nitrogen per ASTM D 4629, and 0.5 volume percent aromatics per ASTM D 1319 are not present before charging the hydrocarbon contents of the Drum to the batch and/or continuous distillation still(s).

(9) Conduct an ASTM D 2887 simulated distillation on each of the naphtha, diesel, and soft wax product cuts collected during each batch and/or continuous distillation of the Drum contents for acceptance testing prior to composite blending of individual naphtha, diesel, and soft wax products.

(10) Due to the corrosive nature (High Total Acid Number) of the neat F-T naphtha products and the neat F-T diesel products, no carbon steel containers was used for collection and storage of the neat F-T product cuts. Use of glass containers with polyethylene-lined caps and/or polyethylene lined steel drums depending upon sample retain size requirements was recommended.

(11) The IBP to 466K (380°F) neat F-T naphtha products and 466K (380°F) to 644K (700°F) neat F-T diesel products will be retained and stored in glass or polyethylene-lined container (s). The 644K (700°F) plus neat F-T soft wax products will be stored in new clean 208 liter (55-gal) carbon steel drum(s) and will be checked for the presence of iron solids. The F-T Light Product was collected as a condensed vapor along with water in an ISOtainer product receiver and therefore is believed to be free of iron solids(<10 ppmw). This was confirmed by metals analyses of the 644K (700°F) plus neat F-T soft wax products.

(12) The composite blends of the neat F-T naphtha product cut(s), the neat F-T diesel product cut(s), and the neat F-T soft wax product cuts obtained from each batch and/or continuous distillation(s) of a Drum will be tested for the presence of sulfur by ASTM D 5453, nitrogen by ASTM D 4629, aromatics by ASTM D 1319, and metals.

(13) The composite blends of the neat F-T naphtha product cut(s) and of the neat F-T diesel product cut(s) will be collected from batch and/or continuous distillation(s) of the Drum and be kept segregated from future composite blends of neat F-T naphtha product cuts, neat F-T diesel product cuts, and neat F-T soft wax product cuts obtained from the distillation of Drums from each of the three F-T Light Product receipts (The eight drums from the ISOtainer for Subtask 2.5.7.1.a, designated Drum One for Subtask 2.5.7.1.b, and designated Drum 2 for Subtask 2.5.7.1.c). Only after inspection testing has been conducted will approval be given to prepare composite blends with each product cut retain obtained from the three F-T Light Product receipts.

(14) The EECP team requested cold ~ 272K (30°F) storage of the neat F-T naphtha product cut(s) and cool storage ~286K (55°F) of the neat F-T diesel product cut(s) to avoid the loss of light ends during intermediate storage prior to their end use in Task 2.5 and Task 2.6 product evaluations. The neat F-T soft wax product cut(s) should be stored indoors to avoid potential exposure to weather elements.

(15) The batch and/or continuous distillation conditions will be set as necessary (e.g. use of vacuum) to insure that thermal cracking of the 644K (700°F) plus neat F-T soft wax fraction contents of the Drum is minimized to maintain the integrity and qualities of the overhead neat F-T naphtha product cut(s) and the neat F-T diesel product cut(s).

(16) A performance target of ± 2% mass balance closure for each of the batch and/or continuous distillation run(s) conducted on the contents of a Drum has been set.

(17) The True Boiling Point (TBP) product cut point targets for the batch and/or continuous distillation(s) are an IBP to 466K (380°F) neat F-T naphtha product cut(s), a 466K (380°F) to 644K (700°F) neat F-T diesel product cut(s), and a 644K (700°F) plus neat F-T soft wax product bottom(s).

(18) The fractionation efficiency of the batch and/or continuous distillation run(s) will be judged on the basis of the gap and overlap between product cuts. The gap between the ASTM D-86 temperatures at 95 vol % off of the neat F-T naphtha product cut versus the ASTM D-86 temperature at 5 vol % off of the neat F-T diesel product cut will be a minimum of 30°F. The overlap between the ASTM D-86 temperature at 95 vol % off of the neat F-T diesel product cut versus the ASTM D-86 temperature at 5 vol % off of the neat F-T soft wax product cut will be a maximum of 30°F.

(19) All LaPorte AFDU demonstration F-T Light Product and F-T Heavy Product along with feed and products generated during Task 2.5 product evaluations which are not consumed in destructive inspection testing will be saved.

Results and Discussion

Subtask 2.5.7.1.a Naphtha Fractionation of LaPorte AFDU ISOtainer

Inspection of Shipping Drums

The eight 208 liter (55-gal) drums of ~1217.75 liter (322 gal) of F-T Light Product originating from the LaPorte AFDU demonstration ISOtainer product receiver were each inspected. The inside of all eight drums were visually inspected and found to have deformed liners. Aliquots were pulled from each of the eight drums to establish the baseline sulfur and nitrogen levels present. The sulfur and nitrogen levels of the eight drums of F-T Light Product ranged from 0.09

ppmw to 0.14 ppmw in sulfur contents and from 14.8 ppmw to 19.4 ppmw in nitrogen contents. The eight drums were inspected for the presence of free water and no free water was observed.

Blending Kettle and Distillation Stills

Equipment should be cleaned expressly for the F-T Light Product to be handled, and rinse solvents should be analyzed for sulfur, nitrogen, and aromatics. All equipment involved with Subtask 2.5.7.1.a was thoroughly cleaned with new toluene then thoroughly rinsed new hexane and nitrogen dried. This equipment consisted of a 3785 liter (1000 gal) blending kettle, a batch distillation still designated Pilot Plant 51, and a continuous distillation still designated Pilot Plant 114. Aliquots of the new Toluene and new Hexane were submitted for sulfur and nitrogen analyses to establish a base line. Aliquots of the final rinse hexane were submitted sulfur and nitrogen analyses confirming that all equipment employed for this project met the cleanliness specifications. Tabulated below are the results of the background checks.

Subtask 2.5.7.1.a Equipment	Rinse solvent sulfur, ppmw	Rinse solvent nitrogen, ppmw
3785 liter (1000 gal) Blending Kettle	0.04	0.10
Batch Distillation Still	0.10	0.18
Continuous Distillation Still	0.11	0.10

Blending Kettle Operation for a Composite Blend F-T Light Product

The composite blending of the eight drums of the F-T Light Product which originated from the ISOtainer product receiver of the LaPorte AFDU demonstration along with the ILT retain samples remaining from individual drum inspection testing was performed in the cleaned 3785 liter (1000 gal) reactor kettle employing thoroughly cleaned stainless steel hoses and pump. The eight drums were weighed prior to charging the F-T Light Product contents to the blending kettle, the empty drums were tared and all weights recorded were compared with weights recorded on the drums. The reactor kettle was purged with nitrogen before charging and a nitrogen blanket was maintained throughout the process. The composite blend for Subtask 2.5.7.1.a was prepared at 322K (120°F) with agitation for approximately two hours. The agitator was shut off and the composite blend was allowed to settle at 322K (120°F) for two and half hours. The composite blend was checked for free water (none observed) before discharging to new 208 liter (55-gal) drums with phenolic resistance liners. The tare weights of the new drum containers and the corresponding weights of the F-T Light Product contents of each drum were documented by ILT personnel before transferring the contents of the eight drums to a blending kettle. A total of 1085 kilograms (kgs) (2,388 pounds (lbs)) of F-T Light Product was charged from the eight drums into the blending kettle. A Phaudler glass lined 3785 liters (1000 gal) reactor kettle with an agitator and baffle, heated with hot water or steam to 436K (325°F) with a riser, condenser, and a 767 liter (200 gal) glass-lined receiver vessel. The unit can operated at atmospheric or under vacuum (760 millimeters (mm) of mercury (Hg) to 10 mm of (Hg)). A total of 1074 kgs (2,363 lbs) of F-T Light Product was recovered from the blending kettle operation to prepare a composite blend these kgs represents a 99.2 wt% recovery from the drum removal/ blending kettle process. Out of the 1074 kgs (2,363 lbs) of F-T Light Product, 1016 kgs (2235.5 lbs) were distilled under Subtask 2.5.7.1.a using both batch and continuous distillation technologies. A remaining 3.1 kgs (6.8 lbs) or about 3.785 liters (one gal) was set aside for inspection testing needs. A remaining 59.5 kgs (131 lbs) of F-T Light Product were set aside as a feed blend component for Subtask 2.5.2 entitled "Lab Batch Fractionation." The 59.5 kgs (131 lbs) of F-T Light Product was used to prepare a ratio-of-production blend with 214.5 kgs (472 lbs) of F-T Heavy Product to be distilled under Subtask 2.5.2 into neat F-T naphtha, neat F-T diesel, and neat F-T wax products. The mass balance closure is tabulated below.

Description of F-T Light Product Receipt	Weight, Kgs (Lbs)
Contents In eight drums from ISOtainer	1085.4 (2,387.8)
Subtask 2.5.2 ratio-of-production blend retain	59.5 (131)
One 3.785 liter(1 gal) retain for Inspection Testing	3.1 (6.8)
Subtask 2.5.7.1.a Feed for Batch Distillation	1016.1 (2235.5)
Losses from handling	6.6 (14.5)
Mass Balance Closure	99.4 wt%

The 1016.1 kgs (2235.5 lbs) of composite blend prepared in the blending kettle charging the eight drums of F-T Light Product were submitted for the inspection tests presented in Table 1 below.

Table 1-Subtask 2.5.7.1.a F-T Light Product from ISOtainer

Composite Blend of F-T Light Product	
Inspection Tests	Results
Gravity,	
API	43.4
Specific	0.8090
Sulfur, ppmw	0.14
Nitrogen, ppmw	16.4
Aromatics, wt%	Not detected
Karl Fisher Water, wt%	0.22
D2887 Distillation, °K (°F)	
IBP	336 (146)
5%	396 (253)
10%	422 (300)
30%	488 (419)
50%	570 (566)
70%	651 (713)
90%	699 (798)
95%	706 (811)
EP	787 (957)

Batch Distillation of Composite Blend of F-T Light Product

The decision was made for Subtask 2.5.7.1a to conduct an initial batch distillation at atmospheric pressure to distill off the IBP to 466K (380°F) neat F-T naphtha product contained in the 1016.1 kgs (2235.5 lbs) of composite blend of F-T Light Product.

Product Yields from ASTM D-2887 Distillation

An ASTM D-2887 simulated distillation on the composite blend of F-T Light Product indicated that with perfect fractionation the F-T Light Product contains around 22% of IBP to 466K (380°F) neat F-T naphtha product, 46.5% of 466K (380°F) to 644K (700°F) neat F-T diesel product, and 31.5% of neat F-T soft wax product.

Product Yields from Laboratory Scale Distillation Trial

The laboratory scale atmospheric distillation trial was performed to observe the composite blend of F-T Light Product for foaming potential and bumping due to the presence of water, and to develop a correlation distillation for the larger production scale batch and continuous distillations to follow. This laboratory scale distillation developed moisture droplets in the reboiler flask neck at approximately a 369K (205°F) reboiler temperature at atmospheric pressure. The distillate take-off was started at 324K (124°F) distillate temperature at a reflux ratio of 5:1 and the reboiler temperature was 452K (354°F) at atmospheric pressure. The neat F-T naphtha and neat F-T diesel product cuts were completed without any foaming or bumping problems. The neat F-T naphtha product cut contained approximately 1 to 2 milliliters (ml) of brownish colored water. The tabulation below provides the mass balance closure for the laboratory scale distillation trial.

Stream Identity	Weight(Wt), grams(oz.)	wt% basis Feed	Gravity, API	Gravity, Specific
Charge	1618 (57.07)		43.4	0.8090
Naphtha	383.6 (13.53)	23.7	53.2	0.7661
Diesel	676.7 (23.87)	41.8	43.6	0.8081
Soft Wax	537.3 (18.95)	33.2	37.7	0.8363
Column Holdup	17.3 (0.61)	1.1		
Loss	3.1 (0.11)	0.2		
Recovery		98.7		

Table 1 presents the results from the inspection testing conducted on the neat F-T naphtha, neat F-T diesel and the neat F-T soft wax products from the laboratory scale distillation trial on the composite blend of F-T Light Product.

Product Yields from Batch Distillation of F-T Light Product

The Subtask 2.5.7.1.a initial batch atmospheric distillation process to produce the IBP to 466K (380°F) neat F-T naphtha product for end use in Task 2.5 product evaluations was successful completed on the distillation still designated as Pilot Plant 51. There were no signs of foaming or bumping during the batch distillation which was expected based upon the successful laboratory scale distillation trial performed earlier. The tabulation below provides the mass balance closure obtained for the Task 2.5.7.1.a initial batch atmospheric distillation upgrading process step. The 98.7 wt% mass balance is within acceptable limits. The 22 wt% yield of neat F-T naphtha is in good agreement with the 22.1 wt% neat F-T naphtha product yield expected from the ASTM D-2887 simulated distillation results for the F-T Light Product which was the feed to the batch distillation process.

Stream Identity	Wt, kg (lbs)	wt% basis Feed	Vol, liter(gal)	Gravity, API	Gravity, Specific
Feed	1016.1 (2240)		1218.8 (322)	43.4	0.8090
Naphtha	224.4. (494	22.1	295.2 (78)	54.8	0.7595
380F Plus	778.1 (1715)	76.6	942.5 (243)	40.0	0.8251
Water	1.1 (2.43)	0.1			
Loss	12.5 (27.6)	1.2			
Recovery		98.7			

Table 2 presents the results from the inspection testing conducted on the IBP to 466K (380°F) neat F-T naphtha product obtained from the Subtask 2.5.7.1.a batch atmospheric distillation processing step. The quality and yield of neat F-T naphtha was judged acceptable for use in product evaluations in Task 2.5 entitled "F-T Product Upgrading."

Table 2-Subtask 2.5.7.1.a Batch and Continuous Distillation Product Results

Subtask 2.5.7.1a **Fraction Analyses**	**Composite Blend of F-T Light Product**	**Lab Scale Distillation Trial Naphtha Product**	**Batch Distillation Naphtha Product Composite**	**Lab Scale Distillation Trial Diesel Product**	**Continuous Distillation Diesel Product Composite**	**Lab Scale Distillation Trial Soft Wax Product**	**Continuous Distillation Soft Wax Product Composite**
API Gravity	43.4	53.2	54.8	43.6	40.8	37.7	36.7
Specific Gravity	0.8090	0.7661	0.7595	0.8081	0.8212	0.8363	0.8413
Fraction, wt% basis Feed		23.7	22.1	41.8	30.7[1]	33.2	32.2
Karl Fischer Water, wt%	0.22	0.40	0.23	na	Na	Na	Na
Nitrogen, Other ppmw	16.35	1.471		7.067		42.07	
Nitrogen, Chemiluminescene, ppmw			<1		9.9		39.7
Sulfur, Chemiluminescene, ppmw			2		2.4		11.4
Sulfur, Dohrmann, ppmw	<1			<1			
Sulfur, Antek, ppmw				<1		1.2	
Sulfur, Other, ppmw		<6.0		<6.0		<6.0	
Aromatics, wt%			None detected		None detected		None detected
D2887/D86/D1160, °K (°F)	D2887	D2887/D86	D2887/D86	D2887/D86	D2887/D86	D2887/D1160	D2887/D1160
IBP	336 (146)	303 (86) /162	328 (131) /172	461 (371) /424	479 (402) /491	632 (679) /747	611 (641) /641
5	396 (253)	362 (193) /232	367 (201) /244	478 (401) /448	506 (452) /510	652 (715) /755	645 (701) /733
10	422 (300)	369 (204) /250	371 (209) /257	488 (419) /456	523 (482) /519	663 (734) /760	660 (729) /750
20	460 (369)	396 (254) /262	396 (254) /270	507 (454) /471	544 (519) /533	681 (767) /771	682 (768) /764
30	488 (419)	408 (275) /277	414 (285) /283	526 (488) /492	560 (549) /549	691 (784) /778	691 (785) /778
40	526 (487)	422 (300) /287	422 (300) /295	544 (520) /514	576 (577) /565	696 (793) /784	696 (794) /786
50	570 (566)	424 (304) /299	425 (305) /306	562 (552) /537	590 (603) /581	699 (799) /787	700 (800) /788
60	612 (642)	440 (333) /309	444 (340) /317	585 (593) /563	605 (629) /597	702 (805) /793	703 (806) /794
70	651 (713)	446 (344) /320	446 (343) /328	602 (625) /588	618 (653) /612	707 (813) /809	707 (813) /801
80	690 (782)	449 (349) /331	459(366) /339	617 (652) /609	630 (675) /628	719 (834) /870	715 (827) /810
90	699 (798)	467 (382) /346	467 (382) /352	631 (677) /630	644 (699) /647	762 (912) /937	759 (907) /880
95	706 (811)	469 (384) /355	469 (385) /362	641 (694) /643	654 (717) /664	812 (1003) /----	801 983) /-----
EP	787 (957)	496 (434) /375	555 540() /382	657 (724) /656	689 (781) /682	944 (1240) /----	960 (1269) /953
ICP Metals, ppmw							
Iron (FE)	16.6						125

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[1] Weight percent low by approximately 12% due to front-end of diesel lost during processing

Product Yields from Continuous Distillation of F-T Light Product

Following the successful recovery and quality of neat F-T naphtha product from an initial batch atmospheric distillation process step on Pilot Unit 51, the remaining 1711 lbs (777.7 kgs) of 466K (380°F) plus product bottoms from the previous batch distillation was charged to the continuous vacuum distillation still designated as Pilot Plant 114 operating under vacuum to recovery a 466K (380°F) to 644K (700°F) neat F-T diesel product and a 644K (700°F) plus neat F-T soft wax product. Task 2.5.7.1.a continuous distillation under vacuum to recover diesel and soft wax products encountered problems which resulted in only an 83.3 wt% mass balance closure. A loss of 129.7 kgs (286 lbs) was calculated based on the 466K (380˚F) plus F-T Light Product charged to the continuous distillation still. Upon investigation of the run data, the neat F-T diesel product overhead condensers (3 Heat Exchangers) were controlled at too hot a temperature of 344K (160°F) instead of the desired colder ambient temperature (of approximately 297K (75°F)). Because of this elevated temperature full condensing of the neat F-T diesel product stream did not occur causing an irretrievable loss of the front-end of the diesel fraction through the vacuum system. About 29 wt% almost a third of the expected neat F-T diesel product was lost during Subtask 2.5.7.1.a. Based upon the previous yield predictions available for the neat F-T diesel from both the ASTM D-2887 distillation, laboratory scale distillation trial, and the batch distillation results the low recovery of diesel yield being observed should have been detected early on by operating personnel during the start of the continuous distillation operation and corrective actions taken immediately to negate the magnitude of the loss. The tabulation below provides the mass balance closure for the continuous distillation process step completed for Task 2.5.7.1.a. The mass balance closure of 83.4 wt% falls outside acceptable standards.

Stream Identity	Wt, km (lb)	wt% basis Feed	Vol, liter (gal)	Gravity, API	Gravity, Specific
380F Plus Feed[1]	777.7 (1715)		942.5 (249.0)	40.0	0.8251
Heavy Diesel	311.5 (687)	40.1	384.9 (101.7)	40.8	0.8212
Soft Wax	327 (721)	42.1	389.1 (102.8)	36.7	0.8413
Column Holdup	9.1 (20)	1.2			
Recovery		83.4 before loss			
Loss Light Diesel	130.1	16.7			

Note 1: Weight percents are based on charge weight of the 380˚F (466˚K) Plus F-T Light Product cut from the previous batch atmospheric distillation and not the F-T Light Product.

Table 1 presents the results from the inspection testing conducted on the 505K (450°F) to 644K (700°F) neat heavy F-T diesel product obtained from the Subtask 2.5.7.1.a continuous vacuum distillation processing step. The quality and yield of the neat heavy F-T diesel and neat F-T soft wax products was judged acceptable for use in select product evaluations in Task 2.5 entitled "F-T Product Upgrading."

The neat F-T diesel product from Task 2.5.7.1.a is referred to as the neat heavy F-T diesel product in Task 2.5 product evaluations. The neat heavy F-T diesel had a D-2887 temperature at

5% off of 505K(450°F) compared to a D-2887 temperature at 5% off of 478K (400°F) for the neat F-T diesel product from the laboratory scale distillation trial. The neat heavy F-T diesel product had an API gravity of 40.8 compared to the 43.6 API gravity of the neat F-T diesel product from the laboratory scale distillation. The heavy neat F-T diesel product was used as a feed component in the preparation of a ratio-of-production feed blend representing F-T Light Product and F-T Heavy Product for feed to Subtask 2.5.3 entitled "Hydrocracking Pilot" and as feed to Subtask 2.5.4 entitled "Wax Finishing Pilot." The neat heavy F-T diesel product from Subtask 2.5.7.1.a was used in the Subtask 2.5.6 entitled "Diesel Blending Tests." The neat heavy F-T diesel of Subtask 2.5.7.1.a was not used in the product evaluations of Task 2.6 entitled "Fuel/Engine Performance and Emissions." The neat heavy F-T diesel product of Subtask 2.5.7.1.a was not used in Subtask 2.5.7.6 entitled "Neat Diesel Hydrotreating." which produced an end use product for Task 2.6. As discussed later the neat F-T diesel products from Subtask 2.5.7.1. b&c entitled "Naphtha Fractionation" were used for Task 2.6 product evaluations.

Subtask 2.5.7.1.b Naphtha Fractionation of LaPorte AFDU Drum One

The contents of Drum One of the F-T Light Product drained from an overhead product receiver on the LaPorte AFDU demonstration unit was visually inspected and considered in reasonable condition with a rusty top and the side dented but there was no evidence of product leakage. All equipment coming in contact with the F-T Light Product in Drum One was thoroughly cleaned with toluene and hexane then dried with nitrogen.

Free Water Removal from LaPorte AFDU Drum One

Before distilling the contents of Drum One of the F-T Light Product it was determined that free water needed to be removed. The process of removing the free water from Drum One of F-T Light Product was accomplished using a fork lift with a drum handling attachment. A clean drum valve was installed securely in the large drum bung opening before the Drum One was raised and tilted at 135° from perpendicular facing the top of drum towards the ground at a 45° angle with the valve at the lowest point. A new open-top 208 liter (55-gal) drum with a phenolic resistant liner was placed under the suspended Drum One of F-T Light Product to contain any unintentional releases and for decanting the water. After approximately 20 hours of settling at ambient temperature in this position, 26.4 kgs (58 lbs) of free water was removed. The tabulation below provides the mass balance closure for the free water removal process.

Drum Number One from LaPorte AFDU	
Net Weight of Drum One with free water	135.3 kilograms (297.7 lbs)
Free Water Removed (19.5 wt %)	26.3 kgs (58.0 lbs)
F-T Light Product	109 kgs (239.7 lbs)
Recovery	100.0 wt%

A 3.785 liter (1 gal) retain was set aside of the F-T Light Product from Drum One after free water removal for inspection testing and for a laboratory scale distillation trial on a 2 liter (.53 gal) still. Table 3 below provides the results of the inspection testing conducted on the F-T Light Product from Drum One of the LaPorte AFDU demonstration after free water removal.

Table 3 – Subtask 2.5.7.1.b F-T Light Product from Drum One Test Results

Subtask 2.5.7.1.b F-T Light Product from Drum One Inspection Tests	
Gravity, API	41.2
Gravity, Specific	0.8193
Karl Fisher Water, wt%	0.46
Nitrogen, ppmw	7
Sulfur, ppmw	1.5
Aromatics, wt%	Not detected
D2887 Simulated Distillation, °K (°F)	
IBP	370 (206)
5%	420 (297)
10%	445 (342)
30%	530 (494)
50%	604 (628)
70%	691 (785)
90%	710 (819)
95%	756 (902)
EP	938 (1229)

Upon completion of inspection testing the unused retain from the 3.785 liter (1 gal) sample of the F-T Light Product from Drum One after free water removal was recombined with its larger sample retain to yield a total of 107 kgs (235.4 lbs) for future Subtask 2.5.7.1.b batch atmospheric distillation.

Product Yields from ASTM D-2887 Distillation

An ASTM D-2887 simulated distillation on the F-T Light Product from Drum One after free water removal indicated that with perfect fractionation the F-T Light Product from Drum One contains around 14.5% of IBP to 466°K (380°F) neat F-T naphtha product, 43.6% of 466°K (380°F) to 644°K (700°F) neat F-T diesel product, and 41.9% of neat F-T soft wax product.

Product Yields from Initial Laboratory Scale Distillation Trial

An initial laboratory scale distillation trial was performed to observe the F-T Light Product from Drum One after free water removal for foaming potential and bumping due to the presence of residual water, and to develop a correlation distillation for the larger production scale batch distillation of Subtask 2.5.7.1.b to follow. The distillation still pot employed for the initial laboratory scale distillation trial had heavy particulate residue that raised concerns of potential hot spots forming during the Subtask 2.5.7.1.b batch distillation processes. These hot spots may cause degradation of the distillation charge consisting of the F-T Light Product compromising the distillation results.

The initial laboratory scale distillation trial ran at atmospheric pressure and under vacuum without burping or foaming being present. The distillate take-off was started at 336K (146˚F) distillate temperature at a reflux ratio of 5:1 and the reboiler temperature was 475K (396˚F) at atmospheric pressure. The neat F-T naphtha product was obtained at a 380°F (466K) distillate temperature with a 570K (566°F) reboiler temperature. There was approximately 25 milliliters (ml) of water collected in the distillate and was accounted for accordingly in the distillation summary report. The neat F-T diesel product was obtained operating the column under 50 milliliters (mL) of mercury (Hg) without any foaming or bumping problems. Even though this initial laboratory scale distillation trial did not demonstrate any degradation tendencies, a second laboratory scale distillation trial was warranted on the F-T Light Product after free water removal and after filtration to reduce particulates. The tabulation below presents a comparison of product yields from the ASTM D-2887 simulated distillation performed on the F-T Light Product of Drum One from the LaPorte AFDU demonstration as received and the initial laboratory scale distillation trial conducted after free water removal from the F-T Light Product in Drum One. One reason for the differences observed below may be due to the weight percents for the product yields shown for the as received Drum One were estimated from the D-2887 distillation and did not take into account any water that may have been suspended in the as received sample.

Subtask 2.5.7.1.b F-T Light Product from LaPorte AFDU Drum One Product Yield Comparisons	D2887 Distillation on Drum One prior to free water removal	Initial Laboratory Scale Distillation Trial after free water removal
IBP to 466°K (380°F) Naphtha, wt%	14.5	12.7
466°K (380°F) to 644°K (700°F) Diesel, wt%	43.6	40.0
644°K (700°F) plus Soft Wax, wt%	41.9	46.1
Recovery, wt%	100	98.8

Filtration Process for Solids Removal from LaPorte AFDU Drum One

While the initial laboratory scale distillation trial (FSL 9455) was being performed the decision was made to filter the F-T Light Product from Drum One after free water removal through a 5-micron absolute filter to remove particulates that may cause “Hot Spots” during the future Subtask 2.5.7.1.b batch fractionation work that may also lead to premature thermal degradation. It became evident quite early in the filtration of particulates that the 5-micron absolute filter was too fine for this product to start with. The filter was changed to a 25-micron nominal filter and the process was resumed without any problems. After approximately 24 hours of filtering with the 25-micron filter, the filter was switched back to a 5-micron absolute then to a 10-micron absolute filter for the final filtration of particulates, because the differential pressure using 5-micron filter was too high indicating that the product contained a high amount of particulates. The tabulation below presents the results of the mass balance closure around the filtration of particulate processes.

Subtask 2.5.7.1.b Drum One from LaPorte AFDU F-T Light Product after free water removal	
Drum One after free water removal	107.0 kgs (235.4 lbs)
25-Micron filter Product Hold-up	11.8 kgs (26.0 lbs)
Pump and hoses Product Hold-up	1.3 kgs (2.8 lbs)
Net F-T Light Product after 25-micron filtration	93.6 kgs (206.6 lbs)
Recovery, wt% from 25-Micron Filtration	87.8
Net F-T Light Product after 25-micron filtration	93.6 kgs (206.6 lbs)
5 and 10-Micron filter, pump, hose Product Hold-up	9.2 kgs (20.3 lbs)
3.785 liter (1 gal) sample retain for testing	3.1 kgs (6.8 lbs)
Net F-T Light Product after solids filtration processes	81.6 kgs (179.5 lbs)
Recovery, wt% from 5 and 10-Micron filtration	86.9

Product Yields from Second Laboratory Scale Distillation Trial

A second laboratory scale distillation trial was performed to observe the F-T Light Product from Drum One after both free water and particulate removal for foaming potential and bumping due to the presence of residual water and particulates, and to develop a correlation distillation for the larger production scale batch distillation of Subtask 2.5.7.1.b to follow and to identify the effects the particulates may have caused in the initial laboratory scale distillation trial._The second laboratory scale distillation trial ran at atmospheric pressure and under vacuum without burping or foaming being present. The distillate take-off was at 328°K (131°F) distillate temperature at a reflux of 2:1 to accommodate for any water that may be present, and the reboiler temperature was 482K (408˚F) at atmospheric pressure. A reboiler temperature of 533K (500°F) was reached before the neat F-T naphtha product cut point of 466K (380°F) was obtained and the laboratory scale distillation operation was temporarily shutdown to cool the distillation bottoms product before operating the column under vacuum at 50 millimeters (mm) of Mercury (Hg). The neat F-T naphtha product was obtained at an the Atmospheric Equivalent Temperature of 466K (380°F) distillate with a 457K (363°F)reboiler temperature. There was approximately 14milliliters (ml) of water collected in the distillate and accounted for appropriately in the summary report. The 466K (380°F) to 644K (700°F) neat F-T diesel product was also completed under vacuum without any foaming or bumping problems. The tabulation below presents a comparison of product yields from the initial laboratory scale distillation trial conducted after free water removal from the F-T Light Product in Drum One versus the second laboratory scale distillation trial conducted after both free water and particulate removal from the F-T Light Product in Drum One.

Subtask 2.5.7.1.b F-T Light Product from LaPorte AFDU Drum One Product Yield Comparisons	Initial Laboratory Scale Distillation Trial after free water removal	Second Laboratory Scale Distillation Trial after free water & particulate removal
IBP to 466K (380°F) Naphtha, wt%	12.7	12.0
466K (380°F) to 644K (700°F) Diesel, wt%	40.0	44.7
644K (700°F) plus Soft Wax, wt%	46.1	43.3
Recovery, wt%	98.8	100

The tabulation below presents the results of the inspection tests performed on the IBP to 466K (380°F) neat F-T naphtha product, the 466K (380°F) to 644K (700°F) neat F-T diesel product, and on the 644K (700°F) plus neat F-T soft wax products obtained from the second laboratory scale distillation trial performed on the F-T Light Product from Drum One after free water and particulate removal.

Task 2.5.7.1.b F-T Light Product from Drum One after water and particulate removal	Second Lab Scale Distillation Trial Naphtha Product	Second Lab Scale Distillation Trial Diesel Product	Second Lab Scale Distillation Trial Soft Wax Product
Gravity, API	54.1	44.5	38.2
Gravity, Specific	0.7624	0.842	0.8338
Yield, wt%	12.0	42.7	43.3
Karl Fisher water, wt%	1.8	No test	No test
Sulfur, ppmw	5	2	6
Nitrogen, ppmw	0.8	0.4	18
Aromatics, wt%	Not detected	Not detected	Not detected
D2887/D86/D1160, K (°F)	D2887/D86	D2887/D86	D1160
IBP	329 (133) / 183	446 (343) / 415	669 (744)
5%	366 (200) / 249	470 (386) / 445	680 (764)
10%	383 (230) / 257	487 (418) / 455	682 (768)
30%	409 (277) / 278	527 (489) / 496	690 (782)
50%	422 (301) / 296	562 (552) / 541	694 (790)
70%	445 (341) / 316	597 (615) / 583	701 (802)
90%	463 (374) / 343	630 (675) / 626	748 (887)
95%	467 (381) / 354	640 (693) / 643	764 (915)
EP	486 (416) / 378	657 (723) / 654	na

Product Yields from Batch Distillations of F-T Light Product

For ease of handling the 81.6 kgs (179.5 lbs) of F-T Light Product from Drum One after free water and particulate removal processing steps was transferred into six clean 18.9 liter (5 gal) containers with phenolic resistance liners in preparation for carrying out three batch distillation runs charging between 30 liters (7.93 gals) to 35 liters (9.25 gals) to the individual batch distillation still pots. The Subtask 2.5.7.1.b three batch distillations to produce the IBP to 466K (380°F) neat F-T naphtha product, a 466K (380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax for end use in Task 2.5 product evaluations were successful completed on 22.9 centimeters(cm) (9 inch(in)) by 5.1 cm (2 in.) clean protruded packed distillation columns. There were no signs of foaming or bumping during the three batch distillation runs which was expected based upon the successful removal of free water and particulates and the two laboratory scale distillation trials performed earlier. The tabulation below presents a comparison of the product yield results obtained with the various laboratory scale distillation trials and with the composite results from the three Task 2.5.7.1.b batch distillations. The product yields on the F-T Light Product from Drum One after free water and particulate removal compare very well with the second laboratory scale distillation trial results and the composite results from the three Task 2.5.7.1.b batch distillations.

Task 2.5.7.1.b F-T Light Product Of Drum One Yield Comparisons	D-2887 Distillation on Drum One as received	Initial Lab Scale Distillation Trial after free water removal	Second Lab Scale Distillation Trial after free water and particulate removal	Composite of Three Batch Distillations
Naphtha, wt%	14.5	12.7	12.0	12.4
Diesel, wt%	43.6	40.0	44.7	45.1
Soft Wax, wt%	41.9	46.1	43.3	42.2
Recovery, wt%	100	98.8	100	99.7

Table 4 below presents the results of the inspection tests performed on the IBP to 466K (380°F) neat F-T naphtha product, the 466K (380°F) to 644K (700°F) neat F-T diesel product, and on the 644K (700°F) plus neat F-T soft wax products obtained on the composite products from the three batch distillation runs performed on the F-T Light Product from Drum One.

Table 4- Subtask 2.5.7.1.b Batch Distillation Product Results

Task 2.5.7.1.b F-T Light Product from Drum One after water and particulate removal	Batch Distillations Composite of Naphtha Products	Batch Distillations Composite of Diesel Products	Batch Distillations Composite of Soft Wax Products
Gravity, API	55.2	43.7	38.3
Gravity, Specific	0.7579	0.8076	0.8333
Yield, wt%	12.4	45.1	42.2
Karl Fisher water, wt%	0.9	No test	No test
Sulfur, ppmw	<1	1.3	4.1
Nitrogen, ppmw	1.0	2	18
Aromatics, wt%	Not detected	Not detected	Not detected
D2887/D86/D1160, K (°F)	D2887/D86	D2887/D86	D2887/D1160
IBP	330 (134) / 189	445 (341) / 426	629 (672) / 403
5%	367 (201) / 245	469 (384) / 447	657 (724) / 696
10%	384 (232) / 257	487 (417) / 454	671 (749) / 766
30%	413 (284) / 281	527 (489) / 498	694 (789) / 779
50%	425 (305) / 302	565 (558) / 543	700 (800) / 791
70%	446 (343) / 322	599 (618) / 585	707 (814) / 803
90%	466 (380) / 348	630 (675) / 631	766 (920) / 866
95%	469 (384) / 360	641 (695) / 652	826 (1028) / 905
EP	507 (453) / 374	669 (745) / 663	933 (1220) / 932

Subtask 2.5.7.1.c Naphtha Fractionation of LaPorte AFDU Drum Two

The contents of Drum Two of the F-T Light Product drained from an overhead product receiver on the LaPorte AFDU demonstration unit was visually inspected and considered in reasonable condition with a rusty top and no evidence of product leakage. All equipment coming in contact with the F-T Light Product in Drum Two was thoroughly cleaned with toluene and hexane then dried with nitrogen.

Free Water Removal from LaPorte AFDU Drum Two

Before distilling the contents of Drum Two of the F-T Light Product it was determined that free water needed to be removed. The process of removing the free water from Drum Two of F-T Light Product was accomplished using a fork lift with a drum handling attachment. A clean drum valve was installed securely in the large drum bung opening before the Drum Two was raised and tilted at 135˚ from perpendicular facing the top of drum towards the ground at a 45˚ angle with the valve at the lowest point. A new open-top 208 liter (55-gal) drum with a phenolic resistant liner was placed under the suspended Drum Two of F-T Light Product to contain any unintentional releases and for decanting the water. After approximately 17 hours of settling at ambient temperature in this position, 10.5 kgs (23.1 lbs) of free water was removed. The tabulation below provides the mass balance closure for the free water removal process.

Drum Number Two from LaPorte AFDU	
Net Weight of Drum Two with free water	145.4 kgs (319.8 lbs)
Free Water Removed (7.2 wt %)	10.5 kgs (23.1 lbs)
F-T Light Product	134.9 kgs (296.7 lbs)
Recovery	100.0 wt%

A 3.785 liter (1 gal) retain was set aside of the F-T Light Product from Drum Two after free water removal for inspection testing and for a potential laboratory scale distillation trial on a two liter still. The laboratory scale distillation trial was not performed. Table 5 below provides the results of the inspection testing conducted on the F-T Light Product from Drum Two of the LaPorte AFDU demonstration after free water removal.

Table 5 – Subtask 2.5.7.1.c F-T Light Product from Drum Two Test Results

Subtask 2.5.7.1.c F-T Light Product from Drum Two Inspection Tests	
Gravity, API	42.2
Gravity, Specific	0.8146
Karl Fisher Water, wt%	0.46
Nitrogen, ppmw	8.3
Sulfur, ppmw	<1
Aromatics, wt%	Non detected

Filtration Process for Solids Removal from LaPorte AFDU Drum Two

The decision was made to filter the F-T Light Product from Drum Two after free water removal through a 25-micron absolute filter to remove particulates that may cause “Hot Spots” during the future Subtask 2.5.7.1.c batch fractionation work that may also lead to premature thermal degradation. After approximately 36 hours of filtering with the 25-micron filter, the filter was switched back to a 5-micron absolute for the final filtration of particulates. The tabulation below presents the results of the mass balance closure around the filtration of particulate processes.

Subtask 2.5.7.1.c Drum Two from LaPorte AFDU Demonstration F-T Light Product after free water removal	
Drum Two after free water removal	134.9 kgs (296.7 lbs)
25-Micron filter, pump, hose Product Hold-up	11.2 kgs (24.6 lbs)
Net F-T Light Product after 25-micron filtration	123.7 kgs (272.1 lbs)
Net F-T Light Product after 25-micron filtration	123.7 kgs (272.1 lbs)
5-Micron filter, pump, hose Product Hold-up	7.5 kgs (16.6 lbs)
One gal (3.785 liter) sample retain for testing	2.9 kgs (6.4 lbs)
Net F-T Light Product after solids filtration processes	113.2 kgs (249.1 lbs)

Product Yields from Batch Distillations of F-T Light Product

Based on the lessons learned from the laboratory scale distillation trials conducted for Subtask 2.5.7.1.b, a determination was made that the F-T Light Product from Drum Two after free water and particulate removal was of comparable quality and would perform satisfactory in the Subtask 2.5.7.1.c batch distillations. Therefore, no laboratory scale distillation trial was conducted prior to Task 2.5.7.1.c batch distillations. For ease of handling the 113.2 kgs (249.1 lbs) of F-T Light Product from Drum Two after free water and particulate removal processing steps was transferred into nine clean 18.9 liter (L) (5 gal) containers with phenolic resistance liners in preparation for carrying out four batch distillation runs charging between 30 liters (9.73 gals) to 37 liters (9.77 gals) to the individual batch distillation still pots. The Subtask 2.5.7.1.c four batch distillations to produce the IBP to 466K(380°F) neat F-T naphtha product, a 466K(380°F) to 644K (700°F) neat F-T diesel product, and a 644K (700°F) plus neat F-T soft wax for end use in Task 2.5 product evaluations were successful completed on 22.9 cm (9 in) by 5.1 cm (2 in.) clean protruded packed distillation columns. There were no signs of foaming or bumping during the four batch distillation runs. The tabulation below presents a comparison of the product yields from the composite results from the three Subtask 2.5.7.1.b batch distillations performed on the F-T Light Product from Drum One and the composite results from the four Subtask 2.5.7.1.c batch distillations performed on the F-T Light Product from Drum Two.

Task 2.5.7.1.b&c F-T Light Products From Drums One & Two Product Yield Comparisons	Composite of Three Batch Distillations of Drum One	Composite of Four Batch Distillations of Drum Two
Naphtha, wt%	12.4	12.6
Diesel, wt%	45.1	49.7
Soft Wax, wt%	42.2	37.3
Recovery, wt%	99.7	99.6

Table 6 below presents the results of the inspection tests performed on the IBP to 466°K(380°F) neat F-T naphtha product, the 466K(380°F) to 644K (700°F) neat F-T diesel product, and on the 644K (700°F) plus neat F-T soft wax products obtained on the composite products from the four batch distillation runs performed on the F-T Light Product from Drum Two after free water and particulate removal. The Subtask 2.5.7.1.b results on the naphtha, diesel, and soft wax products obtained from the distillation of the F-T Light Product from Drum Two are in close agreement with the previously reported Subtask 2.5.7.1.b results on the naphtha, diesel, and soft wax products obtained from the distillation of the F-T Light Product from Drum One.

Table 6 – Subtask 2.5.7.1.c Batch Distillation Product Test Results

Task 2.5.7.1.c F-T Light Product from Drum Two after water and particulate removal	Batch Distillations Composite of Naphtha Products	Batch Distillations Composite of Diesel Products	Batch Distillations Composite of Soft Wax Products
Gravity, API	54.7	43.7	37.1
Gravity, Specific	0.7599	0.8076	0.8393
Yield, wt%	12.6	49.7	37.3
Karl Fisher water, wt%	3.97	No test	No test
Sulfur, ppmw	<1	<1	<2
Nitrogen, ppmw	<1	2	22
Aromatics, wt%	Not detected	Not detected	Not detected
D2887/D86/D1160, K (°F)	D2887/D86	D2887/D86	D2887/D1160
IBP	341 (155) / 202	446 (343) / 423	633(680) / 747
5%	367 (202) / 261	469 (384) / 444	652 (715) / 755
10%	390 (242) / 271	487 (417) / 454	664 (736) / 761
30%	420 (297) / 292	526 (488) / 494	692 (786) / 778
50%	432 (318) / 311	561 (550) / 539	700 (801) / 790
70%	446 (343) / 329	595 (611) / 580	709 (816) / 805
90%	467 (381) / 353	629 (672) / 622	777 (939) / 897
95%	469 (385) / 364	639 (691) / 640	833 (1040) / 953
EP	508 (455) / 385	663 (734) / 656	930 (1215) / 1023

Preparation of End Use Products for Task 2.5 and Task 2.6

The F-T Synthesis liquid products from the LaPorte AFDU demonstration must be distilled to the required fuel or specialty wax product boiling range specifications. There are technical and economic risks to the EECP if the F-T Synthesis products undergo degradation or liquid yield losses during the distillation process.[1] Subtask 2.5.7.1.a&b&c technical risks are the degree of laboratory fractionation efficiency, recovery of products and possible contamination of distilled products. These technical and economic risks to the EECP are mitigated if the distilled products achieve desired yield recoveries and qualities meeting fuel or specialty product boiling range specifications in order to satisfy the end use evaluation needs of Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emissions."

Composite Blending of Neat FT Naphthas from Task 2.5.7.1a&b&c

Table 7 below presents a comparison of the results obtained from simulated distillations, specific gravities, total sulfur, total nitrogen, and total aromatic contents of each of the IBP-466K (380°F) neat F-T naphtha products obtained from Subtask 2.5.7.1a&b& c. These results of these inspection tests indicated that all three naphtha products are suitable to blend together to generate a neat F-T naphtha composite sample suitable for end use in Task 2.5 product evaluations.

Table 7 –Subtask 2.5.7.1.a&b&c Batch Distillation Naphtha Composite Test Results

Task 2.5.7.1.a&b&c Distillation of F-T Light Products	Subtask 2.5.7.1.a Batch Distillations Composite of Naphtha Products	Subtask 2.5.7.1.b Batch Distillations Composite of Naphtha Products	Subtask 2.5.7.1.c Batch Distillations Composite of Naphtha Products
Gravity, API	54.8	55.2	54.7
Gravity, Specific	0.7595	0.7579	0.7599
Yield, wt%	22.1	12.4	12.6
Karl Fisher water, wt%	0.23	0.9	3.97
Sulfur, ppmw	2	<1	<1
Nitrogen, ppmw	<1	1.0	<1
Aromatics, wt%	None detected	None detected	None detected
D2887/D86, °F (K)	D2887/D86	D2887/D86	D2887/D86
IBP	328 (131) /172	330 (134) / 189	341 (155) / 202
5%	367 (201) /244	367 (201) / 245	367 (202) / 261
10%	371 (209) /257	384 (232) / 257	390 (242) / 271
30%	414 (285) /283	413 (284) / 281	420 (297) / 292
50%	425 (305) /306	425 (305) / 302	432 (318) / 311
70%	446 (343) /328	446 (343) / 322	446 (343) / 329
90%	467 (382) /352	466 (380) / 348	467 (381) / 353
95%	469 (385) /362	469 (384) / 360	469 (385) / 364
EP	555 (540) /382	507 (453) / 374	508 (455) / 385

Composite Blending Results for Neat F-T Naphthas

All equipment involved with the transferring, blending and storage of the neat F-T naphtha composite blend were thoroughly cleaned with new hexane and nitrogen dried and verified that the background contamination levels from testing of solvent rinses were <1 ppmw sulfur and <1 ppmw nitrogen.

With the blending kettle having ambient temperature (~291K (65°F)) water circulating through the jacket and being nitrogen blanketed the two drums of Task 2.5.7.1a IBP-466K(380°F) neat F-T naphtha product containing 224.4 kgs (493.7 lbs) was pumped into the blending kettle. While obtaining the tare weight of these two empty drums the technicians found that the phenolic resistant drum liners were separated from the drum walls raising the possibility of phenolic resistant lining particles being present in the neat F-T naphtha composite blend. The decision was made to complete the composite blending of the neat F-T naphtha products and filter the final composite blend of neat F-T naphtha product during the transfer process to new polyethylene drums and/or containers. The remaining 10 kgs (21.9 lbs)of Subtask 2.5.7.1.b neat F-T naphtha product and the 14 kgs (30.8 lbs) Subtask 2.5.7.1.c neat F-T naphtha products were added by weight with a note indicating that water was observed in these two neat F-T naphtha composite blend components. The tabulation below presents the quantities of each of the Subtask 2.5.7.1.a&b&c neat F-T naphtha products that when into the preparation of the neat F-T naphtha composite blend. Each of the three neat F-T naphtha products are considered highly corrosive and are currently being stored in drums with phenolic resistance liners prior to composite blending. The three neat F-T naphtha product retains are in cold storage until ready for composite blending and the composite blending will be done in such a manner to avoid the lost of light ends.

Subtask	**Subtask Reported Wt, kgs (lbs)**	**Subtask Reported Vol, liters (gals)**	**Blend Component, wt.%**
2.5.7.1a	224.4 (493.7)	294.9 (77.9)	90.3
2.5.7.1b	10.0 (21.9)	13.3 (3.5)	4.1
2.5.7.1c	14.0 (30.8)	18.6 (4.9)	5.6
Totals	248.4 (546.4)	326.6 (86.3)	100.0

The total neat F-T naphtha composite blend weight was 245.8 kgs (540.8 lbs), 2.5 kgs (5.6 lbs) short of expectations. This represents a mass balance closure of 99 wt% for the transfer/blending processes which is considered acceptable considering the normal product hold-up expected in the containers, the pump and hoses employed.

The blending kettle was secured and the nitrogen blanket was turned off to prevent any vapor losses and the neat F-T naphtha was left to settle out any water for 48 hours. A .47 liter (.125 gal) sample was drawn from the bottom of the kettle to check for free water and apparently not seeing any the sample was poured back into the kettle. The agitator was started for one hour then shut off and the filtering process started.

Filtration Process on Composite Naphtha Blend to Remove Particles

Apparently the high acid content of this naphtha product affected the phenolic resistance drum liner of the 208 liter (55gal) drums much like the whole liquid product affected the linings of the drums it was deliver in. New polyethylene drums and containers were ordered for use on all neat F-T naphtha products. A 5-micron absolute filter system was employed to remove any phenolic resistance drum liner pieces that may have been present in the neat F-T naphtha product composite blend. The neat F-T naphtha composite blend was filtered into the new polyethylene containers to the specified weights for end use in Task 2.5 product evaluations as close as possible. The filtering process had a total loss of 2.58 kgs (5.7 lbs), of which 2.27 kgs (5.0 lbs) were accounted for in equipment hold-up. The composite blending and filtration processes went well. Unfortunately, pulling only a .47 liter (.125 gal) sample to check for free water was not enough. Subsequent separation steps were required to remove the presence of free water from the neat F-T naphtha composite blend prior to its end use in Task 2.5 product evaluations

Neat F-T Naphtha Composite Blend Distribution to Task 2.5

The Subtask 2.5.7.1.a&b&c composite blend of neat F-T naphtha is intended for use in four future Task 2.5 product evaluations. The Subtask 2.5.7.1.a&b&c composite blend will be blended with about 14.4 kgs (31.6 lbs) or about 18.9 liters (5 gals) of the neat F-T naphtha product obtained from Subtask 2.5.2 entitled "Lab Batch Fractionation." Details on the preparation of the Subtask 2.5.2 neat F-T naphtha product can be found in the Subtask 2.5.2 Topical Report that is appended to the Task 2.5 Topical Report prepared for the DOE. The total amount of the composite blend of neat F-T naphtha product from both Subtask 2.5.7.1b&c and Subtask 2.5.2 will come to 254.7 kgs (560.4 lbs) or ~ 335 liters (88.5 gals).
The Subtask 2.5.7.1.a&b&c composite blend of neat F-T naphtha is intended for use in four Task 2.5 product evaluations. The Subtask 2.5.7.1.a&b&c composite blend of neat F-T naphtha and the composite blend of neat F-T naphtha from Subtask 2.5.2 entitled "Lab Batch Fractionation" were blended together. The tabulation below presents the required sample needed by each Subtask of Task 2.5 entitled "F-T Product Upgrading." The four retains of the composite blend of neat F-T naphtha product went to cold storage to avoid the lost of light ends until ready for use at the ChevronTexaco Integrated Laboratory Technology Company (ILT) or for shipment to offsite technology providers.

Subtask	Subtask Name	Wt, kgs (lbs)	Vol, liters (gals)	wt.%
2.5.5	ASTM Testing Schedule	3.7 (8.23)	4.9 (1.3)	1.47
2.5.7.2	Neat Naphtha Hydrotreating	199.2 (438.21)	261.9. (69.2)	78.19
2.5.3	Hydrocracking Pilot Test	25.9 (56.98)	34.1 (9.0)	10.17
2.5.4	Wax Finishing Pilot Test	25.9 (56.98)	34.1 (9.0)	10.17
Totals		254.0(7560.40)	335.0 (88.5)	100.00

Composite Blending of Neat FT Diesel from Task 2.5.7.1.b&c

Table 8 below presents a comparison of the results obtained from simulated distillations, specific gravities, total sulfur, total nitrogen, and total aromatic contents of each of the 466°K (380°F) to 644°K (700°F) neat F-T diesel products obtained from Subtask 2.5.7.1.b& c. The results of these inspection tests indicated that both diesel products are suitable to blend together to generate a neat F-T diesel composite sample suitable for end use in Task 2.5 and Task 2.6 product evaluations.

Table 8- Subtask 2.5.7.1b&c Batch Distillation Diesel Composite Test Results

Task 2.5.7.1.b&c Distillation of F-T Light Products	Subtask 2.5.7.1.b Batch Distillations Composite of Diesel Products	Subtask 2.5.7.1.c Batch Distillations Composite of Diesel Products
Gravity, API	43.7	43.7
Gravity, Specific	0.8076	0.8076
Yield, wt%	45.1	49.7
Karl Fisher water, wt%	No test	No test
Sulfur, ppmw	1.3	<1
Nitrogen, ppmw	2	2
Aromatics, wt%	Not detected	Not detected
D2887/D86, °K (°F)	D2887/D86	D2887/D86
IBP	445 (341) / 426	446 (343) / 423
5%	469 (384) / 447	469 (384) / 444
10%	487 (417) / 454	487 (417) / 454
30%	527 (489) / 498	526 (488) / 494
50%	565 (558) / 543	561 (550) / 539
70%	599 (618) / 585	595 (611) / 580
90%	630 (675) / 631	629 (672) / 622
95%	641 (695) / 652	639 (691) / 640
EP	669 (745) / 663	663 (734) / 656

All equipment involved with the transferring, blending and storage of the neat F-T diesel composite blend were thoroughly cleaned with new hexane and nitrogen dried and verified that the background contamination levels from testing of solvent rinses were <1 ppmw sulfur and <1 ppmw nitrogen. Each of the two neat F-T diesel products are considered highly corrosive and are currently being stored in drums with phenolic resistance liners prior to composite blending in one drum. The two neat F-T diesel product retains are in cool storage until ready for composite blending and the composite blending will be done in such a manner to avoid the lost of light ends

The small quantities of neat F-T diesel products from Subtask 2.5.7.1.b and Subtask 2.5.7.1.c allow for blending in a single 208 liter (55-gal) drum with a phenolic resistant liner. The remaining 36.2 kgs (79.7 lbs) of Subtask 2.5.7.1.b neat F-T diesel product and the 55.2 kgs (121.4 lbs) Subtask 2.5.7.1.c neat F-T diesel products were added by weight. The total neat F-T diesel composite blend weight was 91.4 kgs (201.1 lbs). The tabulation below presents the quantities of each of the Subtask 2.5.7.1. b&c neat F-T diesel products that when into the preparation of the neat F-T diesel composite blend.

Subtask	**Subtask Reported Wt, Kgs (lbs)**	**Subtask Reported Vol, liters (gals)**	**Blend Component, wt.%**
2.5.7.1b	36.2 (79.7)	44.7 (11.8)	39.6
2.5.7.1c	55.2 (121.4)	68.1 (18.0)	60.4
Totals	91.4 (201.1)	112.8 (29.8)	100.0

Neat F-T Diesel Composite Blend Distribution to Task 2.5

The Subtask 2.5.7.1.b&c composite blend of F-T neat diesel is intended for use in five future Task 2.5 and Task 2.6 product evaluations. The Subtask 2.5.7.1.b&c composite blend will be blended with about 27.7 kgs (61 lbs) or 34.8 liters (9.1 gals) of the neat F-T diesel product obtained from Subtask 2.5.2 entitled "Lab Batch Fractionation." Details on the preparation of the Subtask 2.5.2 neat F-T diesel product can be found in the Subtask 2.5.2 Topical Report that is appended to the Task 2.5 Topical Report prepared for the DOE. The total amount of the composite blend of neat F-T diesel product from both Subtask 2.5.7.1b&c and Subtask 2.5.2 will come to 119.1 kgs (262 lbs) or ~ 147.1 liters (38.9 gals). The tabulation below presents the required neat F-T diesel sample needed by each Subtask of Task 2.5 entitled "F-T Product Upgrading" and Task 2.6 entitled "Fuel/Engine Performance and Emission Testing." The five retains of the composite blend of neat F-T diesel product went to cool storage to avoid the lost of light ends until ready for use at the ChevronTexaco Integrated Laboratory Technology Company (ILT) or for shipment to offsite technology providers.

Subtask	**Subtask Name**	**Wt, kgs (lbs)**	**Vol, liters (gals)**	**wt.%**
2.5.5	ASTM Testing Schedule	2.8 (6.1)	3.4 (0.9)	2.3
2.5.7.6	Neat Diesel Hydrotreating	48.6 (106.9)	60.2 (15.9)	40.8
2.6.1	Lubricity Additive Testing	0.3 (0.7)	0.4 (0.1)	0.3
2.6.2	Hot-Start Emission Testing	67.5 (148.3)	83.3 (22.0)	56.6
2.6.3	Solvent Extraction of PM			
Totals		119.1 (262)	147.3 (38.9)	100.0

Neat Heavy F-T Diesel Composite Blend Distribution to Task 2.5

The 505K (450°F) to 644K (700°F) composite blend of neat F-T heavy diesel product from the Subtask 2.5.7.1.a continuous distillation operation was designated for use in Subtasks for Task 2.5 product evaluations. While the 466K (380°F) to 644K (700°F) neat F-T diesel product from Subtask 2.5.7.1.b&c and Subtask 2.5.2 was designated for use in Subtasks for Task 2.6 product evaluations. Table 9 below presents the results of the inspection testing done on the Subtask 2.5.7.1.a neat F-T heavy diesel product.

Table 9 – Subtask 2.5.7.1.a Continuous Distillation Heavy Diesel Test Results

Subtask 2.5.7.1a Inspection Tests	Continuous Distillation of F-T Light Product Neat F-T Heavy Diesel Product Composite
API Gravity	40.8
Specific Gravity	0.8212
Nitrogen, ppmw	9.9
Sulfur, ppmw	2.4
Aromatics, wt%	None detected
D2887/D86, °K (°F)	D2887/D86
IBP	479 (402)/491
5	506 (452) /510
10	523 (482) /519
30	560 (549) /549
50	590 (603) /581
70	618 (653) /612
90	644 (699) /647
95	654 (717) /664
EP	689 (781) /682

The neat F-T heavy diesel was a feed component in a ratio-of-production feed blend representing F-T Light Product and F-T Heavy Product. The ratio-of-production feed blend was charged to Subtask 2.5.3 entitled "Hydrocracking Pilot" and to Subtask 2.5.4 entitled "Wax Finishing Pilot." The neat F-T heavy diesel product was also designated for use in Subtask 2.5.6 entitled "Diesel Blending Tests." The tabulation below presents the required Subtask 2.5.7.1.a neat F-T heavy diesel sample needed by the Subtasks of Task 2.5 entitled "F-T Product Upgrading."

Subtask	Subtask Name	Wt, kgs (lbs)	Vol, liters (gals)	wt.%
2.5.5	ASTM Testing Schedule	3.1 (6.7)	3.8 (1.0)	2.62
2.5.3	Hydrocracking Pilot	52.1 (114.6)	64.3 (17.0)	44.75
2.5.4	Wax Finishing Pilot	52.1 (114.6)	64.3 (17.0)	44.75
2.5.6	Diesel Blending Tests	9.2 (20.2)	11.4 (3.0)	7.88
Totals		116.4 (256.1)	143.8 (38.0)	100.00

Neat F-T Soft Wax Composite Blend Distribution to Task 2.5

The 644K (700°F) plus neat F-T soft wax products from the Task 2.5.7.1.b and Subtask 2.5.7.1c batch distillations were found to be contaminated with high levels of iron solids (>2000 ppmw) and were not retained for end use in the Task 2.5 product evaluations. Only the 644K (700°F) plus neat F-T soft wax product from the Task 2.5.7.1.a continuous distillation of the eight drums of F-T Light Product from the LaPorte AFDU demonstration ISOtainer product receiver was used for Task 2.5 product evaluations. Table 10 below presents the results of the inspection performed on the Subtask 2.5.7.1.a neat F-T soft wax product.

Table 10- Subtask 2.5.7.1.a Continuous Distillation Soft Wax Test Results

Subtask 2.5.7.1a Inspection Testing	**Continuous Distillation of F-T Light Product Neat F-T Soft Wax Product Composite**
API Gravity	36.7
Specific Gravity	0.8413
Fraction, wt% basis Feed	32.2
Nitrogen, ppmw	39.7
Sulfur, ppmw	11.4
Aromatics, wt%	None detected
D2887/D86/D1160, °K (°F)	D2887/D1160
IBP	611 (641) /641
5	645 (701) /733
10	660 (729) /750
30	691 (785) /778
50	700 (800) /788
70	707 (813) /801
90	759 (907) /880
95	801 (983) /-----
EP	960 (1269) /953
ICP Metals, ppmw	
Iron (FE)	125

The neat F-T soft wax was a feed component in a ratio-of-production feed blend representing F-T Light Product and F-T Heavy Product. The ratio-of-production feed blend was charged to Subtask 2.5.3 entitled "Hydrocracking Pilot" and to Subtask 2.5.4 entitled "Wax Finishing Pilot." The tabulation below presents the required Subtask 2.5.7.1.a neat F-T soft wax sample needed by the Subtasks of Task 2.5 entitled "F-T Product Upgrading."

Subtask	**Subtask Name**	**Wt, kgs (lbs)**	**Vol, liters (gals)**	**wt.%**
2.5.5	ASTM Testing Schedule	3.2 (7)	3.8 (1.0)	4.34
2.5.3	Hydrocracking Pilot	35.0 (77)	41.6 (11.0)	47.83
2.5.4	Wax Finishing Pilot	35.0 (77)	41.6 (11.0)	47.83
Totals		73.2 (161)	87.1 (23.0)	100.00

Conclusions

1. Subtask 2.5.7.1. a&b&c provided the necessary yields and qualities of neat F-T naphtha, neat F-T diesel, and neat soft F-T wax products from its feed slate while meeting necessary fuel and specialty wax boiling range specifications for end use products in Task 2.5 and Task 2.6.

2. The end use neat F-T naphtha, neat F-T diesel, and neat F-T soft wax products generated from Subtask 2.5.7.1.a&b&c. contributed to the success of all Phase II RD&T Task 2.5 and Task 2.6 product evaluations.

Bibliography

1. United States of America Patent Number 5,904,834 entitled “Synthetic Wax for Food Applications”, assigned to inventors Messrs. Joachim Ansorge, Arend Hoek, Willem Pieter Leenhouts, and Robert Anthony John Priston of the Shell Research Limited, May 18, 1999.

List of Acronyms and Abbreviations

AGR – acid gas removal unit
API – American Petroleum Institute
ASTM – American Society for Testing and Materials
ASU – Air Separation Unit
CO_2 – Carbon Dioxide
CO – Carbon Monoxide
cm – centimeters
DCRP – Delaware City Repowering Project
DOE – Department of Energy
EECP – Early Entry Coproduction Plant
°F – Temperature in degrees Fahrenheit
FE – Iron
F-T -Fischer-Tropsch
ft – feet
g – gram
gal – gallon
GE – General Electric
H2S – Hydrogen Sulfide
Hg – Mercury
HRSG – Heat Recovery Steam Generator
Hydrocarbons – HC
IGCC – Integrated Gasification Combined Cycle
in – inch
°K – Temperature in degrees Kevin
kg – kilogram
KBR – Kellogg Brown & Root
lbs – pounds
MDEA-methyldiethanolamine
ml – milliliters
mm – millimeter
L – liter
oz – ounce
O2 – carbon dioxide
Oxides of Nitrogen – NOx
psia – pounds force per square inch absolute
ppmw – parts per million (weight per volume)
RD&T – Research, Development, and Testing
SO2 – Sulfur Dioxide
SOW – Scope of Work
SRU – Sulfur recovery unit
SwRI – Southwest Research Institute

SWS – Sour Water Stripper
TES – Texaco Energy Systems a subsidiary of ChevronTexaco
TGTU – Tail gas recovery unit
Vol – Volume
Wt – Weight
wt% – weight percent

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix G - Test Report

Subtask 2.5.7.2: FISCHER-TROPSCH NAPHTHA HYDROTREATING

Reporting Period: December 2002 - May 2003

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Background

In the EECP concept, one of the product upgrading options is hydrotreating of the Fischer-Tropsch (F-T) naphtha range material to produce low sulfur feed for ethylene cracking and fuel cell reforming feedstock.

Hydrotreating is perhaps the most widely practiced refining process in the world today. It is used to upgrade petroleum distillates and residuum to refinery intermediate streams and also to finished products. ChevronTexaco has extensive experience operating hydrotreaters in its own refineries. ChevronTexaco also licenses its state-of-the-art, proprietary ISOTREATING technology and ISOTREATING® catalysts to the refining industry worldwide.

ISOTREATING® catalysts are single-function catalysts, containing only a hydrogenation function. The hydrogenation sites remove impurities from and saturate any double bonds in the feed molecules to produce clean, hydrogen-rich products.

As part of the RD&T Plan from Phase II of the EECP, F-T products from the La Porte demonstration run were fractionated to produce a naphtha range material. A commercially-proven ISOTREATING® catalyst was selected to hydrotreat the raw F-T naphtha to finished products meeting industry specifications. The hydrotreated naphtha range material was analyzed and tested to confirm its properties and performance as a feedstock for ethylene cracking and fuel cell reforming.

Experimental

Process Description

ChevronTexaco Technology Marketing (TEMA) performed Pilot Plant Run 34-91 for the Fischer-Tropsch naphtha hydrotreating test. Figure 2.5.7.2-1 is the schematic diagram of the pilot plant used for the hydrotreating test.

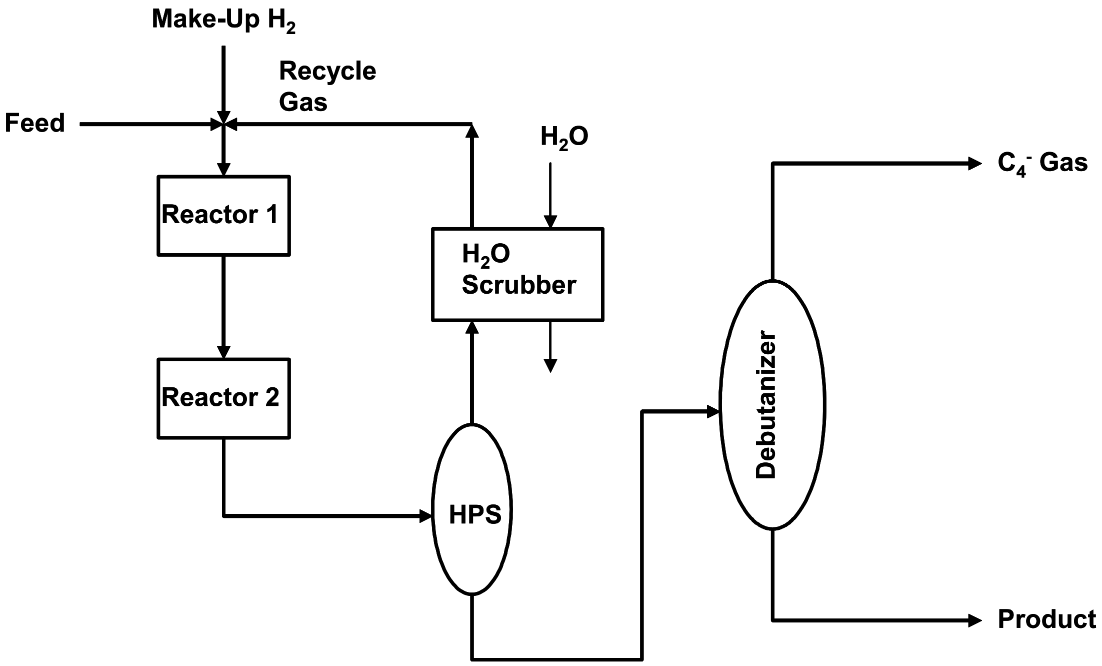


Figure 2.5.7.2-1 Naphtha Hydrotreating Pilot Plant Block Flow Diagram

The naphtha feed combined with the Make-Up Hydrogen and Recycle Gas is fed to the hydrotreating reactors. The two hydrotreating reactors are in series. The reactor effluent is separated into liquid and vapor in the High Pressure Separator (HPS). The liquid is then fractionated in a debutanizer where the naphtha product is collected on the bottom and the C4's and lighter go overhead. The separated vapor from the HPS, composed mainly of the hydrogen, is scrubbed with water to remove the traces of ammonia (NH_3) from nitrogen in the feed. The vapor is then recycled back to the reactors.

Feedstock

The Fischer-Tropsch (F-T) demonstration at the Alternative Fuels Demonstration Unit (AFDU) in La Porte, TX produced a mixture of light F-T hydrocarbons and water. The mixture was separated by a contract laboratory and the light F-T hydrocarbons were sent to ChevronTexaco Integrated Laboratory Technologies (ILT). The light F-T hydrocarbons were then fractionated into Soft Wax, Neat Diesel and Neat Naphtha cuts. 0.22 m^3 (60 gallons) of the Neat Naphtha was used as the feed for the naphtha hydrotreating runs. Table 2.5.7.2-1 gives the properties of the naphtha feed.

Table 2.5.7.2-1

Naphtha Feed Properties for Hydrotreating Pilot Plant

ID		WOW9288	
Gravity, °API		54.7	
Specific Gravity		0.76	
Nitrogen	wt, ppm	1.3	
Sulfur	wt, ppm	3.3	
Oxygen By NAA	wt %	4.3	
AED Analyses			
Oxygen	wt %	not available	
Alcohol	wt %	not available	
Olefins	wt %	not available	
TAN	mg KOH / g	13	
Simulated Distillation, LV%		Temperature (K)	(°F)
	IBP	311	101
	0.5%	334	142
	5%	366	199
	10%	371	208
	30%	411	281
	50%	424	303
	70%	445	341
	90%	466	380
	95%	468	383
	99%	485	413
	EP	530	494

Naphtha Product Qualities

The naphtha hydrotreating production goal was to hydrotreat all 58 gallons of naphtha feed. The original target for the hydrotreated naphtha was less than 10 ppm oxygen content. This requirement was set by the Task 2.5.7.3: Ethylene Cracking vendor. However, after many inquiries and laboratory tests by Southwest Research Institute (SWRI) and ChevronTexaco, no reliable method to measure this low level of oxygen was found. Instead, an alternate test was selected as the criterion for the hydrotreated naphtha. A Total Acid Number (TAN) of the less than 0.05 milligram of potassium hydroxide (KOH) per gram of sample was selected as the target for the hydrotreated naphtha product. Later, based on discussions with the ethylene cracking vendor, it was found that a TAN of less than 0.1 mg KOH/g was sufficient as the target. The feed naphtha had a TAN of 13 mg KOH/g.

Results and Discussion

The pilot plant results of the hydrotreating activity, yields, and product qualities are discussed in the following and are given in Table 2.5.7.2-2.

Table 2.5.7.2-2

Yields (Calculated by D2887) for Hydrotreating Naphtha

Feed	**WOW9288**			
Run Number	34-91		34-91	
Run Hours	114-126		426-438	
No Loss Prod. Yields	WT. %	VOL. %	WT. %	VOL. %
Total C4-	1.0		1.6	
Total C5+	95.9	100.8	95.3	100.4
H2 Consumption SCF/B	(sm^3/m^3)	(SCF/B)	(sm^3/m^3)	(SCF/B)
	154	865	153	861
Material Balance Closure, wt%	100		101	
Product Properties				
Specific Gravity	0.72		0.72	
Gravity, °API	64.6		64.2	
TAN, mg KOH / g	<0.05		0.07	
Simdist (D2887) (Volume %)	Temperature			
	(K)	(°F)	(K)	(°F)
St	271	28	269	25
5	332	139	329	132
10	347	165	341	155
30	399	259	398	257
50	424	303	423	302
70	447	345	446	344
90	469	384	467	382
95	470	386	469	384
99.5	479	403	478	401

After hydrotreating all of the naphtha feed, all of the naphtha products were blended together. Approximately 58 gallons of hydrotreated F-T naphtha product was collected. The blend was labeled as WOW9307. The TAN of the blended naphtha was 0.09 mg KOH/g. Although this is higher than the original target of 0.05 mg KOH/g, it was found that a TAN of less than 0.1 mg KOH/g was acceptable for the ethylene cracking subtask.

The hydrotreating shifted the material lighter (higher API for the hydrotreated naphtha). This was mostly likely due to the hydrogenation of oxygenates rather than hydrocracking.

0.106 m^3 (28 gallons) of the hydrotreated naphtha was sent for the Ethylene Cracking Test (Task 2.5.7.3) and $0.00379m^3$ (1 gallon) was sent for the Fuel Cell Reformer Test (Task 2.5.7.4). The product properties are given in Table 2.5.7.2-3.

Table 2.5.7.2-3

Hydrotreated Naphtha Properties

ID		WOW9307	
Gravity, °API		64.2	
Specific Gravity		0.723	
Sulfur	wt, ppm	pending	
Nitrogen	wt, ppm	0.2	
TAN	mg KOH/g	0.09	
PONA	Aromatic (vol %)	pending	
	Olefin (vol %)	2.0	
	Par/Np (vol %)	95.8	
Research Octane		<40	
Simulated Distillation	LV%	Temperature (K)	(°F)
	IBP	295	71
	0.5%	340	153
	5%	369	205
	10%	371	208
	30%	412	282
	50%	425	306
	70%	447	346
	90%	469	384
	95%	476	398
	99%	486	415
D86 Distillation	IBP	340	152
	5%	377	219
	10%	390	242
	30%	413	284
	50%	428	311
	70%	441	334
	90%	452	355
	95%	459	366
	EP	479	403

Conclusions

ChevronTexaco Technology Marketing performed a hydrotreating pilot plant run on the Fischer-Tropsch naphtha produced from the La Porte Alternative Fuels Demonstration Unit. The run generated approximately 58 gallons of hydrotreated Fischer-Tropsch naphtha which met the product specification target of a TAN less than 0.1 mg KOH/g. Some of the hydrotreated naphtha products were sent to the Ethylene Cracking Test and the Fuel Cell Reformer Test.

List of Acronyms and Abbreviations

°API	degree(s) API
°F	degree(s) Fahrenheit
AFDU	Alternative Fuels Demonstration Unit
API	American Petroleum Institute
C#	hydrocarbons with # number of carbons
C#-	hydrocarbons with less than # number of carbons
C#+	hydrocarbons with more than # number of carbons
EECP	Early Entrance Co-Production
EP	End Point
F-T	Fischer-Tropsch
g	gram
gal	gallons
H_2	Hydrogen
H_2O	Water
HPS	high pressure separator
IBP	Initial Boiling Point
IC	iso-hydrocarbon with # number of carbons
ID	Identification
ILT	ChevronTexaco Integrated Laboratory Technologies
K	kelvin(s)
KOH	potassium hydroxide
LHSV	Liquid Hourly Space Velocity
LV%	liquid volume percent
m^3	cubic meter(s)
mg	milligram
NAA	Neutron Activation Analysis
NC	normal hydrocarbon with # number of carbons
NH_3	ammonia
ppm	parts per million
Prod.	Product
psig	pounds per square inch gauge
RD&T	Research, Development and Testing
SCF/B	standard cubic feet per barrel
SWRI	Southwest Research Institute
TAN	Total Acid Number
TEMA	ChevronTexaco Technology Marketing
TX	Texas
vol%	volume percent
wt	Weight
wt%	Weight percent

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix H - Test Report

Subtask 2.5.7.3: ETHYLENE CRACKING

Reporting Period:	June 2003
Contributors:	Jennifer Adams (Kellogg Brown & Root)

1.0 Introduction

Quantities of the Hydrotreated Neat Fischer-Tropsch Synthesis hydrotreated neat naphtha product (FT Naphtha) were generated from the Neat Naphtha Hydrotreating test program. In an effort to evaluate a potential use for this product, Chevron Texaco contracted with Kellogg Brown & Root to characterize the material as a steam cracking feedstock and to evaluate its performance as a pyrolysis feed in a pilot-scale test unit measuring: (a) product yields, and (b) making observations on the relative cracking coil coking rate

2.0 Summary

The test program was designed to meet three basic objectives:

A. Characterization of the FT Naphtha as a steam cracking feedstock,

B. Evaluation of FT Naphtha steam cracking performance, specifically to determine the yields by pyrolysis over a range of cracking severities and estimate commercial performance.

C. Evaluation of FT Naphtha coking tendency.

To accomplish these objectives, the FT Naphtha was first analyzed in detail and using that analysis, experts at KBR were able to characterize the feed as extremely well suited for the production of olefins by steam cracking. A 24hr run with Alpha-7 Naphtha was performed on a conditioned 3/8” 800H SHC-40 reactor with the purpose to obtain material balance closure and ensure the operability of the pilot plant. The smaller reactor was selected for the ability to reach a .2 second residence time with limited FT Naphtha feedstock. Yield data was collected from high ethylene to high propylene production (P/E range of about 0.4-0.65). The yields for the Alpha-7 Naphtha matched closely with historical pilot plant data on the feedstock. This established the baseline for subsequent runs. The reactor was then de-coked and CO/CO2 yields were measured to give a coking comparison for the FT Naphtha feed. FT Naphtha was then introduced into the system targeting similar P/E ratios. Due to low gas make at the higher P/E ratio, an additional run was completed with a higher feed and steam rate to decrease residence time similar to that being run in the commercial KBR SCORE Furnace. At the conclusion of the 24hr run, the reactor was burned out and the coking rate was calculated

3.0 Conclusions

In this test program, the steam cracking performance of the FT Naphtha feed was successfully characterized. In the initial phase of the test, the FT Naphtha feed was cracked over a range of operating conditions to characterize the naphtha as a steam cracking feedstock.

The results of this program show that:

1. This FT Naphtha feed is well suited for the production of olefins (ethylene and propylene) by pyrolysis, which we attribute to the high feed paraffin content.

2. Comparison to the Alpha-7 naphtha shows that cracking of this feed is at least as selective to the production of ethylene, propylene and butadiene.

3. Cracking this feed in a KBR commercial furnace (SCORE furnace) designed to operate at a more typical residence time closer to 120 milliseconds would produce even higher yields of ethylene.

4. The coking test shows that, the coking tendency for this feed is similar to typical naphthas. KBR would expect, even when operating at higher severity, run lengths in a commercial furnace cracking the FT Naphtha feed would be as long as operation with other naphthas.

4.0 Experimental

4.1 Feedstocks:

Steam cracking process is a series of complex interactions between hardware, feed, and products. Feedstock properties determine the ability to produce olefins. High Paraffins and Iso-paraffins are desirable, while aromatics and naphthenes are unfavorable. Higher boiling range material tends to have lower gas yields. For this program the feedstocks were two full range naphthas. FT Naphtha was characterized by KBR, using the PIANO method, as having high paraffin content, some aromatics and relatively low naphthenic content. The Alpha-7 Naphtha has significantly lower n-paraffins in comparison, however lower total aromatics and lower boiling range. A list of the properties of these feeds is provided in Table 4.1. Detailed analysis including component list for each feed is included in the Appendix.

Table 4.1 Feedstock

Lab No.	**Alpha Seven**	**FT Naphtha**
•GCSD		
Percent off	Weight % off °F	Weight % off °F
IBP	136	<32
5	156	154
10	159	206
15	171	209
20	189	246
25	208	260
30	217	261
35	225	287
40	243	304
45	258	305
50	271	306
55	295	307
60	316	333
65	332	346
70	346	347
75	357	348
80	372	349
85	386	383
90	395	386
95	417	387
FBP	803	435
•Sulfur	<10	<10
•Density @20C	0.7406	.7168
•Total Oxygen (Wt%)		0.11
•PIANO (Wt%)		
Aromatics	1.0	4.1
I-Paraffins	43.7	13.2
Naphthenes	21.3	2.3
Olefins	0.4	0.4
Paraffin	28.7	78.7
Oxygenates	0	0
Unidentified	5.0	1.3

4.2 Apparatus:

KBR maintains a hydrocarbon Pyrolysis Pilot Plant for the purpose of evaluating yields for commercial olefins plant design. Feedstocks from ethane and other light hydrocarbons, through naphthas, to very heavy vacuum gas oils can be run. The unit as seen in the Pyrolysis Flow Sheet, located in the Appendix consists of automated feed systems, a zoned electrical furnace-reactor section, product quench and recovery sections, and on-line analytical and data gathering systems.

The reactor is suspended in the three-zone electric furnace to allow the imposition of a predetermined temperature profile on the pyrolysis tube and so simulate the actual temperature profile followed in an industrial pyrolysis furnace. In this way, the Pyrolysis Pilot Plant matches closely the performance of an industrial pyrolysis furnace in yield structure and in operability characteristics.

A given pyrolysis reactor is capable of good, sustained operation over a wide hydrocarbon residence time range. By changing reactors, residence times covering 20-600 milliseconds with ethane feedstock (which exceeds the range of essentially all modern commercial pyrolysis furnaces) can be obtained. Throughput can be up to about 3 BPSD of liquid feed.

For this program, the reactor tube was 12 foot long constructed from a 3/8-inch 800H SCH-40 pipe to which the inlet and outlet connections were welded. The residence times for these tests ranged from approximately 120-250 milliseconds. KBR commercial steam cracking furnaces are designed to operate closer to 120 milliseconds contact times; this leads to greater selectivity to olefins.

4.3 Procedure:

4.3.1Startup:

Adjusting temperatures in the three furnace zones controlled reactor severity. The external skin temperatures on the reactor tube were the control points. The temperature profile data are presented in Table 4.3a for the Alpha-7 feedstock and Table 4.3b for the FT Naphtha feedstock.

Table 4.3a Run Conditions Summary

Run #		**H-2271-B**		**H-2271-C**
P/E		**0.58**		**0.40**
Temperature Profile				
Zone 1		**1405**		**1488**
Zone 2		**1508**		**1584**
Zone 3		**1455**		**1534**

Table 4.3b Run Conditions Summary

Run #		**H-2272-C**		**H-2272-D**
P/E		**0.42**		**0.40**
Temperature Profile				
Zone 1		**1545**		**1634**
Zone 2		**1643**		**1716**
Zone 3		**1594**		**1667**

Before feed was introduced into the unit, the steam rate was lined out with nitrogen flowing at about one half the final feed rate. With the furnace set at about 1200°F, the feed was introduced replacing the nitrogen. After the feed reached full rate, the skin temperatures were ramped to the predicted run temperatures as quickly as possible up to a maximum rate of 200°F per hour. A GC was shot every 5 minutes in order to monitor the product gas and observe the P/E ratio.

The reactor effluent was quenched to 1150°F by direct steam injection at the reactor outlet. The outlet pressure of the reactor was controlled to 12 psig. Differential pressure transmitters were used to measure the pressure drop across the reactor.

4.3.2 Operation:

FT Naphtha was fed to the top of the reactor tube at a rate of 3.5kg/hr. Steam was generated from distilled water and was mixed with the feed well upstream of the reactor inlet. The steam rate was held at 1.75 kg/hr (0.5 H2O/kg Naphtha).

The feed was heated to a set temperature and fed to the top of the 800H reaction tube. After the process gas passed through the reactor, it was quenched with 90 to 120 psi of steam, reducing the temperature to 1150 F. The process gas then passed through a tar pot, which removes high boiling tars. The process gas was then cooled in a series of heat exchangers to room temperature. Here, the bulk of the water and condensable oils were removed and measured hourly. The remaining gas passed through two chillers to remove trace amounts of water. The bulk of the gas stream passed through a wet test meter, which has a nominal capacity of 600 CFH. A small slipstream was passed through an online GC to determine product gas composition.

4.3.3 Shut Down:

Once the run was complete, the feed was replaced with nitrogen to flush the system of hydrocarbons. The furnace temperature was set to 1500F. The steam and nitrogen were left on until the furnace cooled down. Once the furnace was cooled down, the unit was either burned out or placed in standby.

4.3.4 Analytical:

The analysis of the product gas stream was performed on a HP Micro GC with a sample analysis time of 5 minutes. The GC was calibrated regularly to ensure that the equipment was operating acceptably. The chromatogram was integrated by a computer, which calculated the peak areas. Peak areas were then converted to weight percent component yields and the average molecular weight of the gas was calculated. Normally for calculations, the C_5+ is assumed to have the C/H ratio and molecular weight of benzene. Component product yields are reported as the weight of the component produced per 100 grams of feed. At the end of each run, the burnout gas was analyzed for CO_2 and CO to determine the amount of carbon in the tube. CO_2 and CO was measured using a Siemens Ultramat 6 analyzer. This analyzer operates according to the NDIR two-beam alternating light principle and measures gases highly selective whose absorption bands lie in the infrared wavelength range from 2 to 9 µm.

4.3.5 Decoking:

The reactor was decoked after each of the two runs. During decoking, 7500 g/hr of steam was fed to the reactor. The furnace was set to 1500°F on the air space temperatures. Initially, nitrogen was fed to the reactor. The nitrogen was gradually replaced with oxygen in a series of ten steps. The oxygen was introduced either as industrial air or industrial oxygen, depending on the step. The burnout gas was analyzed for CO_2 and CO to determine the amount of carbon in the tube. The flow was changed to the next step after the level of CO_2 had decreased to below 4wt%. The last step of the burnout was held for 1 hour to ensure oxidation of the coating. The amount of carbon in the tube was calculated by the amount of CO_2 and CO analyzed.

5.0 Discussion of Results

5.1 Characterization of FT Naphtha as a Steam Cracking Feedstock

The results of the analyses of the Chevron Texaco FT Naphtha are shown in Table 5.1. This FT Naphtha stream can be characterized as a good feed for pyrolysis due to its high paraffinic content and relatively low naphthenic content. In addition, the comparatively higher ratio of normal-paraffins to iso-paraffins also makes it an excellent feed for ethylene production.

In contrast, the overall properties of the Alpha-7 naphtha are compared to those of the FT Naphtha in Table 5.1:

Table 5.1 Comparison of Alpha-7 to FT Naphtha

Properties/Feed Type	**Alpha-7**	**FT Naphtha**
Density (20 ºC)	0.7406	0.7168
PIONA (wt.%)	-	-
N-Paraffins	28.7	78.7
I-Paraffins	43.7	13.2
Olefins	0.4	0.4
Naphthenes	21.3	2.3
Aromatics	1.0	4.1
Unknown	5.0	1.3
GCSD [ºF]	-	-
IBP	136	<32
10%	159	206
30%	217	261
50%	271	306
70%	346	347
90%	395	386
EP	803	435

5.2 Evaluation of FT Naphtha Steam Cracking Performance

The material balance was a check to ensure that the feed and product measurements are correct. The overall material balances and hydrogen balances fall within normal limits ranging from 97% to 103%.

The data and yield slates for each run are tabulated in the Appendix along with the material and hydrogen balances. Hourly readings of reactor pressure, temperature, and product gas composition are included. Table 5.2a and Table 5.2b summarizes the overall results.

KBR typically designs its commercial cracking furnaces to operate in the range of 0.1 to 0.14 seconds contact time. This was the shortest contact time of any commercially available furnace technology, and operation at shorter residence time directly results in greater selectivity in cracking to olefins, especially ethylene. During the pilot plant study, the feed and steam rate were increased to measure the difference in yields as a result of lower residence time. The effect of this shorter residence time is depicted in Table 5.2b.

Thus, at equivalent methane yield (typical indicator of cracking severity), the yield of ethylene increased and butadiene yield increased while there was little change in propylene, netting an overall improvement in olefins yield. This overall improvement in yields, and thus plant economics, is the reason KBR has developed its pyrolysis technology to operate at these short residence times.

Table 5.2a Alpha-7 Results Summary

Run #		H-2271-B	H-2271-C
Feed		Alpha-7 Naphtha	Alpha-7 Naphtha
Oil Rate		3.5 kg/hr	3.5 kg/hr
Steam Rate		1.75 kg/hr	1.75 kg/hr
Normalized Yields			
	Gas	66.59%	77.06%
	Liquid	33.41%	22.94%
Material Balance		98.60	98.53
Time (msec)		231	211
Run #		H-2271-B	H-2271-C
hydrogen		0.73	0.90
Carbon Monoxide		0.06	-
carbon dioxide		0.02	0.02
Methane		11.69	12.48
ethane		3.46	4.19
ethylene		23.42	30.93
acetylene		0.47	0.65
H2S		-	-
propane		0.54	0.62
propylene		13.51	12.51
Propadiene		0.36	0.34
methyl acetylene		0.37	0.49
n-butane		0.18	0.23
iso-butane		0.10	0.19
trans-2-butene		0.47	0.61
1-butene		2.39	2.77
iso-butene		2.52	2.73
cis-2-butene		0.43	0.48
1,3-butadiene		3.70	4.28
C5	P	0.25	0.19
	I	0.25	0.19
	N	0.00	0.00
	O	2.43	2.49
C6	A	2.39	5.54
	Other	5.12	2.66
C7	A	1.74	2.62
	Other	5.38	1.87
C8	A	0.95	0.92
	Other	4.04	1.38
C9+, Unknown		13.04	7.73

Table 5.2b FT Naphtha Results Summary

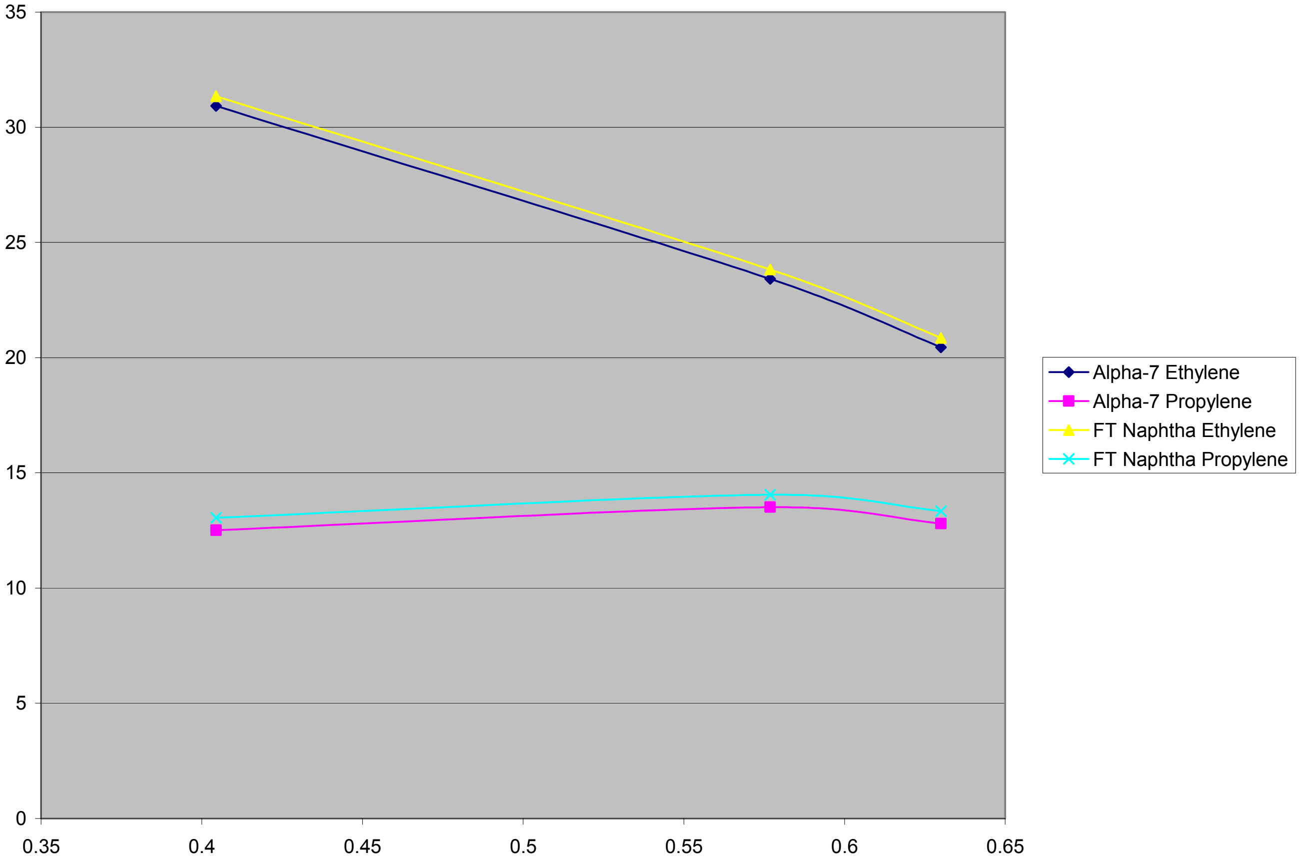
Run #	H-2272-C		H-2272-D
Feed	FT Naphtha		FT Naphtha
Oil Rate	3.5 kg/hr		6.0 kg/hr
Steam Rate	1.75 kg/hr		3.0 kg/hr
Normalized Yields			
	76.60%		80.36%
	23.40%		19.64%
Material Balance	101.77		103.04
Time (msec)	205		138
Run #	H-2272-C		H-2272-D
hydrogen	0.78		0.84
Carbon Monoxide	0.06		-
carbon dioxide	0.02		0.02
Methane	12.70		13.06
ethane	3.72		3.93
ethylene	31.34		33.27
acetylene	0.52		0.61
H2S	-		-
propane	0.57		0.58
propylene	13.05		13.17
Propadiene	0.31		0.32
methyl acetylene	0.47		0.46
n-butane	0.22		0.21
iso-butane	0.11		0.17
trans-2-butene	0.54		0.54
1-butene	2.38		2.46
iso-butene	2.47		2.42
cis-2-butene	0.43		0.43
1,3-butadiene	3.97		4.02
C5 P	0.50		0.14
I	0.29		0.01
N	0.01		0.01
O	2.40		0.75
C6 A	0.83		0.72
Other	2.56		1.46
C7A	0.55		0.04
Other	2.88		2.54
C8 A	0.13		0.02
Other	4.28		3.00
C9+, Unknown	11.89		14.79

Table 5.3 Comparison of FT Naphtha Yields with Alpha-7 Naphtha

Run #	H-2271-C	H-2272-C
Feed	Alpha-7 Naphtha	FT Naphtha
Oil Rate	3.5 kg/hr	3.5 kg/hr
Steam Rate	1.75 kg/hr	1.75 kg/hr
Normalized Yields		
	77.06%	76.60%
	22.94%	23.40%
Material Balance	98.53	101.77
Run #	H-2271-C	H-2272-C
Zone 1	1,488°F	1,545°F
Zone 2	1,584°F	1,643°F
Zone 3	1,534°F	1,594°F
Time (msec)	211	205
Run #	Alpha-7 Naphtha	FT Naphtha
hydrogen	0.90	0.78
Carbon Monoxide	-	0.06
carbon dioxide	0.02	0.02
Methane	12.48	12.70
ethane	4.19	3.72
ethylene	30.93	31.34
acetylene	0.65	0.52
H2S	-	-
propane	0.62	0.57
propylene	12.51	13.05
Propadiene	0.34	0.31
methyl acetylene	0.49	0.47
n-butane	0.23	0.22
iso-butane	0.19	0.11
trans-2-butene	0.61	0.54
1-butene	2.77	2.38
iso-butene	2.73	2.47
cis-2-butene	0.48	0.43
1,3-butadiene	4.28	3.97
C5 P	0.19	0.50
I	0.19	0.29
N	0.00	0.01
O	2.49	2.40
C6 A	5.54	0.83
Other	2.66	2.56
C7A	2.62	0.55
Other	1.87	2.88
C8 A	0.92	0.13
Other	1.38	4.28
C9+, Unknown	7.73	11.89

This range of conditions of propylene-to-ethylene (P/E) weight ratio from 0.7 to 0.4 was selected to span typical commercial cracking severities for naphtha feedstocks. While trying to obtain the P/E ratio much above 0.4, the gas yields on the FT Naphtha dramatically decreased. This would not be expected to occur for commercial operations. The yields for the FT naphtha would trend similarly to the Alpha-7 Naphtha as demonstrated in Figure 5.1.

Figure 5.1 Projected FT Naphtha Yields in Comparison to Alpha-7 Naphtha



KBR's proprietary yield model has been used to estimate the yields for Alpha-7 naphtha and the FT Naptha. The comparison is given in Table 5.3a and Table 5.3b for the Alpha-7 feed and Table 5.4a and 5.4b for the FT Naphtha feed.

Table 5.3a Commercial Prediction Comparison for Alpha-7 Feed at P/E 0.4

	Commercial Predictions	Pilot Plant Yields
Feed	**Alpha-7**	**Alpha-7**
P/E	**0.4**	**0.4**
Methane	**17.49**	**12.5**
Ethylene	**34**	**30.9**
Propylene	**13.6**	**12.5**

Table 5.3b Commercial Prediction Comparison for Alpha-7 Feed at P/E 0.59

	Commercial Predictions	Pilot Plant Yields
Feed	**Alpha-7**	**Alpha-7**
P/E	**.59**	**.59**
Methane	**11.69**	**10.1**
Ethylene	**27.5**	**23.42**
Propylene	**16.2**	**13.51**

Table 5.4a Commercial Prediction Comparison for FT Naphtha Feed at P/E 0.40

	Commercial Predictions	Pilot Plant Yields
Feed	**FT Naphtha**	**FT Naphtha**
P/E	**.40**	**.40**
Methane	**14**	**12.48**
Ethylene	**36.5**	**30.93**
Propylene	**14.6**	**12.51**

Table 5.4b Commercial Prediction for FT Naphtha Feed at P/E 0.59

	Commercial Predictions
Feed	**FT Naphtha**
P/E	**.59**
Methane	**10.1**
Ethylene	**29.7**
Propylene	**17.5**

Note that the yields were estimated based on the same P/E ratio as the pilot plant study. The discrepancy in the commercial yield predictions are more than likely due to lower than expected gas yields in the pilot plant.

5.3 Evaluation of SSN Coking Tendency

The burnout detected a total of 160 grams of coke for the FT Naphtha while the Alpha-7 Naphtha yielded 145 grams of coke. This run demonstrates that the coking tendency of the FT Naphtha, even at relatively high cracking severity, was equivalent to that which we typically encounter with other naphthas. As a consequence, KBR expects that commercial furnace operations (run lengths) should be equivalent to those expected from virgin naphthas cracking at similar severity however KBR recommends that an extended 120-hour coking run be obtained to confirm the coking tendency of the feed.

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix I - Test Report

Subtask 2.5.7.4: Fischer-Tropsch Diesel Fuel Cell Reforming

Reporting Period:	March 2003 to June 2003
Contributors:	Centha A. Davis (ChevronTexaco ERTC) Phyllis D. Hill (Kelly Services) James F. Stevens (ChevronTexaco Technology Ventures)
Date Issued:	June 5, 2003

I. Executive Summary

The suitability of two naphtha cut Fischer-Tropsch (F-T) products, hydrocracked naphtha and hydrotreated naphtha, for hydrogen production was tested under autothermal reforming (ATR) conditions. Two low sulfur, non-F-T, commercially available feed streams, VM&P naphtha and deodorized kerosene were tested under identical conditions. The results indicate that the hydrotreated naphtha is the best ATR feed of the four feed streams tested. The hydrotreated naphtha is a good feed for hydrogen production. The results indicate that the hydrocracked naphtha has a high tendency for carbon formation and would provide ATR process and reactor design challenges greater than the hydrotreated naphtha.

The ATR tests were conducted using a commercially available 0.5% Rhodium (Rh) on alumina catalyst. The air/fuel ratios were controlled to give oxygen (O_2)/carbon (C) ratios of either 0.372 or 0.45. Steam to carbon ratios were held at either 2 or 3. The feed pre-heat temperature was between 673K (400°C) and 718K (445°C). The ATR exit temperature was between 882K (609°C) and 1057K (784°C). The average ATR exit gas composition (dry basis) for the hydrotreated naphtha at an O_2/C ratio of 0.372 and a steam/carbon ratio of 3 was 43.0 mole% hydrogen (H_2), 0.4 mole% methane (CH_4), 9.3 mole% carbon monoxide (CO), 32.1 mole% nitrogen (N_2), 0.4 mole% argon (Ar), and 14.9 mole% carbon dioxide (CO_2).

II. Background

A potential use for Fischer-Tropsch (F-T) products is as a feed for reforming processes producing hydrogen for use in fuel cells. The low sulfur level of F-T products is especially desirable since sulfur poisons catalysts in both reformers and fuel cells. There are three reforming processes used for the conversion of hydrocarbons to the hydrogen rich reformate required by fuel cells. These are steam reforming, partial oxidation, and autothermal reforming (ATR).

The tests conducted in this program used the autothermal reforming process. In this process, air, hydrocarbon, and steam are passed through a catalyst bed. By controlling the air/hydrocarbon ratio the exothermic oxidation reactions are used to supply the energy required by the endothermic steam reforming reactions. Typically the feed to the reforming catalyst is pre-heated to at least 673K (400^{o}C) and the ATR outlet is in the range of 973K (700^{o}C) to 1173K (900^{o}C). In normal applications, the ATR product gas is passed through one or more water-gas shift reactors to reduce the concentration of carbon monoxide and increase the concentration of hydrogen. The tests performed in this work did not include water-gas shift.

Hydrocarbon feeds can challenge the reforming process in several ways. The sulfur content of most refinery streams is a significant challenge. Reforming catalysts, as well as other downstream catalysts, can be poisoned by sulfur which reduces catalyst life and hydrogen yield. There are other catalyst poisons, such as vanadium and arsenic, which must be controlled. Olefins tend to pyrolize and form carbon during the pre-heating process. This problem can be controlled with materials selection and process modifications such as hydrogen recycling, but in general it is preferable to avoid these complications. Highly aromatic feeds can form gums that gradually reduce the activity of the reforming catalyst. These problems can be solved, but avoidance through hydrocarbon feed selection is desirable.

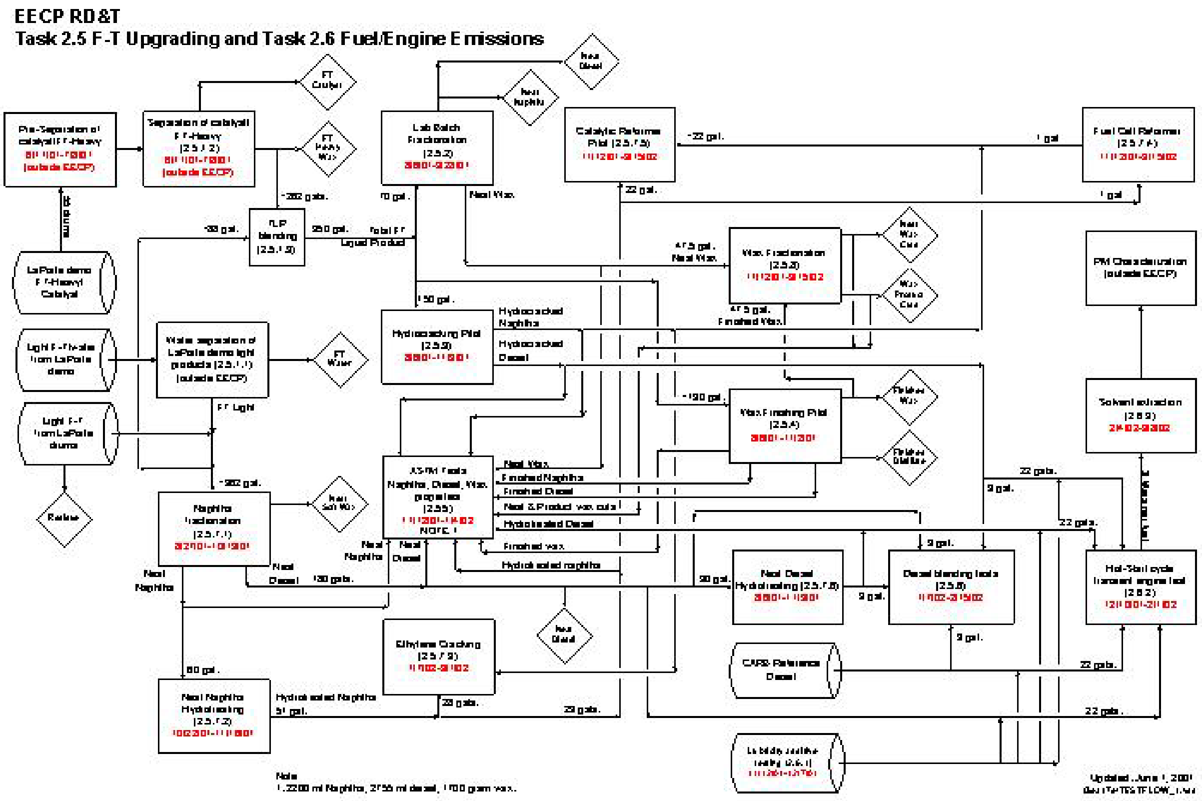
A. Experimental

Four hydrocarbon feeds were tested as part of this work. The feeds were F-T hydrocracked naphtha, F-T hydrotreated naphtha, VM&P naphtha commercially produced by the Sunnyside Corp. of Wheeling, IL, and deodorized kerosene purchased from EM Science of Gibbstown, NJ.

ChevronTexaco Technology Marketing performed a hydrocracking pilot plant run under Task 2.5.3 on the Fischer-Tropsch hydrocarbon liquid blend produced from the La Porte Alternative Fuels Demonstration Unit. The run generated both an initial boiling point (IBP)-466K (IBP-380^{o}F) True Boiling Point (TBP) boiling range hydrocracked naphtha product and a 466K-644K (380^{o}F-700^{o}F) hydrocracked diesel product. The hydrocracked F-T naphtha product met the product specification target of a Total Acid Number (TAN) of less than 0.1 milligrams (mg) potassium hydroxide (KOH) per gram (g). A one gallon retain of the hydrocracked naphtha product was used as a feed under Task 2.5.7.4 for the Fuel Cell Reformer unit. For more details on how the hydrocracked naphtha product was prepared, please see the report for Task 2.5.3 "Hydrocracking Pilot". Schematic diagram 1. shows some of the details of Task 2.5 and the origin of the two F-T products.

ChevronTexaco Technology Marketing performed a hydrotreating pilot plant run under Task 2.5.7.2 on the IBP-466K (IBP-380°F) (TBP) F-T naphtha produced from the La Porte Alternative Fuels Demonstration Unit. The run generated approximately 60 gallons of hydrotreated F-T naphtha and met the product specification target of a TAN of less than 0.1 mg KOH/g. A one gallon retain of the hydrotreated naphtha product was used as a feed under Task 2.5.7.4. for the Fuel Cell Reformer unit. For more details on how the hydrotreated product was prepared, please see the report for Task 2.5.7.2, "Neat Naphtha Hydrotreating".

The physical characteristics of the materials are shown in Table 1.



Schematic 1. Task 2.5 F-T Upgrading and Task 2.6 Fuel/Engine Emissions

Test Material	Density (g/cc)	Carbon Mole %	Hydrogen Mole %	H/C ratio
Hydrocracked F-T Naphtha	0.703	84.78	15.08	2.13
Hydrotreated F-T Naphtha	0.719	84.93	14.82	2.09
Sunnyside VM&P Naphtha	0.747	85.24	14.44	2.03
Deodorized Kerosene	0.76	84.54	15.31	2.17

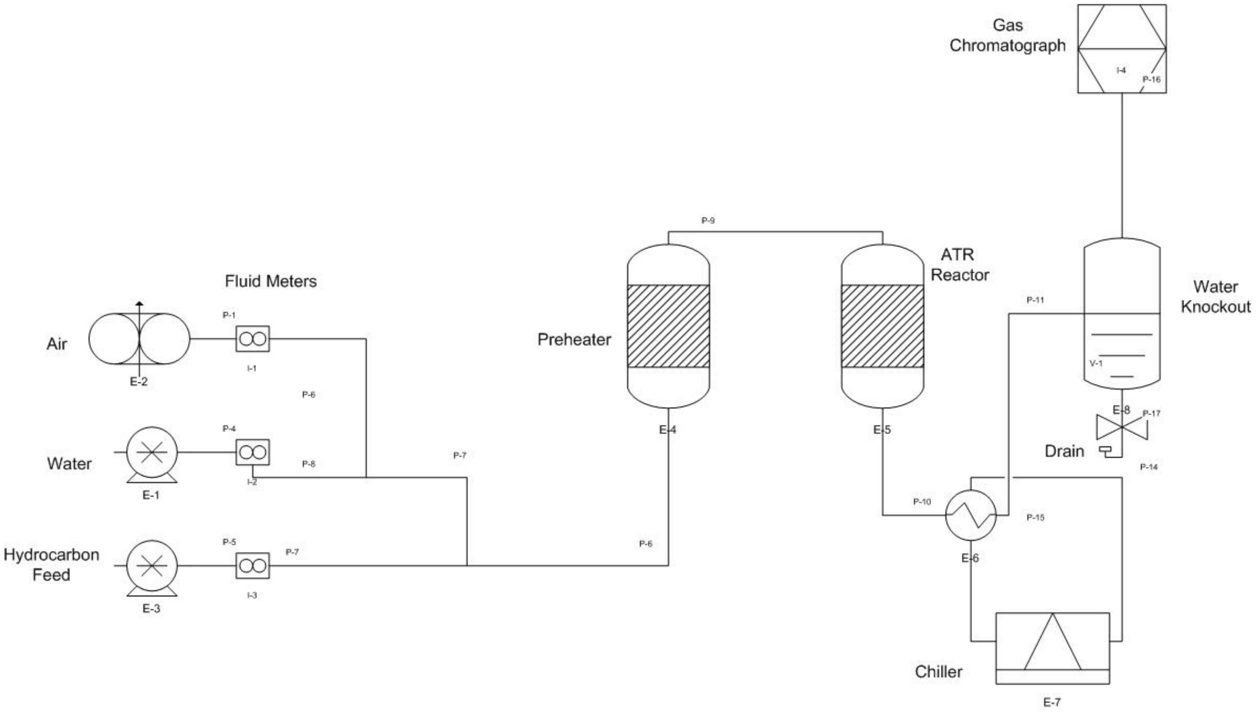
Table 1. Density and compositions of tested materials.

The process flow diagram for the bench scale ATR test apparatus is shown in Schematic 2. In this apparatus deionized water, air, and hydrocarbon are passed through tubing to a mixer inside an electric tube furnace. The temperature of the furnace is adjusted so that the ATR feed mixture is pre-heated to least 673K (400^{o}C). The ATR feed then passes to a 25.4 millimeters (1 inch) diameter tube reactor containing ATR catalyst. The tube reactor is in a second electrically heated furnace. The second electrically heated furnace is used to offset heat losses from the small diameter, high temperature tube reactor. In full scale applications the ATR reactor has relatively low heat losses and is nearly adiabatic.

In the ATR reactor the feed stream passes through a packed catalyst bed. For all tests in this report 60 grams of a commercially available (Engelhard Escat 326) 0.5% Rhodium (Rh) on alumina was used. The nominal particle diameter of the catalyst is 2 mm.

After exiting the ATR reactor the reformate passes through a chilled heat exchanger into a knockout vessel used to separate condensed water from the reformate. The reformate is discharged into a ventilation hood. A slip stream of the product gas is sent to a gas chromatograph for compositional analysis.

For each hydrocarbon feed stream, tests were conducted under eight sets of test conditions. The tests were conducted at two feed rates, two steam/carbon ratios, and two air/fuel (O_2/C) ratios. Multiple measurements of product gas composition were made for each set of test conditions. Raw data for all tests are shown in the Appendix.



Schematic 2. Process flow diagram of bench scale ATR test apparatus.

B. Results and Discussion

The results of the tests are shown in Figures 1 through 26. Multiple gas composition analyses were averaged for each set of test conditions (two feed rates, two steam/carbon ratios, and two air/fuel (O_2/C) ratios) and graphed.

Figure 1 shows the carbon balance for the hydrocracked naphtha at a steam/carbon ratio of 2 and an O_2/C ratio of 0.372. The carbon balance (100*weight of carbon feed rate/weight of carbon in reformate) of less than 100% indicates that the hydrocracked naphtha is pyrolyzing in the reactor. The fact that the carbon balance improves with increasing flow rate indicates that the pyrolysis is occurring in the preheat zone before contacting the reforming catalyst. This conclusion is borne out by the fact that the carbon balance does not improve with increasing steam/carbon ratio (Figure 3) or increasing O_2/C ratio (Figures 5 & 7). The presence of carbon in the reactor zone ahead of the ATR catalyst was confirmed by visual inspection. Figures 2, 4, 6, and 8 show the composition of the reformate from the autothermal reforming of the hydrocracked naphtha.

The high level of pyrolysis seen in all of the tests of the hydrocracked naphtha indicates that it would be a difficult feed to reform. Process modifications such as hydrogen recycle and reactor designs to minimize pyrolysis in the preheat regions would be necessary.

Figures 9, 11, 13, and 15 show that the hydrotreated naphtha is a much better feed stream for reforming. Although carbon formation was shown at the lowest steam/carbon and O_2/C condition no measurable carbon formation was seen at the other seven conditions. The reformate compositions shown in Figure 12 (both feed rates) shows a hydrogen concentration of about 43 mole%. After water-gas shifting and residual carbon monoxide removal this would yield a product gas with a hydrogen content of about 46 mole% (dry basis). The hydrotreated naphtha reformate would be an acceptable feed for a proton exchange membrane fuel cell designed to accept reformate.

Figures 17, 19, 21, and 23 show the results of reforming a commercially available VM&P naphtha. The carbon balance is less than 100%, worsens with increasing flow rate, and improves with increasing O_2/C ratio and increasing steam/carbon flow rate. This is the kind of behavior that is seen when aromatics present in the feed stream form resins in the catalyst. The higher density and lower H/C ratio of the Sunnyside naphtha indicates greater aromaticity in this feed and is the likely cause of the resin formation.

Figure 25 shows the results of reforming a deodorized kerosene. As shown in Table 1 this material had the highest H/C ratio of the four hydrocarbon feeds tested. This type of feed, low sulfur and low aromatics, would also be a good feed for hydrogen production.

Figure 1.
Hydrocracked Naphtha
Steam/Carbon=2
O_2/C=0.372

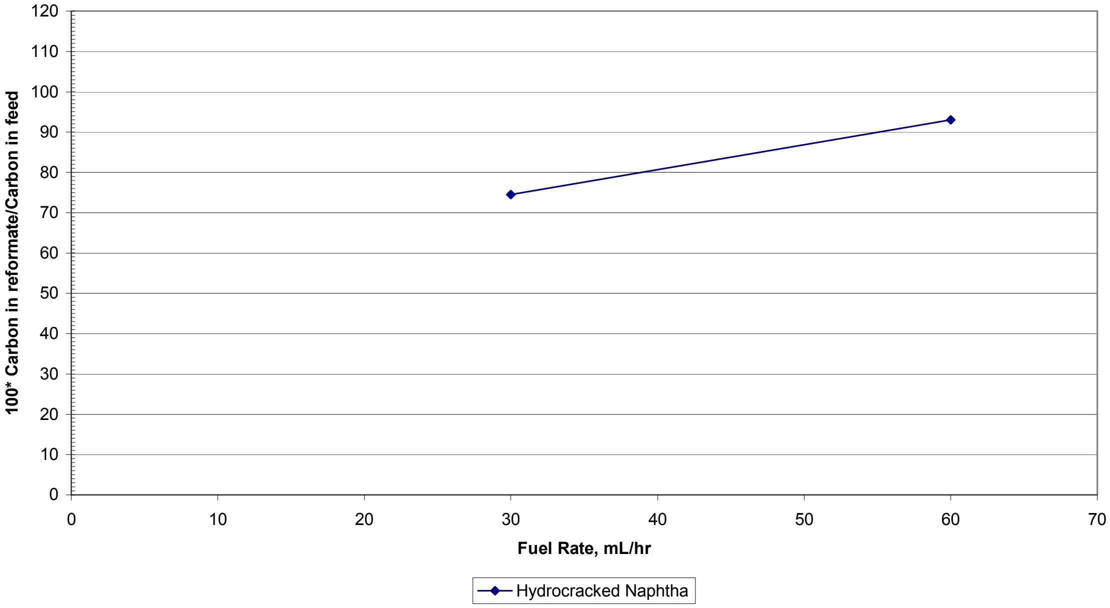


Figure 2
Hydrocracked Naphtha
Steam/Carbon=2
O_2/C=0.372

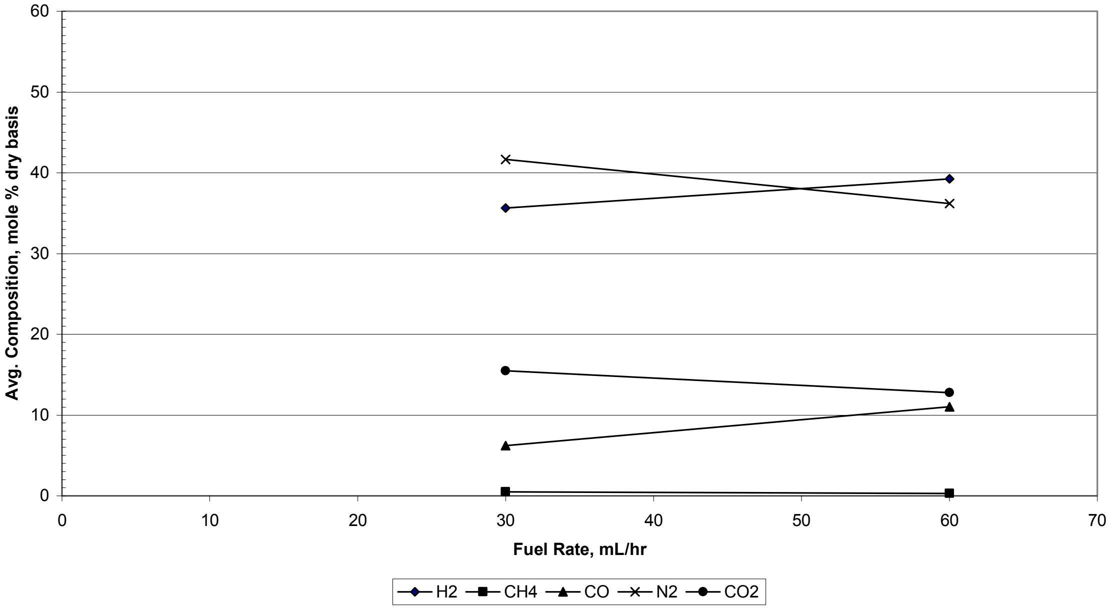


Figure 3
Hydrocracked Naphtha
Steam/Carbon=3
$O_2/C=0.372$

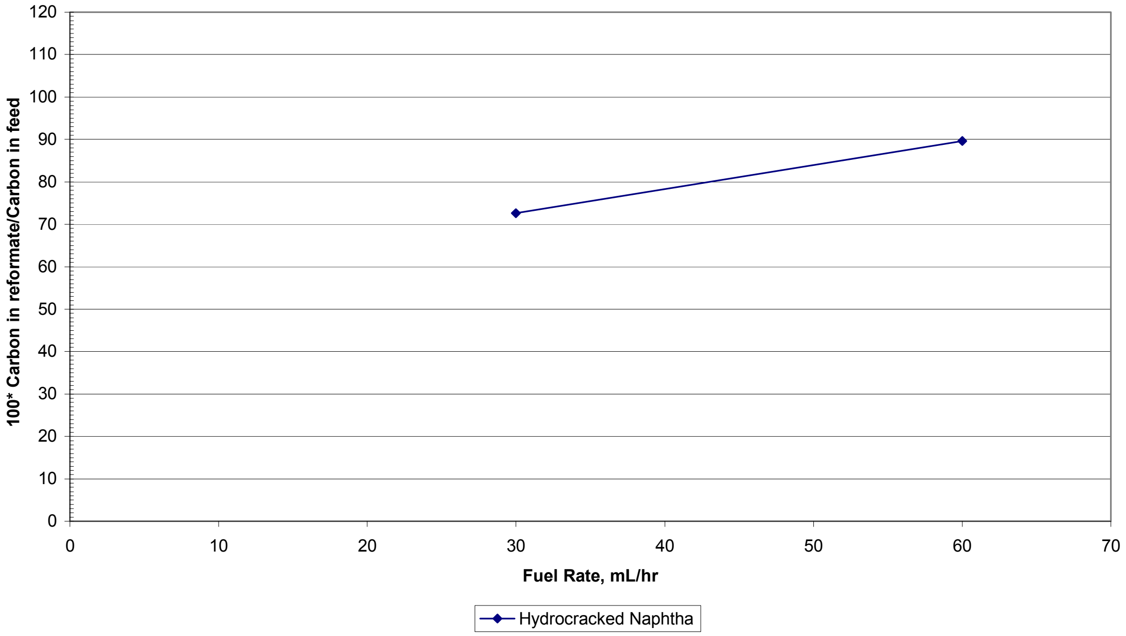


Figure 4.
Hydrocracked Naphtha
Steam/Carbon=3
$O_2/C=0.372$

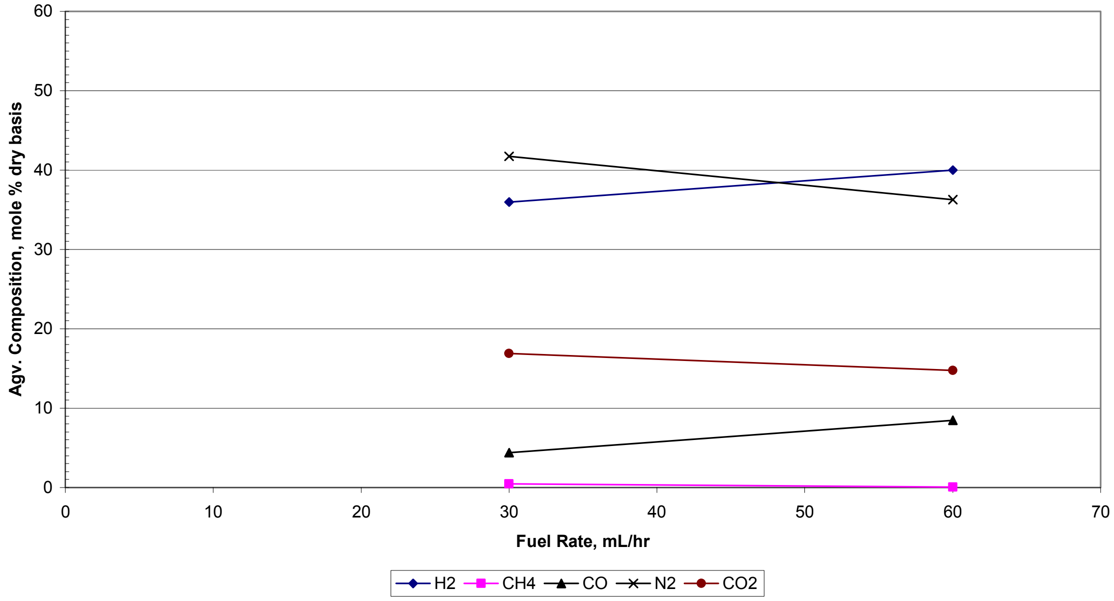


Figure 5.
Hydrocracked Naphtha
Steam/Carbon=2
O_2/C=0.45

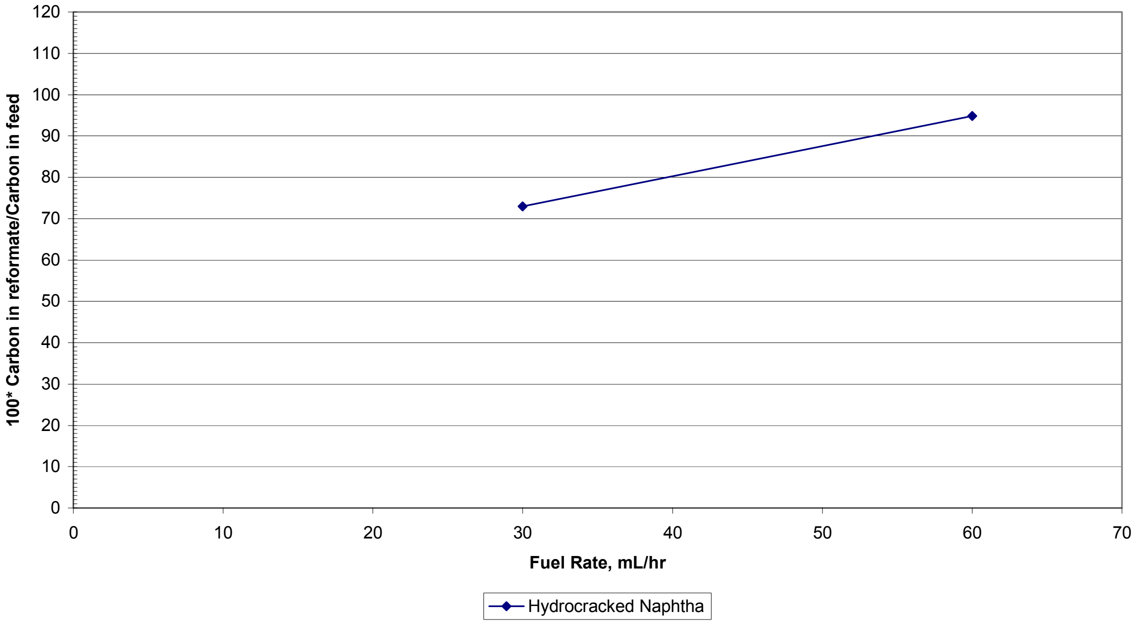


Figure 6.
Hydrocracked Naphtha
Steam/Carbon=2
O_2/C=0.45

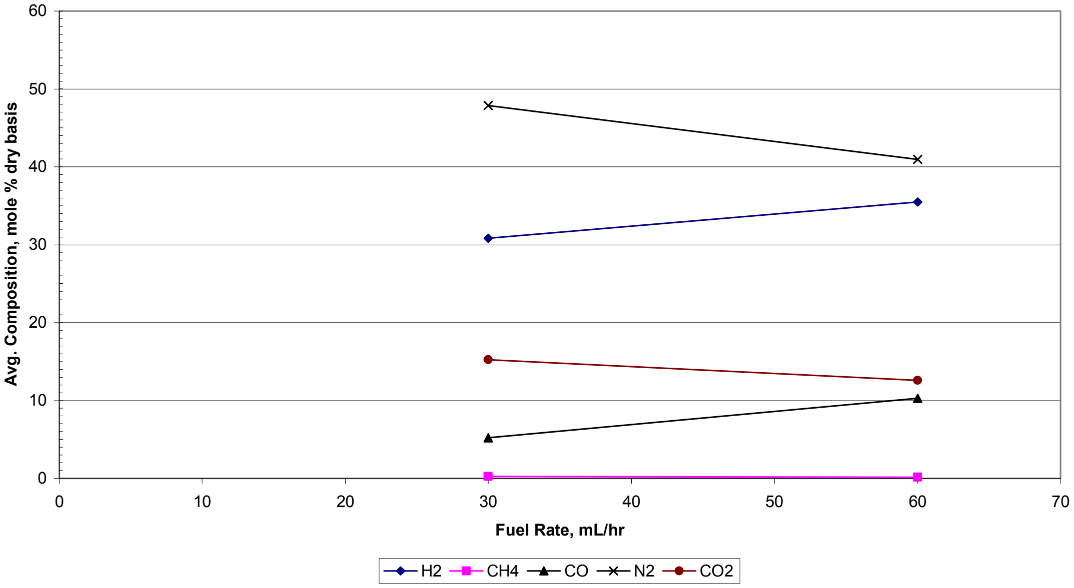


Figure 7.
Hydrocracked Naphtha
Steam/Carbon=3
$O_2/C=0.45$

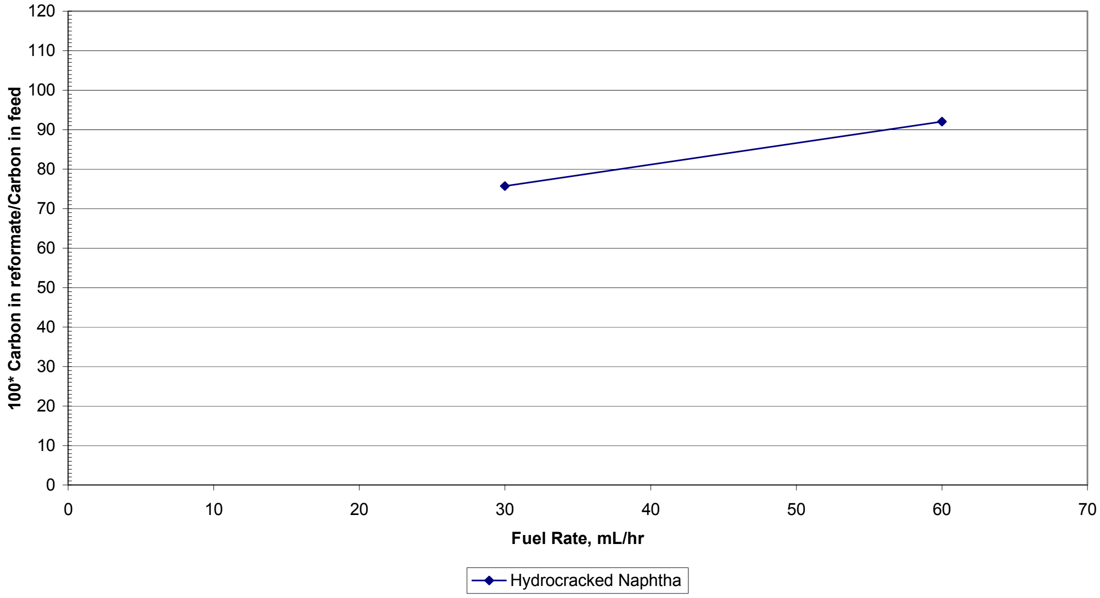


Figure 8.
Hydrocracked Naphtha
Steam/Carbon=3
$O_2/C=0.45$

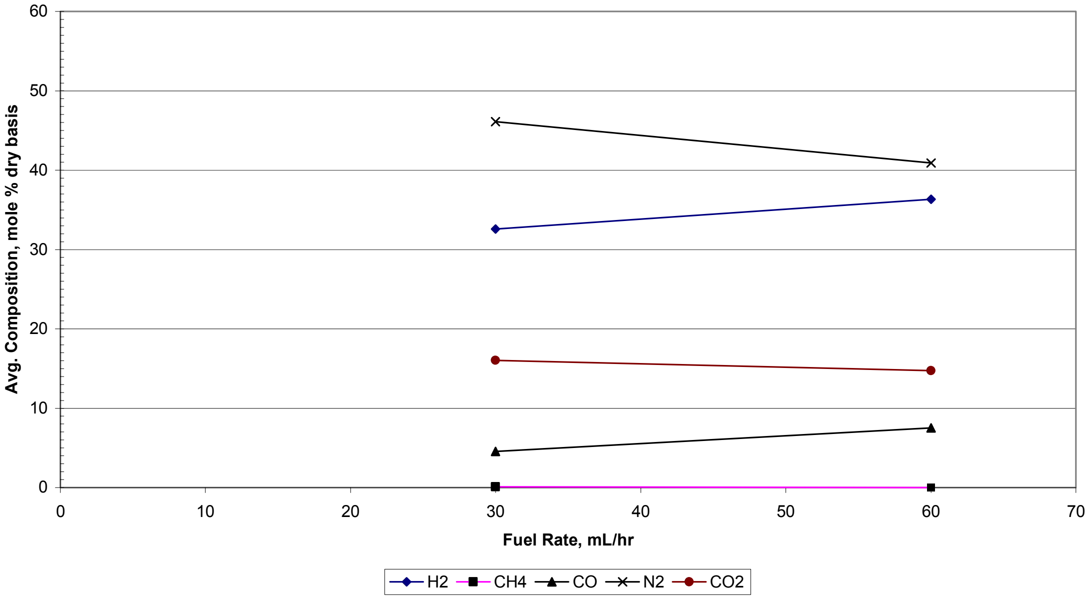


Figure 9.
Hydrotreated Naphtha
Steam/Carbon=2
$O_2/C=0.372$

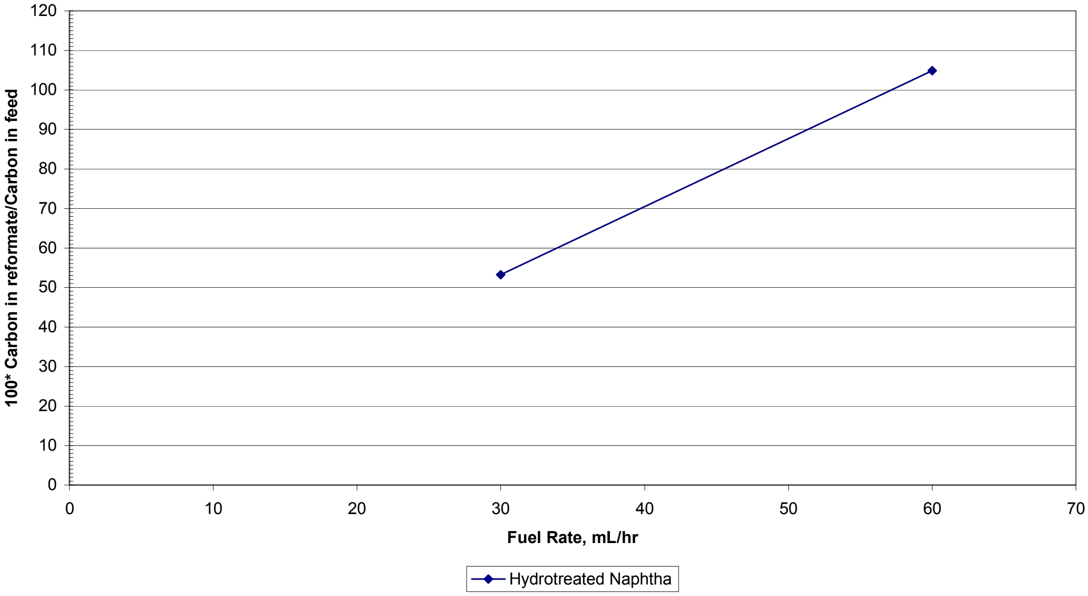


Figure 10.
Hydrotreated Naphtha
Steam/Carbon=2
$O_2/C=0.372$

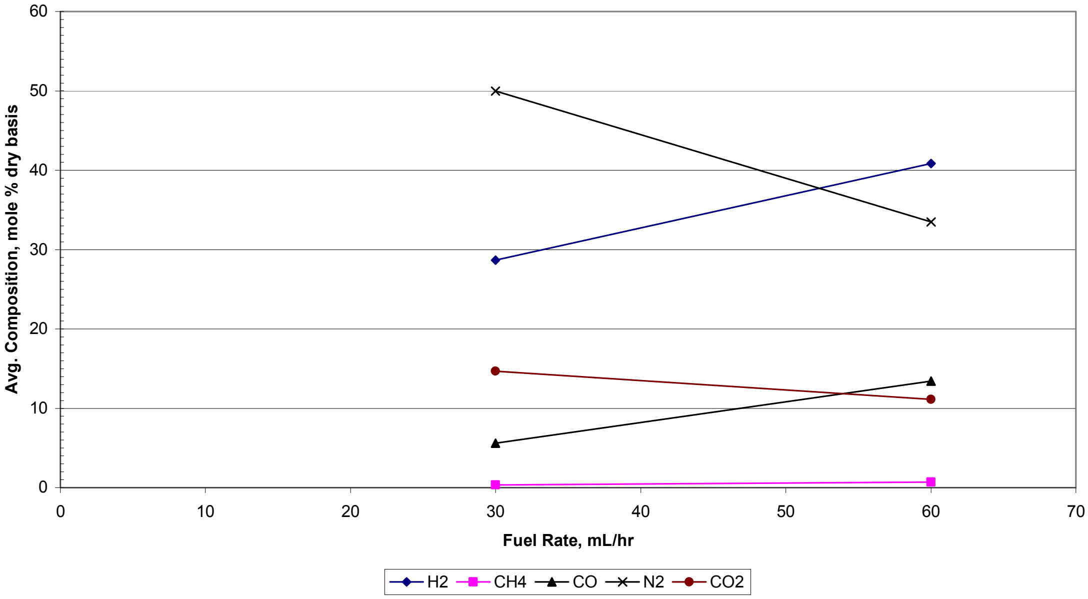


Figure 11.
Hydrotreated Naphtha
Steam/Carbon=3
O_2/C=0.372

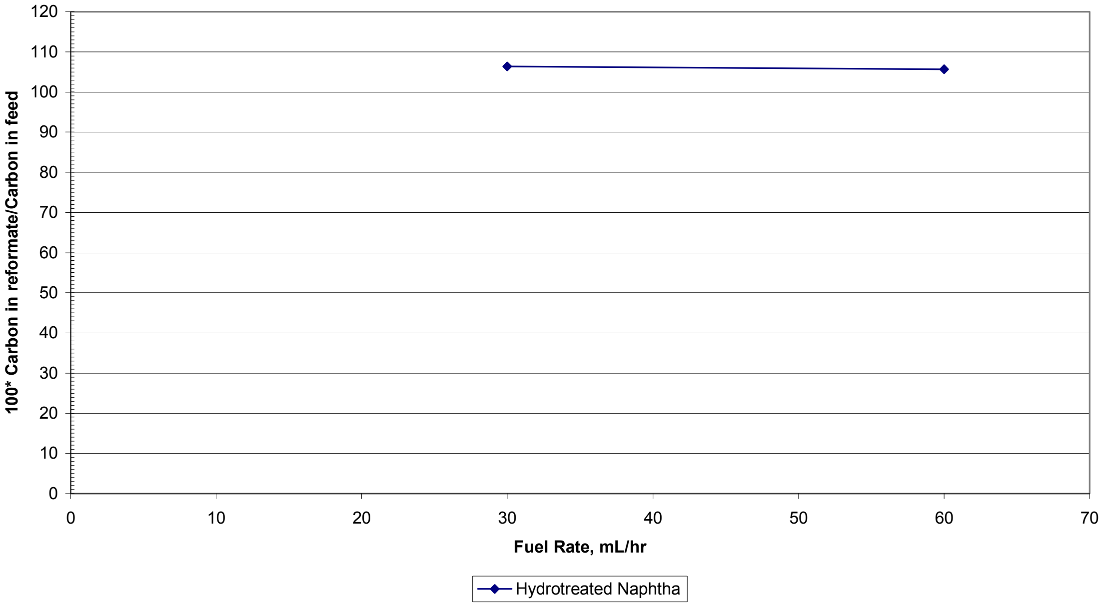


Figure 12. Hydrotreated Naphtha
Steam/Carbon=3
O_2/C=0.372

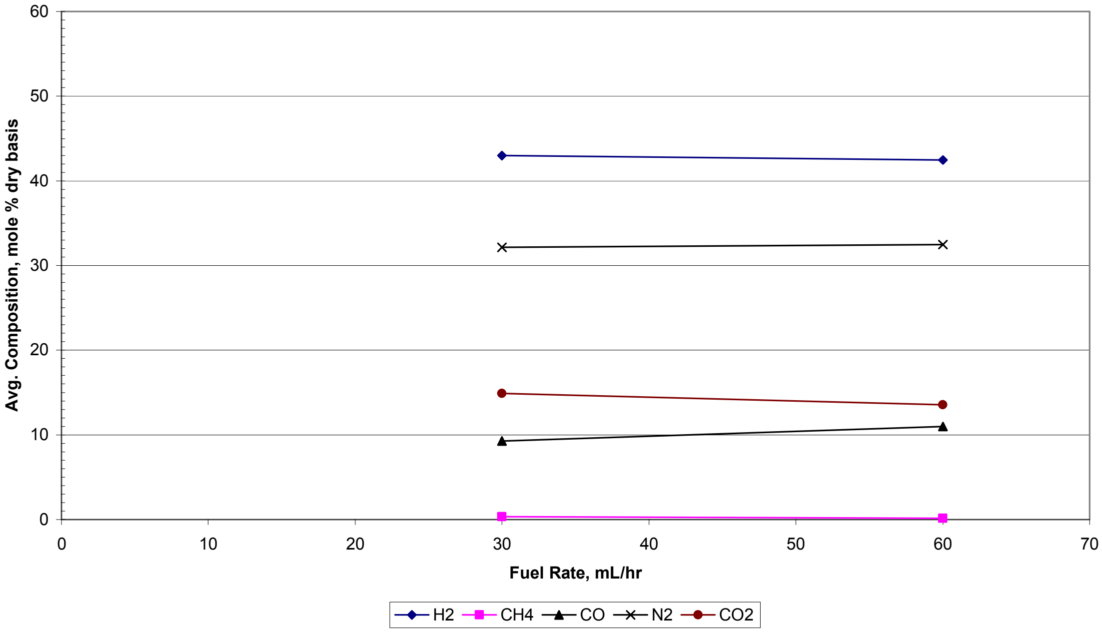


Figure 13.
Hydrotreated Naphtha
Steam/Carbon=2
O_2/C=0.45

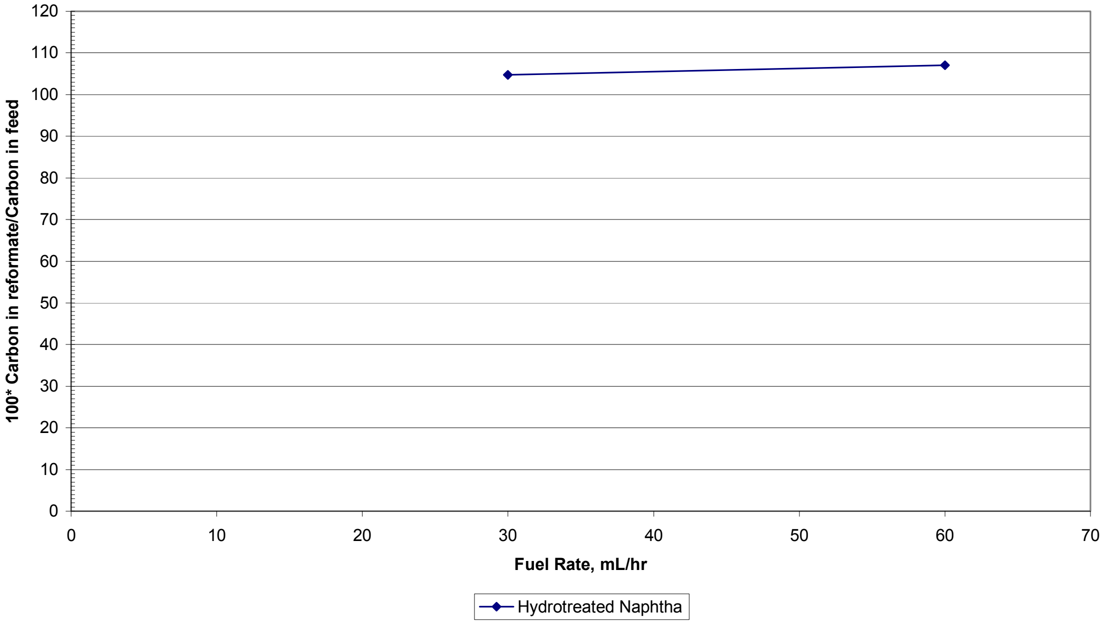


Figure 14.
Hydrotreated Naphtha
Steam/Carbon=2
O_2/C=0.45

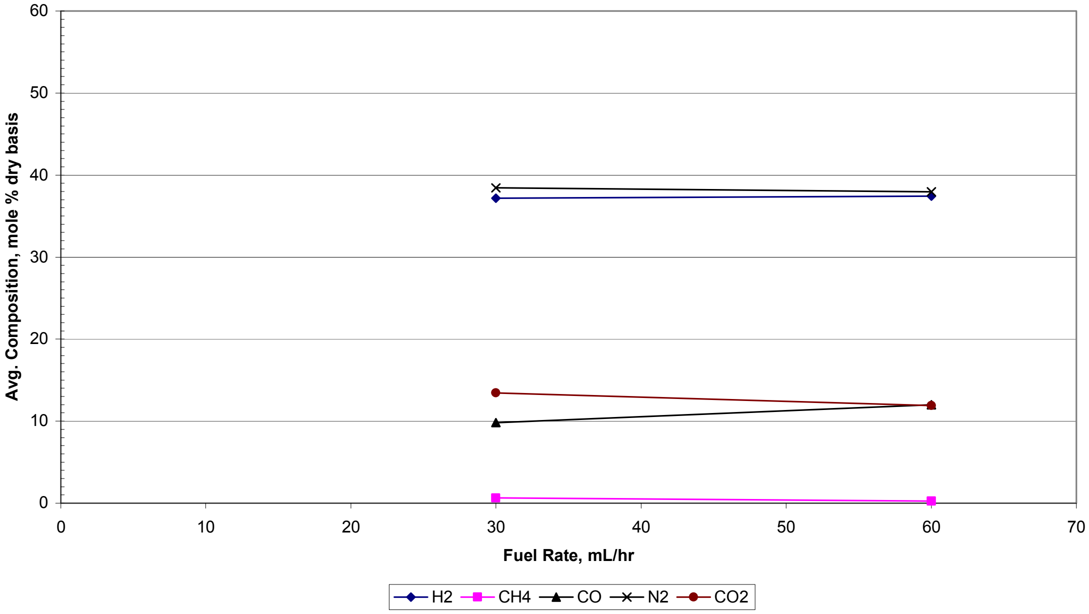


Figure 15.
Hydrotreated Naphtha
Steam/Carbon=3
O_2/C=0.45

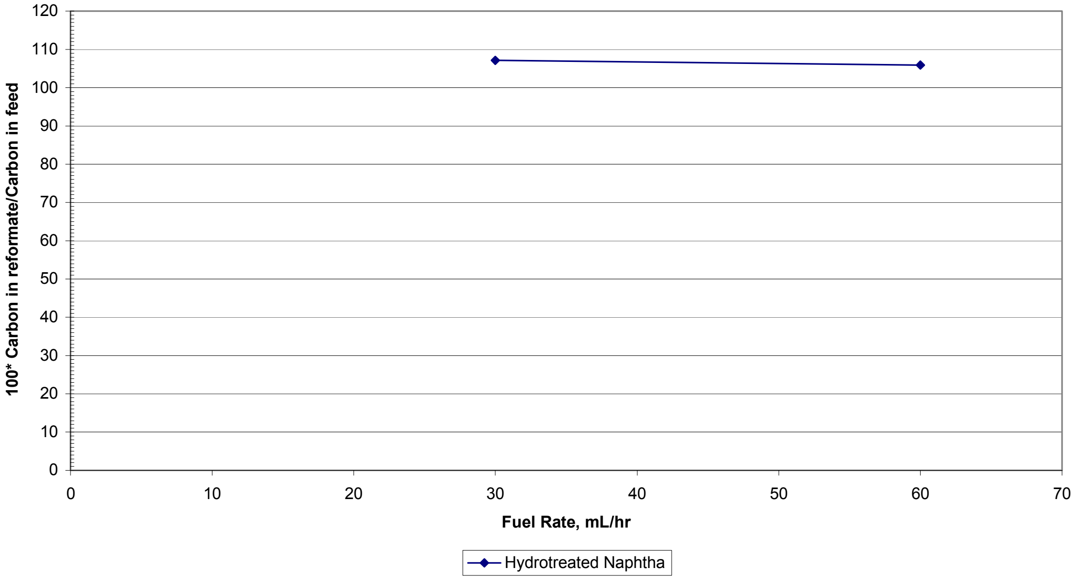


Figure 16.
Hydrotreated Naphtha
Steam/Carbon=3
O_2/C=0.45

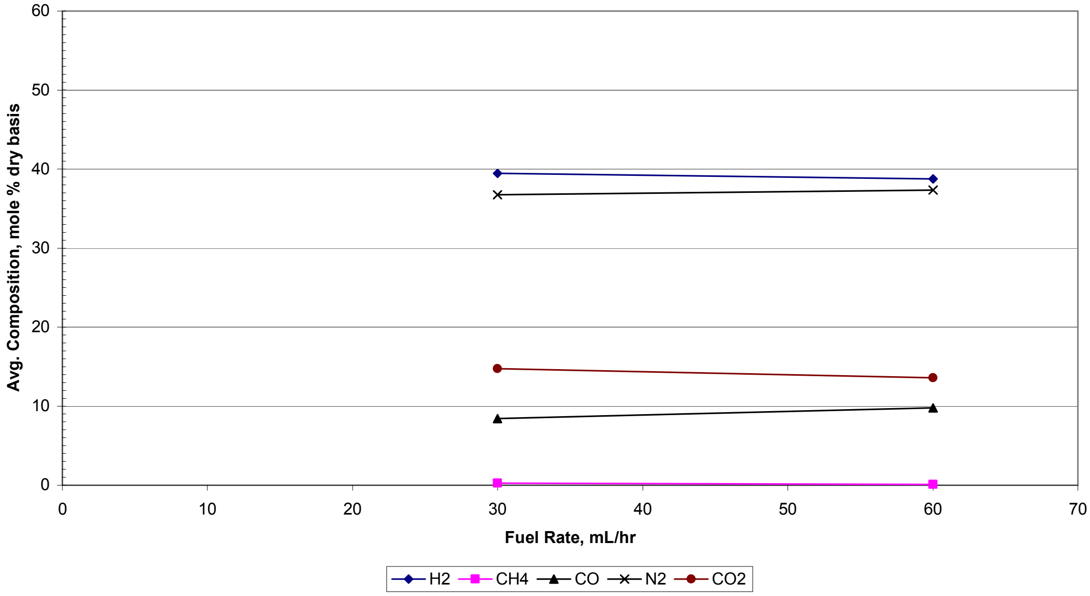


Figure 17.
Sunnyside Naphtha
Steam/Carbon=2
O_2/C=0.372

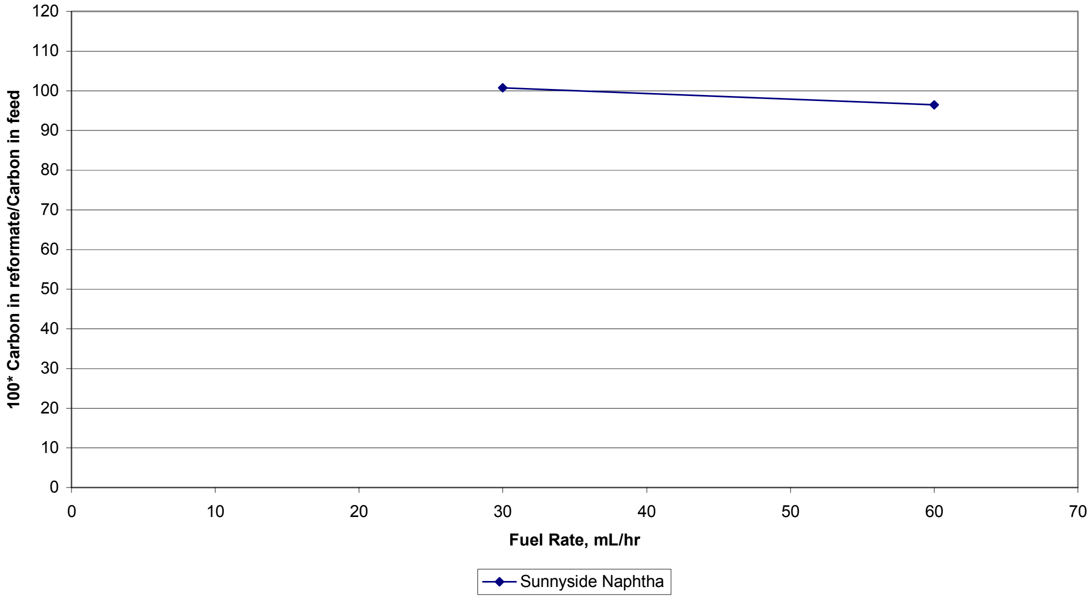


Figure 18.
Sunnyside Naptha
Steam/Carbon=2
O_2/C=0.372

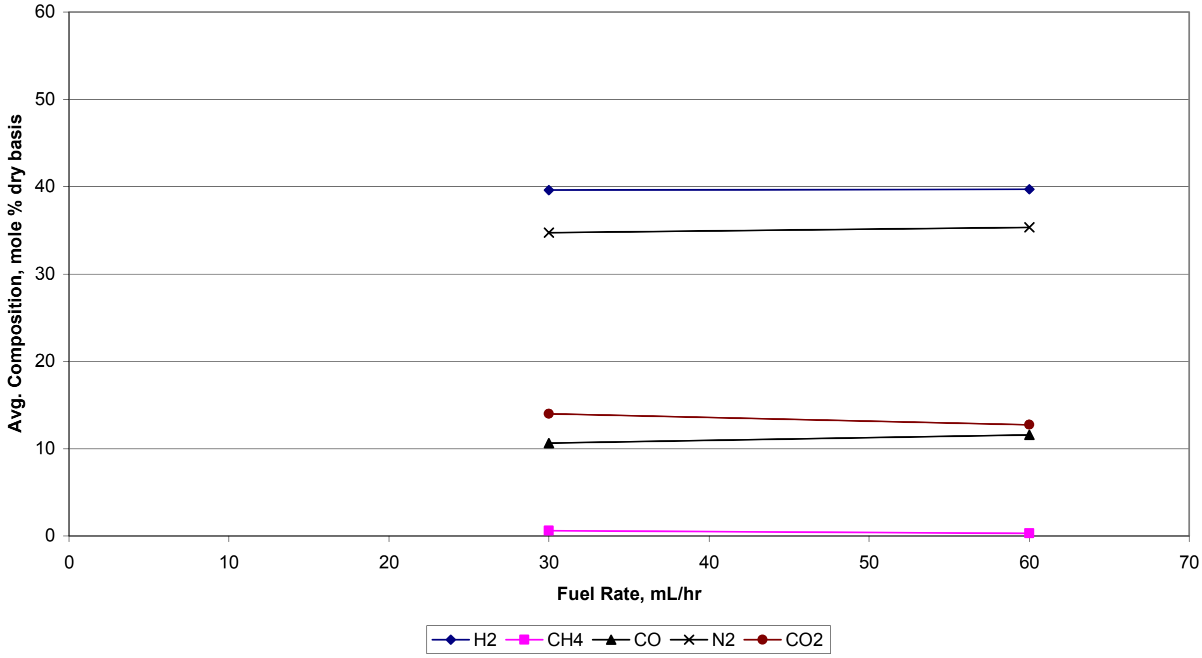


Figure 19.
Sunnyside Naphtha
Steam/Carbon=3
O_2/C=0.372

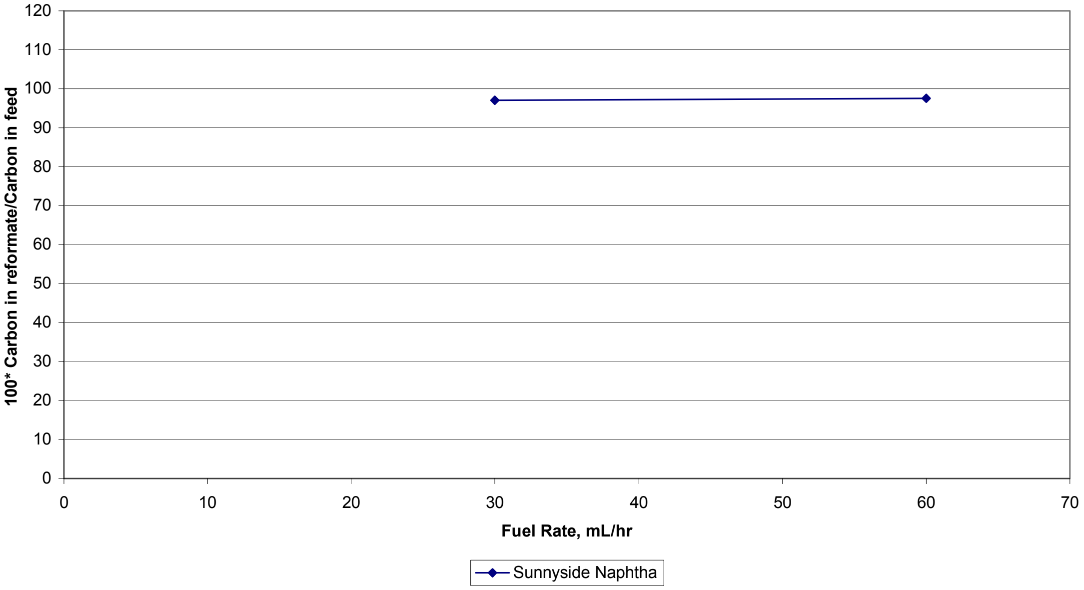


Figure 20.
Sunnyside Naphtha
Steam/Carbon=3
O_2/C=0.372

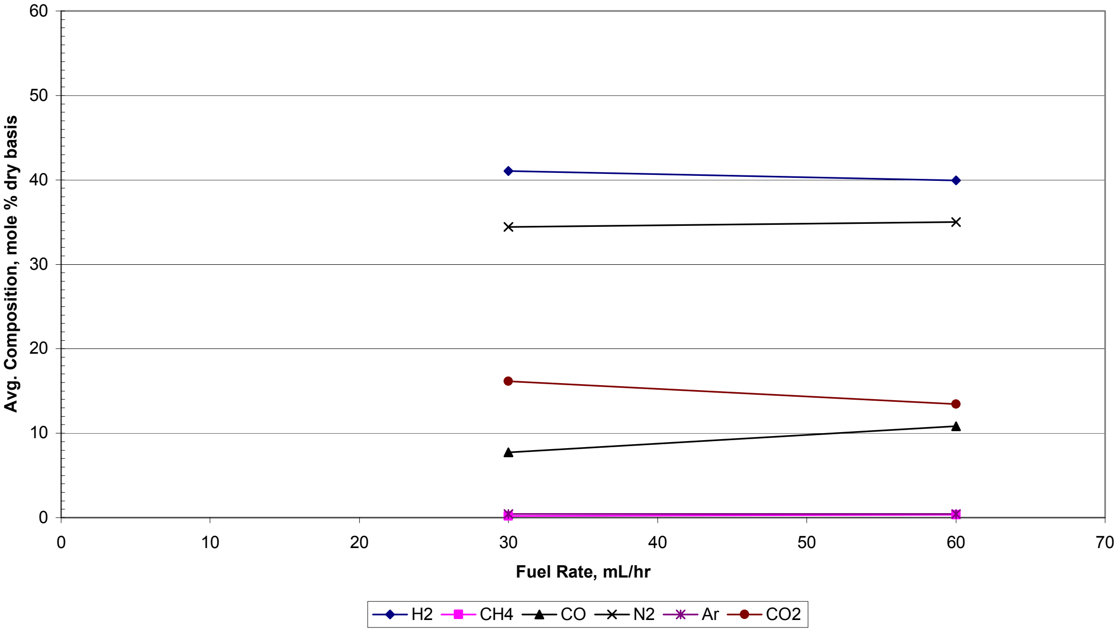


Figure 21.
Sunnyside Naphtha
Steam/Carbon=2
O_2/C=0.45

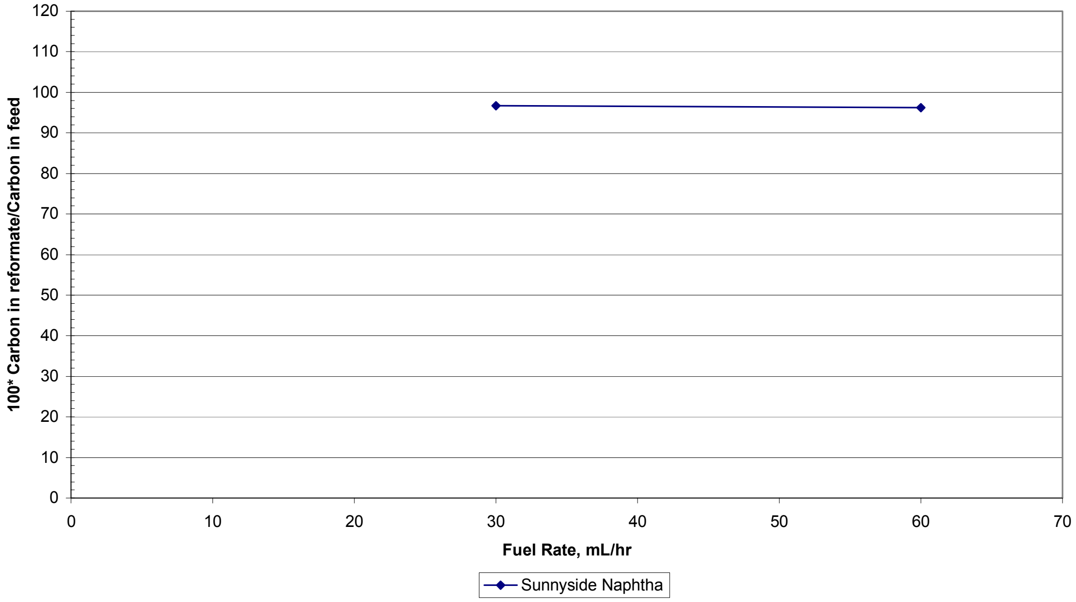


Figure 22.
Sunnyside Naphtha
Steam/Carbon=2
O_2/C=0.45

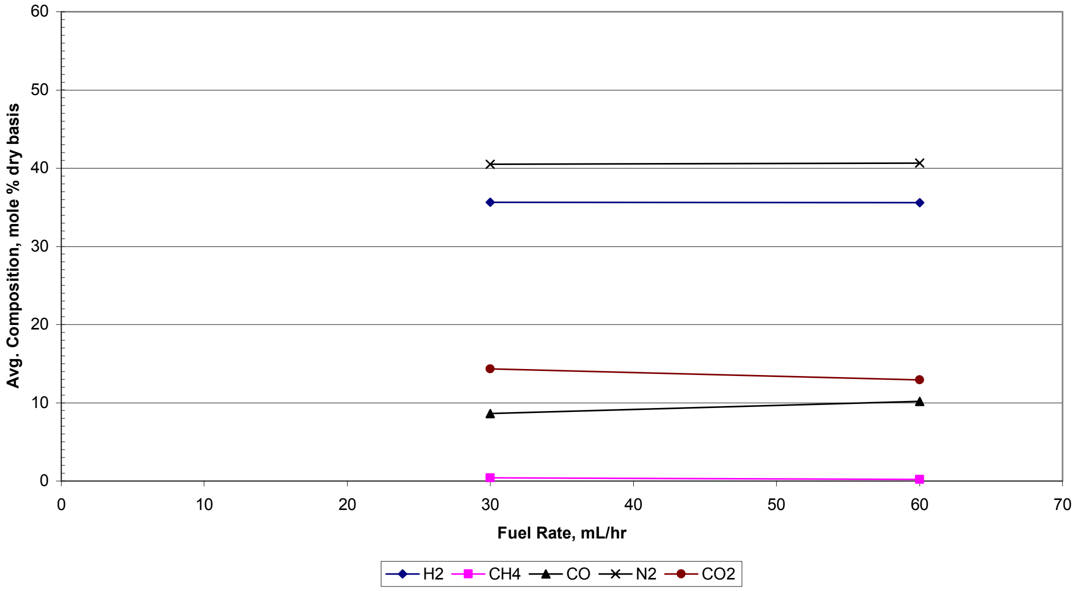


Figure 23.
Sunnyside Naphtha
Steam/Carbon=3
O_2/C=0.45

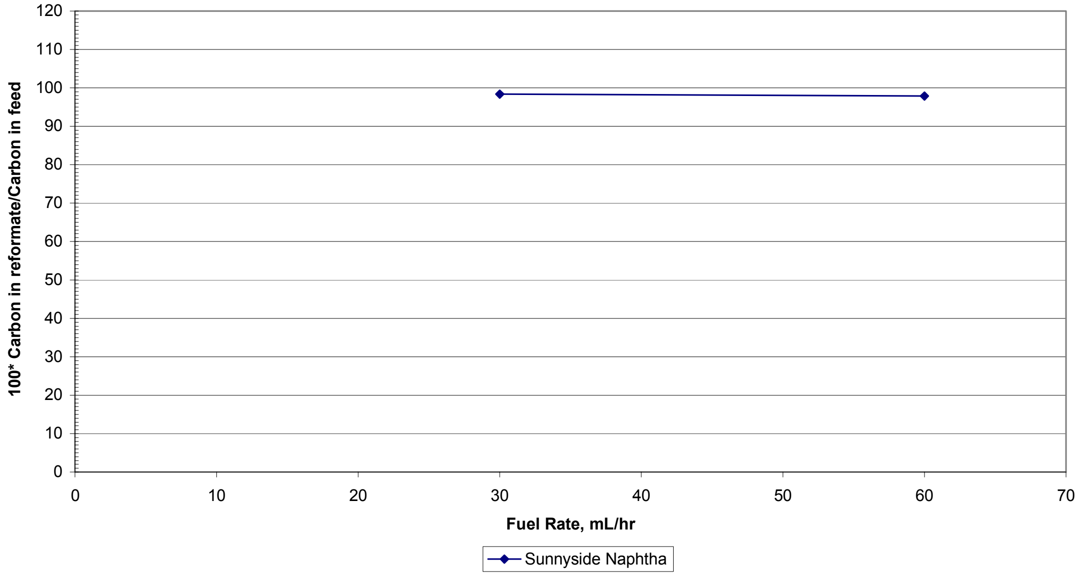


Figure 24.
Sunnyside Naphtha
Steam/Carbon=3
O_2/C=0.45

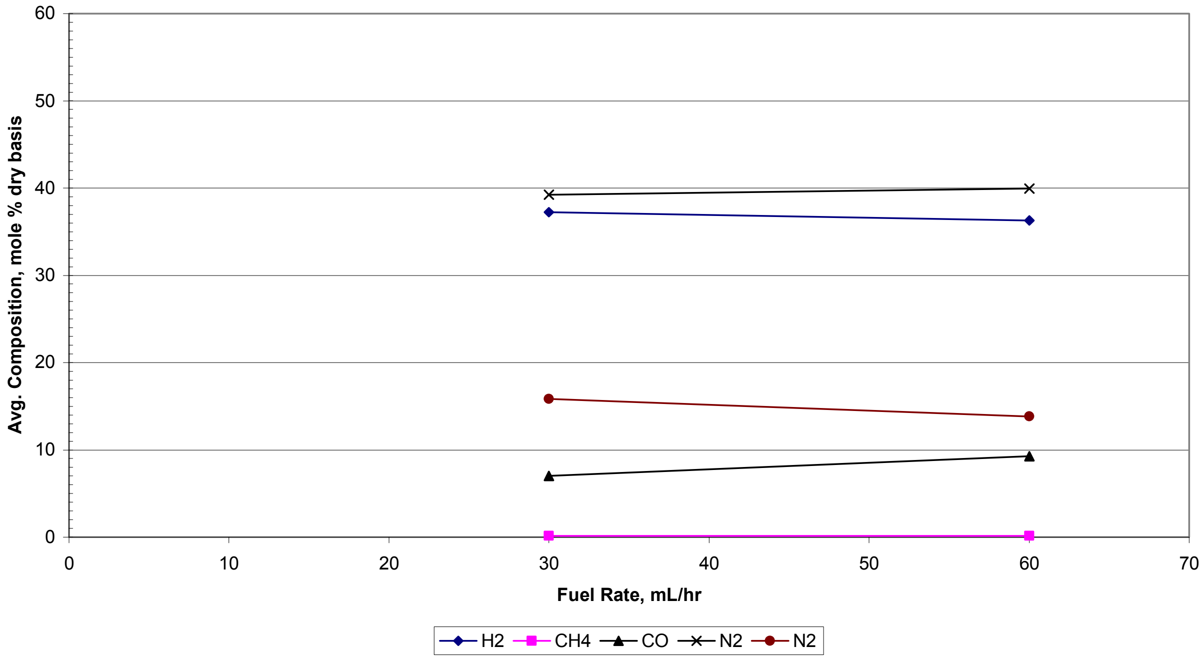


Figure 25.
Desulfurized Kerosene
Steam/Carbon=3
O_2/C=0.372

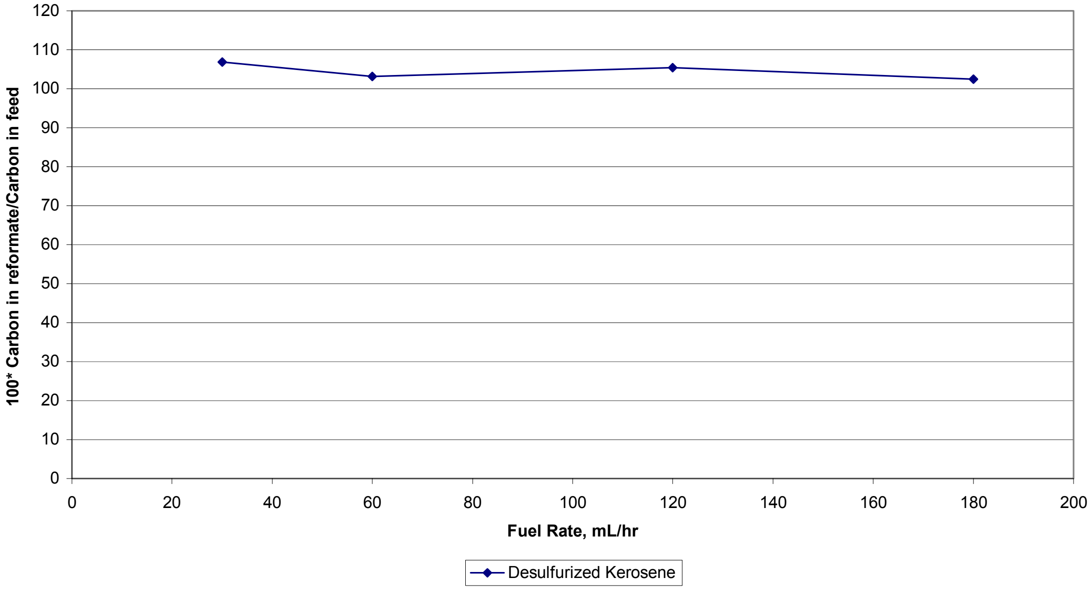
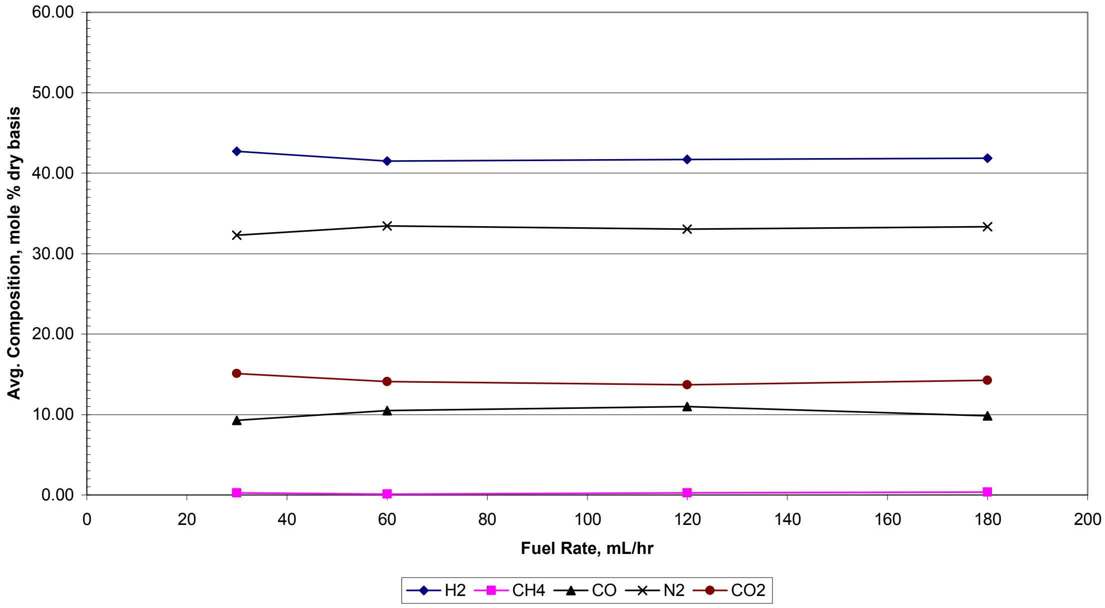


Figure 26.
Desulfurized Kerosene
Steam/Carbon=3
O_2/C=0.372



III. Conclusions

Hydrotreated F-T naphtha is a good reformer feed for hydrogen production. The low levels of sulfur, aromatics, and olefins reduces catalyst poisoning, carbon deposition, and gum formation. The olefin content of the hydrocracked F-T naphtha increases the likelihood of carbon deposition and reduces the desirability of this feed for hydrogen production.

V. List of Acronyms and Abbreviations

Ar - Argon

ATR – Autothermal reforming

CO – Carbon Monoxide

CO_2 – Carbon Dioxide

F-T – Fischer-Tropsch

g – gram

H – Hydrogen

H_2 - Hydrogen

IBP – Initial Boiling Point

KOH – Potassium Hydrdoxide

mg - milligram

N_2 – Nitrogen

Rh - Rhodium

TAN – Total Acid Number

TBP – True Boiling Point

VM&P – varnish maker's and painter's

VI. Appendix - Raw Data

	Hydro cracked Naphtha	H2O	Air	Inlet Temp	Outlet Temp	Sample Time			Varian Micro GC Data				
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/14/2003	30	80.2	58.9	411.6	609.3	13:16	35.03	0.77	4.08	42.52	0.54	17.07	O2/C=0.372; Steam/C=3.
4/14/2003	30	80.2	58.9	408.3	624.1	13:21	35.49	0.53	4.40	42.37	0.51	16.70	
4/14/2003	30	80.2	58.9	405.9	637.1	13:26	36.71	0.34	4.43	41.16	0.50	16.86	
4/14/2003	30	80.2	58.9	403.8	648.8	13:31	36.73	0.26	4.56	40.98	0.49	16.97	
Average							35.99	0.47	4.37	41.76	0.51	16.90	Average
4/14/2003	30	53.5	58.9	400.6	646.8	13:36	36.36	0.53	6.03	40.70	0.49	15.89	O2/C=0.372; Steam/C=2.
4/14/2003	30	53.5	58.9	401.5	647.9	13:41	34.55	0.36	5.69	43.11	0.52	15.77	
4/14/2003	30	53.5	58.9	401.6	651.5	13:46	35.58	0.43	5.96	42.00	0.51	15.54	
4/14/2003	30	53.5	58.9			13:56	35.06	0.42	6.01	42.42	0.51	15.59	
4/14/2003	30	53.5	58.9	406.4	657.1	14:01	36.25	0.64	6.91	40.62	0.49	15.09	
4/14/2003	30	53.5	58.9	407.5	657.6	14:06	35.90	0.53	6.86	41.10	0.50	15.12	
Average							35.62	0.49	6.24	41.66	0.50	15.50	Average
4/14/2003	30	53.5	71.3	408.6	656.0	14:11	32.14	0.34	5.90	46.01	0.56	15.05	O2/C=0.45; Steam/C=2.
4/14/2003	30	53.5	71.3			14:16	29.93	0.22	4.96	48.96	0.59	15.34	
4/14/2003	30	53.5	71.3	410.5	656.7	14:21	30.69	0.26	5.33	48.12	0.58	15.02	
4/14/2003	30	53.5	71.3	409.2	656.8	14:26	31.47	0.25	5.29	47.05	0.57	15.38	
4/14/2003	30	53.5	71.3	411.1	657.9	14:31	29.97	0.18	4.76	49.16	0.59	15.34	
4/14/2003	30	53.5	71.3			14:36	31.06	0.24	5.20	47.72	0.58	15.21	
4/14/2003	30	53.5	71.3	413.6	659.1	14:41	30.61	0.24	5.11	48.20	0.58	15.24	
Average							30.84	0.25	5.22	47.89	0.58	15.23	Average
4/14/2003	30	80.2	71.3	413.8	659.5	14:46	32.45	0.16	4.70	45.99	0.55	16.15	O2/C=0.45; Steam/C=3
4/14/2003	30	80.2	71.3	415.6	669.9	14:51	32.08	0.11	4.44	46.75	0.56	16.06	
4/14/2003	30	80.2	71.3	413.9	675.5	14:56	32.06	0.07	4.21	46.97	0.56	16.13	
4/14/2003	30	80.2	71.3	415.2	674.8	15:01	32.37	0.08	4.24	46.54	0.56	16.21	
4/14/2003	30	80.2	71.3	413.0	674.2	15:06	33.09	0.12	4.59	45.59	0.55	16.07	
4/14/2003	30	80.2	71.3	412.2	677.1	15:11	32.56	0.11	4.71	46.10	0.55	15.97	
4/14/2003	30	80.2	71.3	412.6	677.6	15:16	33.62	0.10	4.86	45.03	0.54	15.85	
Average							32.60	0.11	4.54	46.14	0.56	16.06	Average

	Hydro cracked Naphtha	H2O	Air	Inlet Temp	Outlet Temp	Sample Time	Varian Micro GC Data						
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/14/03	60	106.9	117.9	430.2	723.0	15:26	39.10	0.36	10.02	36.46	0.44	13.61	O2/C=0.372; Steam/C=2.
4/14/03	60	106.9	117.9	437.9	738.3	15:31	39.30	0.37	10.77	36.03	0.44	13.09	
4/14/03	60	106.9	117.9	443.7	746.4	15:36	39.23	0.28	10.72	36.45	0.45	12.87	
4/14/03	60	106.9	117.9	441.8	746.4	15:41	38.87	0.27	11.11	36.49	0.45	12.80	
4/14/03	60	106.9	117.9	438.5	752.0	15:46	39.51	0.23	11.28	36.10	0.44	12.43	
4/14/03	60	106.9	117.9	434.9	755.7	15:51	39.40	0.30	11.75	35.78	0.44	12.34	
4/14/03	60	106.9	117.9	434.4	756.7	15:56	39.51	0.26	11.67	35.87	0.44	12.26	
Average							39.27	0.30	11.04	36.17	0.44	12.77	Average
4/14/03	60	106.9	142.6	433.3	757.4	16:01	35.25	0.16	10.05	41.44	0.50	12.59	O2/C=0.45; Steam/C=2.
4/14/03	60	106.9	142.6	432.2	758.4	16:06	35.32	0.16	10.25	41.10	0.50	12.67	
4/14/03	60	106.9	142.6	432.8	756.8	16:11	35.12	0.18	10.19	41.38	0.51	12.62	
4/14/03	60	106.9	142.6	431.8	756.7	16:16	35.59	0.17	10.44	40.77	0.50	12.54	
4/14/03	60	106.9	142.6	433.0	756.4	16:21	35.48	0.16	10.43	40.92	0.50	12.51	
4/14/03	60	106.9	142.6	433.0	757.4	16:26	35.94	0.16	10.38	40.56	0.50	12.46	
4/14/03	60	106.9	142.6	430.8	758.4	16:31	35.77	0.16	10.39	40.65	0.50	12.53	
Average							35.50	0.16	10.30	40.97	0.50	12.56	Average
4/15/03	60	160.4	117.9		756.0	8:01	40.10	0.10	8.32	36.21	0.44	14.82	O2/C=0.372; Steam/C=3.
4/15/03	60	160.4	117.9		764.5	8:06	40.65	0.08	8.83	35.03	0.43	14.98	
4/15/03	60	160.4	117.9		761.8	8:11	39.05	0.06	8.05	37.52	0.45	14.86	
4/15/03	60	160.4	117.9		765.6	8:16	40.11	0.06	8.51	36.19	0.44	14.68	
4/15/03	60	160.4	117.9		770.1	8:21	39.90	0.04	8.43	36.51	0.44	14.68	
4/15/03	60	160.4	117.9		774.2	8:26	40.08	0.04	8.45	36.33	0.45	14.66	
4/15/03	60	160.4	117.9		776.4	8:31	40.28	0.04	8.60	36.02	0.44	14.63	
Average							40.02	0.06	8.45	36.26	0.44	14.76	Average
4/15/03	60	160.4	142.6		778.5	8:36	36.24	0.03	7.59	40.83	0.49	14.81	O2/C=0.45; Steam/C=3.
4/15/03	60	160.4	142.6		777.4	8:41	36.54	0.03	7.49	40.69	0.50	14.75	
4/15/03	60	160.4	142.6		776.6	8:46	36.83		7.67	40.36	0.49	14.65	
4/15/03	60	160.4	142.6		775.1	8:51	35.71	0.01	7.18	41.77	0.51	14.82	
4/15/03	60	160.4	142.6		774.4	8:56	34.96		6.75	42.76	0.52	15.01	
4/15/03	60	160.4	142.6		774.6	9:01	37.24	0.03	7.97	39.75	0.48	14.53	
4/15/03	60	160.4	142.6		777.3	9:06	36.99		7.92	39.99	0.49	14.62	
Average							36.36	0.02	7.51	40.88	0.50	14.74	Average

Date	Hydro treated Naphtha mL/hour	H2O mL/hr	Air L/hr	Inlet Temp deg C	Outlet Temp deg C	Sample Time	Varian Micro GC Data H2	CH4	CO	N2	Ar	CO2	Comments
4/15/03	30	60.3	54.7		689.0	9:41	30.43	0.37	7.16	47.87	0.59	13.59	O2/C=0.372; Steam/C=2.
4/15/03	30	60.3	54.7			9:46	25.10	0.08	3.67	54.91	0.66	15.59	
4/15/03	30	60.3	54.7		667.1	9:51	33.68	0.44	6.36	44.17	0.52	14.84	
4/15/03	30	60.3	54.7		655.2	10:01	21.67	0.27	3.47	58.99	0.75	14.85	
4/15/03	30	60.3	54.7			10:06	33.63	0.70	7.39	42.73	1.18	14.37	
4/15/03	30	60.3	54.7			10:11	27.44	0.39	5.50	51.19	0.65	14.82	
Average							28.66	0.37	5.59	49.98	0.73	14.68	Average
4/15/03	30	54.7	72.9			10:21	37.28	0.77	9.57	38.40	0.47	13.51	O2/C=0.45; Steam/C=2.
4/15/03	30	54.7	72.9		681.8	10:26	37.19	0.60	9.22	38.70	0.47	13.80	
4/15/03	30	54.7	72.9		684.8	10:31	36.54	0.66	10.02	38.99	0.48	13.32	
4/15/03	30	54.7	72.9		686.1	10:36	37.44	0.67	9.90	38.09	0.46	13.44	
4/15/03	30	54.7	72.9		689.0	10:41	37.18	0.52	9.86	38.44	0.47	13.53	
4/15/03	30	54.7	72.9		689.6	10:46	37.47	0.60	10.37	38.01	0.47	13.09	
Average							37.18	0.64	9.82	38.44	0.47	13.45	Average
4/15/03	30	82.0	60.3		696.6	10:51	42.69	0.43	9.23	32.62	0.40	14.63	O2/C=0.372; Steam/C=3.
4/15/03	30	82.0	60.3		498.1	10:56	43.24	0.39	9.36	31.56	0.38	15.07	
4/15/03	30	82.0	60.3		499.8	11:01	43.01	0.30	8.99	32.31	0.40	15.00	
4/15/03	30	82.0	60.3		704.0	11:06	43.01	0.39	9.61	31.84	0.39	14.77	
4/15/03	30	82.0	60.3		705.3	11:11	42.87	0.30	9.23	32.33	0.39	14.88	
4/15/03	30	82.0	60.3		707.4	11:16	42.97	0.30	9.27	32.09	0.39	14.97	
Average							42.96	0.35	9.28	32.13	0.39	14.89	Average
4/15/03	30	82	72.9		707.7	11:21	39.46	0.24	8.46	36.72	0.45	14.66	O2/C=0.45; Steam/C=3.
4/15/03	30	82	72.9			11:26	39.25	0.23	8.46	36.82	0.45	14.80	
4/15/03	30	82	72.9		705.9	11:31	39.31	0.24	8.32	36.93	0.45	14.75	
4/15/03	30	82	72.9		705.2	11:36	39.49	0.25	8.46	36.67	0.45	14.68	
4/15/03	30	82	72.9		706.3	11:41	39.66	0.24	8.38	36.55	0.45	14.72	
Average							39.43	0.24	8.42	36.74	0.45	14.72	Average

	Hydro treated Naphtha	H2O	Air	Inlet Temp	Outlet Temp	Sample Time	Varian Micro GC Data						
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/15/03	60	109.4	120.5		766.4	11:56	40.89	0.40	13.50	33.23	0.42	11.55	O2/C=0.372; Steam/C=2.
4/15/03	60	109.4	120.5			12:11	40.75	0.83	13.49	33.56	0.40	10.98	
4/15/03	60	109.4	120.5			12:16	40.74	0.79	13.55	33.60	0.39	10.92	
4/15/03	60	109.4	120.5			12:21	41.14	0.55	13.12	33.43	0.40	11.36	
4/15/03	60	109.4	120.5		769.7	12:26	40.94	0.74	13.32	33.49	0.40	11.12	
4/15/03	60	109.4	120.5			12:31	40.63	0.82	13.47	33.72	0.40	10.96	
Average							40.85	0.69	13.41	33.50	0.40	11.15	Average
4/15/03	60	109.4	145.8		771.3	12:41	37.69	0.27	12.10	37.56	0.47	11.91	O2/C=0.45; Steam/C=2.
4/15/03	60	109.4	145.8		767.0	12:46	37.55	0.21	11.80	38.16	0.48	11.80	
4/15/03	60	109.4	145.8		766.6	12:51	37.26	0.26	12.12	38.06	0.47	11.83	
4/15/03	60	109.4	145.8		764.2	12:56	37.36	0.26	12.05	37.93	0.47	11.93	
4/15/03	60	109.4	145.8		756.6	13:01	37.36	0.23	11.86	38.11	0.47	11.97	
Average							37.44	0.25	11.99	37.96	0.47	11.89	Average
4/15/03	60	164	145.8		770.3	13:06	38.83	0.16	10.20	37.31	0.46	13.04	O2/C=0.45; Steam/C=3.
4/15/03	60	164	145.8		775.8	13:16	39.06	0.09	9.74	36.87	0.46	13.78	
4/15/03	60	164	145.8		777.7	13:21	38.58	0.09	9.60	37.52	0.46	13.76	
4/15/03	60	164	145.8		778.7	13:26	38.53	0.07	9.50	37.60	0.46	13.84	
Average							38.75	0.10	9.76	37.32	0.46	13.60	Average
4/15/03	60	164	120.5		778.1	13:31	42.38	0.10	10.60	32.70	0.41	13.80	O2/C=0.372; Steam/C=3.
4/15/03	60	164	120.5		782.2	13:36	42.42	0.13	11.04	32.56	0.41	13.44	
4/15/03	60	164	120.5		783.2	13:41	42.60	0.13	11.08	32.35	0.40	13.45	
4/15/03	60	164	120.5		784.4	13:46	42.68	0.15	11.12	32.11	0.40	13.53	
4/15/03	60	164	120.5		783.4	13:51	42.15	0.14	11.16	32.70	0.41	13.44	
Average							42.45	0.13	11.00	32.48	0.41	13.53	Average

	Sunnyside Naphtha	H2O	Air	Inlet Temp	Outlet Temp	Sample Time	Varian Micro GC Data						
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/16/03	30	56.8	62.6		674.7	10:46	39.10	0.54	10.77	35.40	0.45	13.74	O2/C=0.372; Steam/C=2.
4/16/03	30	56.8	62.6		675.0	10:51	39.16	0.61	10.44	35.20	0.45	14.15	
4/16/03	30	56.8	62.6		675.9	10:56	39.79	0.55	10.37	34.67	0.44	14.18	
4/16/03	30	56.8	62.6		677.6	11:01	40.17	0.76	10.99	33.90	0.42	13.75	
4/16/03	30	56.8	62.6		678.6	11:06	39.83	0.65	10.61	34.48	0.43	14.00	
Average							39.61	0.62	10.64	34.73	0.44	13.96	Average
4/16/03	30	56.8	75.7		678.1	11:11	35.57	0.36	8.43	40.51	0.50	14.63	O2/C=0.45; Steam/C=2.
4/16/03	30	56.8	75.7		677.9	11:16	36.10	0.38	8.78	39.93	0.49	14.32	
4/16/03	30	56.8	75.7		680.6	11:21	35.83	0.41	8.67	40.43	0.50	14.16	
4/16/03	30	56.8	75.7			11:26	35.42	0.37	8.86	40.46	0.50	14.39	
4/16/03	30	56.8	75.7		680.7	11:31	35.23	0.36	8.44	41.27	0.51	14.20	
Average							35.63	0.38	8.64	40.52	0.50	14.34	Average
4/16/03	30	85.2	62.6			11:41	41.02	0.21	7.52	34.59	0.43	16.24	O2/C=0.372; Steam/C=3.
4/16/03	30	85.2	62.6		690.0	11:46	41.00	0.21	7.66	34.41	0.42	16.30	
4/16/03	30	85.2	62.6		691.1	11:51	41.24	0.22	8.05	34.15	0.42	15.93	
4/16/03	30	85.2	62.6			11:56	41.14	0.22	7.96	34.20	0.42	16.06	
4/16/03	30	85.2	62.6			12:01	41.05	0.19	7.53	34.53	0.43	16.27	
4/16/03	30	85.2	62.6			12:06	40.85	0.19	7.62	34.67	0.43	16.24	
4/16/03	30	85.2	62.6			12:11	40.88	0.19	7.76	34.68	0.43	16.06	
4/16/03	30	85.2	62.6			12:16	41.35	0.18	7.87	34.12	0.42	16.06	
4/16/03	30	85.2	62.6		698.1	12:21	40.91	0.21	7.74	34.60	0.43	16.11	
Average							41.05	0.20	7.75	34.44	0.42	16.14	Average
4/16/03	30	85.2	75.7		699.0	12:26	36.99	0.10	6.70	39.74	0.49	15.98	O2/C=0.45; Steam/C=3.
4/16/03	30	85.2	75.7		701.3	12:31	37.12	0.14	6.81	39.45	0.48	15.98	
4/16/03	30	85.2	75.7			12:36	36.89	0.21	7.62	39.17	0.48	15.63	
4/16/03	30	85.2	75.7		699.5	12:41	37.39	0.13	6.97	39.19	0.48	15.85	
4/16/03	30	85.2	75.7			12:46	37.80	0.14	7.02	38.69	0.47	15.89	
4/16/03	30	85.2	75.7		699.3	12:56	37.35	0.15	7.06	39.22	0.48	15.75	
Average							37.26	0.15	7.03	39.24	0.48	15.85	Average

	Sunnyside Naphtha	H2O	Air	Inlet Temp	Outlet Temp	Sample Time	Varian Micro GC Data						
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/16/03	60	113.6	125.2		742.6	13:06	39.41	0.39	11.15	35.64	0.43	12.98	O2/C=0.372; Steam/C=2.
4/16/03	60	113.6	125.2		750.6	13:11	39.63	0.32	11.43	35.33	0.43	12.86	
4/16/03	60	113.6	125.2		755.4	13:16	39.70	0.26	11.34	35.26	0.42	13.02	
4/16/03	60	113.6	125.2		758.7	13:21	39.89	0.25	11.67	35.05	0.42	12.72	
4/16/03	60	113.6	125.2		760.6	13:26	39.89	0.31	11.81	35.03	0.42	12.54	
4/16/03	60	113.6	125.2		761.0	13:31	39.39	0.27	11.60	35.85	0.43	12.45	
4/16/03	60	113.6	125.2		761.7	13:36	40.06	0.29	12.03	34.80	0.42	12.40	
4/16/03	60	113.6	125.2			13:41	39.58	0.25	11.51	35.57	0.43	12.66	
Average							39.69	0.29	11.57	35.32	0.42	12.71	Average
4/16/03	60	113.6	151.5		762.0	13:46	35.69	0.17	10.27	40.48	0.49	12.91	O2/C=0.45; Steam/C=2.
4/16/03	60	113.6	151.5		759.3	13:51	35.47	0.19	10.24	40.73	0.49	12.88	
4/16/03	60	113.6	151.5		759.1	13:56	35.63	0.18	10.00	40.52	0.49	13.19	
4/16/03	60	113.6	151.5		758.8	14:01	35.47	0.21	10.21	40.83	0.49	12.80	
4/16/03	60	113.6	151.5		757.4	14:06	35.72	0.19	10.08	40.60	0.49	12.92	
Average							35.60	0.19	10.16	40.63	0.49	12.94	Average
4/16/03	60	170.4	151.5		766.1	14:21	36.60	0.07	8.49	39.85	0.49	14.49	O2/C=0.45; Steam/C=3.
4/16/03	60	170.4	151.5		764.1	14:26	36.58	0.16	9.36	39.60	0.48	13.82	
4/16/03	60	170.4	151.5		773.0	14:31	36.08	0.15	9.15	40.40	0.49	13.73	
4/16/03	60	170.4	151.5			14:36	36.55	0.17	9.27	39.77	0.49	13.76	
4/16/03	60	170.4	151.5			14:41	36.21	0.20	9.57	39.89	0.49	13.64	
4/16/03	60	170.4	151.5		770.0	14:46	35.97	0.26	9.76	39.90	0.49	13.61	
4/16/03	60	170.4	151.5		769.7	14:51	36.10	0.20	9.31	40.12	0.49	13.78	
Average							36.30	0.17	9.27	39.93	0.49	13.83	Average
4/16/03	60	170.4	125.2		767.3	14:56	40.13	0.30	10.97	34.70	0.43	13.47	O2/C=0.372; Steam/C=3.
4/16/03	60	170.4	125.2		768.4	15:01	39.97	0.32	10.72	34.94	0.43	13.61	
4/16/03	60	170.4	125.2		769.2	15:06	40.04	0.44	10.91	34.88	0.43	13.31	
4/16/03	60	170.4	125.2		768.6	15:11	39.79	0.38	10.89	35.36	0.44	13.14	
4/16/03	60	170.4	125.2		770.3	15:16	40.15	0.37	10.98	34.76	0.43	13.31	
4/16/03	60	170.4	125.2		770.4	15:21	39.84	0.33	10.82	35.08	0.43	13.51	
4/16/03	60	170.4	125.2		768.1	15:26	39.70	0.29	10.54	35.31	0.43	13.74	
Average							39.95	0.35	10.83	35.00	0.43	13.44	Average

Date	Kerosene mL/hour	H2O mL/hr	Air L/hr	Inlet Temp deg C	Outlet Temp deg C	Sample Time	Varian Micro GC Data						Comments
							H2	CH4	CO	N2	Ar	CO2	
4/9/03	30	86.7	63.7	410.9	717.6	13:46	42.05	0.29	8.84	33.02	0.40	15.39	O2/C=0.372; Steam/C=3.
4/9/03	30	86.7	63.7	410.6	725.1	13:51	44.14	0.39	10.05	29.95	0.38	15.09	
4/9/03	30	86.7	63.7	410.8	720.4	13:56	43.24	0.23	9.59	31.71	0.40	14.83	
4/9/03	30	86.7	63.7	409.5	719.0	14:01	42.26	0.27	9.35	32.79	0.42	14.90	
4/9/03	30	86.7	63.7	409.9	719.9	14:06	42.87	0.17	8.76	32.30	0.41	15.48	
4/9/03	30	86.7	63.7	407.5	719.7	14:11	42.33	0.23	9.18	32.73	0.41	15.12	
4/9/03	30	86.7	63.7			14:16	42.22	0.19	8.92	33.25	0.42	15.00	
4/9/03	30	86.7	63.7	411.0	721.8	14:21	43.37	0.18	9.14	31.69	0.40	15.20	
4/9/03	30	86.7	63.7	405.0	720.8	14:26	43.17	0.19	9.53	31.80	0.40	14.91	
4/9/03	30	86.7	63.7	409.8	722.5	14:31	42.24	0.20	9.22	32.86	0.41	15.06	
4/9/03	30	86.7	63.7	409.3	725.2	14:36	42.48	0.26	9.56	32.42	0.41	14.86	
4/9/03	30	86.7	63.7	403.9	722.8	14:41	42.75	0.25	9.59	31.69	0.39	15.34	
4/9/03	30	86.7	63.7	410.3	720.1	14:46	41.88	0.21	9.39	33.46	0.43	14.63	
4/9/03	30	86.7	63.7	408.3	725.7	14:51	42.62	0.22	9.22	32.44	0.41	15.10	
4/9/03	30	86.7	63.7	410.7	720.9	14:56	43.01	0.22	9.40	31.73	0.41	15.24	
4/9/03	30	86.7	63.7	409.9	722.5	15:01	43.04	0.22	9.58	31.60	0.40	15.16	
4/9/03	30	86.7	63.7	409.9	721.1	15:06	42.21	0.20	9.28	32.76	0.41	15.13	
4/9/03	30	86.7	63.7	410.1	722.0	15:11	42.69	0.19	9.07	32.35	0.41	15.30	
4/9/03	30	86.7	63.7	412.2	722.7	15:16	42.40	0.18	8.86	32.89	0.41	15.26	
4/9/03	30	86.7	63.7	405.4	719.7	15:21							
Average							42.68	0.23	9.29	32.29	0.41	15.11	Average
4/10/03	60	173.4	127.4	449.4	787.8	8:26	41.57	0.14	9.74	33.41	0.48	14.67	O2/C=0.372; Steam/C=3.
4/10/03	60	173.4	127.4	447.3	797.6	8:31	41.55	0.12	10.53	32.93	0.47	14.38	
4/10/03	60	173.4	127.4	445.1	800.4	8:36	41.33	0.11	10.70	33.55	0.50	13.83	
4/10/03	60	173.4	127.4	444.1	805.7	8:41	41.52	0.08	10.54	33.48	0.46	13.92	
4/10/03	60	173.4	127.4	443.6	805.6	8:46	41.41	0.06	10.61	33.54	0.44	13.95	
4/10/03	60	173.4	127.4	441.9	808.2	8:51	41.48	0.08	10.86	33.32	0.43	13.82	
4/10/03	60	173.4	127.4	439.4	808.0	8:56	41.49	0.05	10.28	33.72	0.46	14.01	
Average				444.4	801.9		41.48	0.09	10.47	33.42	0.46	14.08	Average

	Kerosene	H2O	Air	Inlet Temp	Outlet Temp	Sample Time	Varian Micro GC Data						
Date	mL/hour	mL/hr	L/hr	deg C	deg C		H2	CH4	CO	N2	Ar	CO2	Comments
4/10/03	120	346.8	254.8	647.7	775.2	13:36	41.55	0.29	11.28	32.91	0.42	13.56	O2/C=0.372; Steam/C=3.
4/10/03	120	346.8	254.8	652.1	778.0	13:41	41.56	0.25	10.99	33.11	0.43	13.67	
4/10/03	120	346.8	254.8	652.6	778.6	13:46	41.57	0.21	11.05	33.12	0.42	13.64	
4/10/03	120	346.8	254.8	649.7	777.1	13:51	41.66	0.23	11.05	33.02	0.42	13.61	
4/10/03	120	346.8	254.8	646.7	778.4	13:56	41.47	0.20	10.88	33.50	0.42	13.53	
4/10/03	120	346.8	254.8	637.7	779.4	14:01	41.79	0.23	10.84	33.06	0.41	13.67	
4/10/03	120	346.8	254.8	635.8	779.1	14:06	41.88	0.32	11.18	32.68	0.40	13.54	
4/10/03	120	346.8	254.8			14:11	41.31	0.38	11.35	33.00	0.41	13.55	
4/10/03	120	346.8	254.8	629.7	780.8	14:16	41.89	0.21	10.99	32.67	0.40	13.83	
4/10/03	120	346.8	254.8	630.7	781.0	14:21	42.05	0.17	10.65	32.94	0.42	13.77	
4/10/03	120	346.8	254.8	631.8	781.5	14:26	41.96	0.18	10.57	33.02	0.41	13.85	
4/10/03	120	346.8	254.8	634.3	782.4	14:31	41.86	0.18	10.59	33.10	0.41	13.87	
Average				640.8	779.2		41.71	0.24	10.95	33.01	0.41	13.67	Average
4/11/03	180	520.2	382.2	630.0	762.0	8:26	41.91	0.36	9.97	33.13	0.40	14.22	O2/C=0.372; Steam/C=3.
4/12/03	180	520.2	382.2	632.6	761.4	8:31	41.87	0.33	9.89	33.30	0.41	14.21	
4/13/03	180	520.2	382.2	635.7	761.1	8:36	41.89	0.39	9.93	33.20	0.40	14.19	
4/14/03	180	520.2	382.2	639.5	760.8	8:41	41.89	0.37	9.86	33.31	0.41	14.17	
4/15/03	180	520.2	382.2	640.0	761.1	8:46	41.92	0.31	9.70	33.40	0.41	14.26	
4/16/03	180	520.2	382.2			8:51	41.65	0.45	10.08	33.22	0.41	14.20	
4/17/03	180	520.2	382.2	645.0	759.8	8:56	41.73	0.42	9.90	33.39	0.41	14.15	
4/18/03	180	520.2	382.2	653.0	772.8	9:01	41.91	0.28	9.66	33.44	0.40	14.31	
4/19/03	180	520.2	382.2	654.8	762.6	9:06	41.72	0.27	9.42	33.80	0.41	14.39	
Average Values.				641.3	762.7		41.83	0.35	9.82	33.35	0.41	14.23	Average

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Appendix J - Test Report

Subtask 2.5.7.6: FISCHER-TROPSCH DIESEL HYDROTREATING

Reporting Period:	December 2003 - May 2003
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Date Issued:	June 21, 2003

Background

In the EECP concept, one of the product upgrading options is hydrotreating of the Fischer-Tropsch (F-T) diesel range material to produce high quality (low sulfur and high cetane) diesel. Hydrotreating is perhaps the most widely practiced refining process in the world today. It is used to upgrade petroleum distillates and residuum to refinery intermediate streams and also to finished products. ChevronTexaco has extensive experience operating hydrotreaters in its own refineries. ChevronTexaco also licenses its state-of-the-art, proprietary ISOTREATING technology and ISOTREATING® catalysts to the refining industry worldwide.

ISOTREATING® catalysts are single-function catalysts, containing only a hydrogenation function. The hydrogenation sites remove impurities from and saturate any double bonds in the feed molecules to produce clean, hydrogen-rich products.

As part of the RD&T Plan from Phase II of the EECP, F-T products from the La Porte demonstration run were fractionated to produce a diesel range material. The hydrotreated diesel range material was analyzed and engine tested to confirm its properties and performance as a high quality diesel fuel. A commercially-proven ISOTREATING® catalyst was selected to hydrotreat the raw F-T diesel to finished products meeting industry specifications.

Experimental

Process Description

ChevronTexaco Technology Marketing (TEMA) performed Pilot Plant Run 34-91 for the Fischer-Tropsch diesel hydrotreating test. Figure 2.5.7.6-1 is the schematic diagram of the pilot plant used for the hydrotreating test.

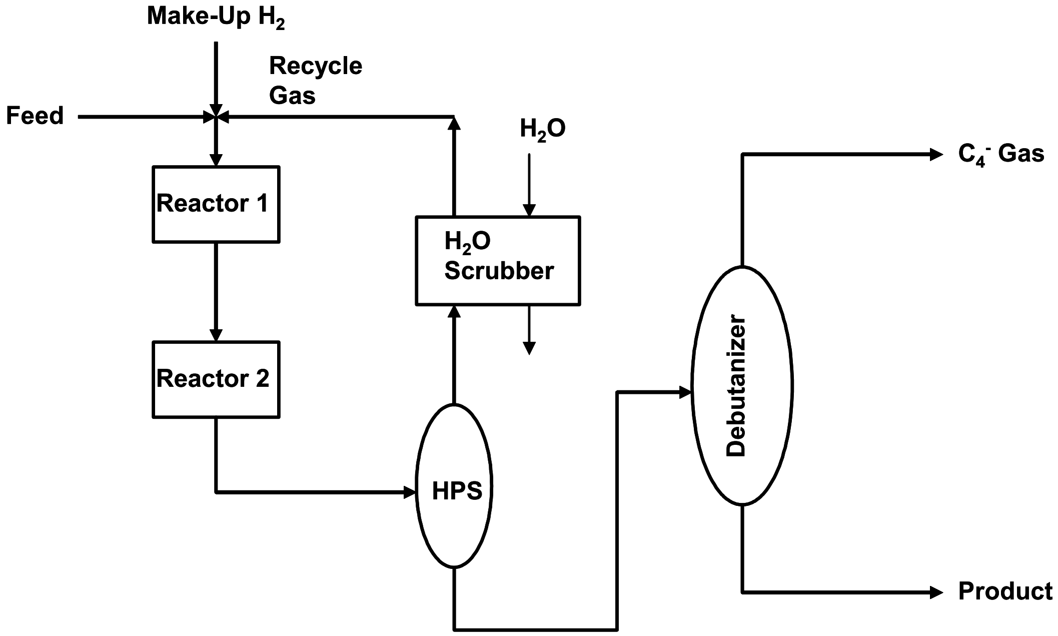

Figure 2.5.7.6-1 Diesel Hydrotreating Pilot Plant Block Flow Diagram

The diesel feed, combined with the Make-Up Hydrogen and Recycle Gas, is fed to the hydrotreating reactors. The two hydrotreating reactors were in series. The reactor effluent is separated into liquid and vapor in the High Pressure Separator (HPS). The liquid is fractionated in a debutanizer where the hydrotreated products are collect on the bottom and the C4's and lighter goes overhead. The separated vapor from the High Pressure Separator (HPS), composed mainly of the hydrogen, is scrubbed with water to remove trace ammonia (NH_3) that formed from nitrogen in the feed. The vapor is then recycled back to the reactors.

Feedstock

The Fischer-Tropsch (F-T) demonstration at the Alternative Fuels Demonstration Unit (AFDU) in La Porte, TX produced a mixture of light F-T hydrocarbons and water. The mix was separated by a contract laboratory and the light F-T hydrocarbons were sent to ChevronTexaco Integrated Laboratory Technologies (ILT). The light F-T hydrocarbons were then fractionated into soft wax, neat diesel and neat naphtha cuts. The neat diesel, with a boiling range of 466 K (380°F) to 644 K (700°F), was used as the feed for the diesel hydrotreating test. A total of 0.053 cubic meter (14 gallons) of the raw diesel was used for this hydrotreating test. Table 2.5.7.6-1 gives the properties of the diesel feed.

Table 2.5.7.6-1

Diesel Feed Properties for Hydrotreating Pilot Plant

Sample ID		WOW9289	
Specific Gravity		0.81	
Gravity, °API		43.5	
Sulfur	wt PPM	3.0	
Nitrogen	wt PPM	7.4	
Oxygen by NAA	wt %	2.9	
AED Analyses			
Oxygen	wt %	not available	
Alcohol	wt %	not available	
Olefins	wt %	not available	
TAN	mg KOH/g	3.69	
		Temperature, K	°F
Simulated Distillation, LV%	IBP	395	251
	0.5%	430	314
	5%	466	380
	10%	485	414
	30%	524	484
	50%	564	556
	70%	600	621
	90%	630	674
	95%	639	690
	99%	651	712
	EP	655	720
D86 Distillation, LV%	IBP	437	328
	5%	475	396
	10%	491	425
	30%	530	495
	50%	568	563
	70%	604	627
	90%	632	679
	95%	643	698
	EP	650	710

Diesel Product Quality Target

The original diesel hydrotreating target was for the hydrotreated diesel to meet a less than 10 ppm oxygen content. However, after many inquiries and laboratory tests by Southwest Research Institute (SWRI) and ChevronTexaco, no reliable method to measure this low level of oxygen was found. Instead, an alternate test was selected as the criterion for the hydrotreated diesel. The Total Acid Number (TAN) of less than 0.05 milligram of potassium hydroxide (KOH) per gram of sample was selected as the target for the hydrotreated diesel product. The starting TAN for the diesel feed was 3.7 mg KOH per gram.

Results and Discussion

Operations

The hydrotreated diesel product contained around 15 volume percent of material with boiling range of 466 K (380ºF) or lower. This light material was probably generated from alcohol saturation and not from hydrocracking. A yield was calculated showing about 85 volume percent diesel yield.

Table 2.5.7.6-2

Yields for Hydrotreating Diesel

Feed		**WOW9289**	
Run Number		34-91	
Run Hours		534-558	
Normalized Prod.Yields		WT. %	VOL. %
Total C4-		0.3	
Total C5+		97.6	101.4
C5-466 K (380°F)		14.5	16.7
466-644 K (380-700°F)		83.1	84.7
H2 Consumption		sm^3/m^3	SCF/B
		111.7	627
Material Balance Closure		101 wt%	
Product Properties			
Specific Gravity		0.78	
Gravity, °API		50.5	
TAN, mg KOH/g		0.05	
		Temperature K	°F
Simdist (D2887) Volume %	St	294	70
	5	370	206
	10	436	325
	30	499	439
	50	544	519
	70	587	598
	90	627	670
	95	637	688
	99.5	651	713

Hydrotreated Diesel Product Properties

Table 2.5.7.6-2 presents the yields and product qualities. The material met the product specification target of a Total Acid Number (TAN) of the less than 0.05 mg KOH per gram of material. The feed material had a TAN of 3.7 mg KOH/g.

Diesel Product Distillation

The diesel products were blended and 0.0511 m^3 (13.5 gallons) were recovered. This blend was labeled as WOW9302. Because the hydrotreated diesel products contained naphtha boiling range material, it was decided to fractionate the product into naphtha range material and diesel boiling range material (466-644 K, 380-700ºF). This was done in three batches, FSL9803, FSL9804 and FSL9805. The naphtha cuts from each batch were then combined together and labeled as PGQ1153, and the diesel cuts from each batch were combined and labeled as PGQ1142. The following Table 2.5.7.6-3 presents what was done with the product blend and distillation.

Table 2.5.7.6-3 Diesel Hydrotreating Product Blend & Distillation

	Hydrotreated Diesel Products	Distilled Hydrotreated Diesel Blends (3 Batches)	Blended Naphtha from Distillation	Blended Diesel from Distillation
Boiling Range	~308-644 K (~95-700°F)	St-466K & 466-644K (St-380 & 380-700°F)	St-466 K (St-380°F)	466-644 K (380-700°F)
ID	WOW9302	FSL9803 FSL9804 FSL9805	PGQ1153	PGQ1142
Further Work				Blended with HCR'd Diesel

The product properties of the Hydrotreated Diesel Products (WOW9302), the Distilled Hydrotreated Diesel Product Blends (FSL9803, FSL9804 & FSL9805) and the Blended Diesel (PGQ1142) are given in Table 2.5.7.6-4.

0.0833 cubic meter (22 gallons) of hydrotreated F-T diesel was needed to perform the Hot Start Cycle Transient Engine Test (Task 2.6.2) and Solvent Extraction (Task 2.6.3). Since there was only 0.0397 m^3 (10.5 gallons) of the hydrotreated diesel in the boiling range of 466-644 K (380-700ºF), a blend was made with 0.0473 m^3 (12.5 gallons) of F-T diesel material from the Hydrocracking Pilot Plant work (Task 2.5.3) for Hot Start Engine Testing (Task 2.6.2) and for Solvent Extraction (Task 2.6.3). The blended material was labeled WOW9306. Its properties are presented in Table 2.5.7.6-4 below. The diesel blend (WOW9306) also met the product specification target of a TAN less than 0.05 mg KOH/g.

Table 2.5.7.6-4 Diesel Hydrotreating Product Properties

Sample ID		WOW9302	FSL 9803 Cut 1	FSL 9803 Cut 2	FSL 9804 Cut 1	FSL 9804 Cut 2	FSL 9805 Cut 1	FSL 9805 Cut 2	PGQ 1153	PGQ1142	WOW 9306
Description		Hydrotreated Diesel Products	Distilled Hydrotreated Diesel Product Blends						Composite of naphtha range Fractions	Composite of diesel range Fractions	Diesel Blend 55% HCR'd Diesel 45% HDT'd Diesel
			Batch 1		Batch 2		Batch 3				
Boiling Temp Range	K		IBP-466	466-644	IBP-466	466-644	IBP-466	466-644	IBP-466	466-644	
	°F		IBP-380	380-700	IBP-380	380-700	IBP-380	380-700	IBP-380	380-700	
Specific Gravity		0.78	0.71	0.79	0.71	0.79	0.72	0.79	0.72	0.79	0.79
Gravity, °API		50.5	67.3	48.4	66.8	48.4	64.7	48.3	66.3	48.4	48.6
Sulfur	wt PPM	< 1		0.59		0.53		<1			< 1
Nitrogen	wt PPM	0.2		0.25		0.17		0.19			< 0.15
Astm Color	none	0.0									0
Pour Point	K (°C)	272 (-1)									263 (-10)
Cloud Point	K (°C)	277 (4)								280 (7)	272 (-1)
Cold Filter Plugging Point	K (°C)	274 (1)									270 (-3)
Aromatics	wt %	pending									pending
Ramsbottom Carbon	wt %	0.06									0.05
TAN	mg KOH/g	< 0.05									< 0.05
Viscosity at 40 °C	cSt	2.2									3.0
Ash Oxide, D482	wt %	< 0.005									< 0.005
Flash Pt	K (°C)	<298 (<25)								372 (99)	354 (81)
		Temperature (K)									
Simulated Distillation, LV%	IBP	272									360
	0.5%	309	271	460	271	459	306	450		460	397
	5%	371	309	469	309	469	340	468		470	467
	10%	423	341	489	341	488	342	487		489	487
	30%	499	372	526	372	525	396	525		526	526
	50%	544	414	560	421	560	422	560		560	560
	70%	588	445	596	446	595	446	598		596	595
	90%	627	468	629	469	629	469	629		629	629
	95%	639	469	640	470	640	470	640		640	637
	99%	651	476	651	487	651	486	651		651	647
	EP	654	484	654	487	654	487	655		657	651
D86 Distillation, LV%	IBP	293									444
	5%	402									479
	10%	450									497
	30%	508									534
	50%	552									567
	70%	595									601
	90%	630									630
	95%	641									638
	EP	644									645
		Temperature (°F)									
Simulated Distillation LV%	IBP	31									189
	0.5%	96	29	369	29	367	92	351		369	256
	5%	208	97	385	97	384	153	383		386	382
	10%	302	154	420	155	419	156	418		420	417
	30%	439	210	487	211	486	253	486		487	487
	50%	520	286	549	298	548	301	548		549	549
	70%	599	342	613	344	612	344	617		614	612
	90%	670	383	673	385	672	384	672		673	672
	95%	691	385	692	386	692	386	692		693	688
	99%	712	398	712	417	712	416	712		713	706
	EP	718	412	717	418	717	417	719		723	713
D86 Distillation LV%	IBP	68									340
	5%	264									402
	10%	351									435
	30%	455									501
	50%	534									562
	70%	611									622
	90%	674									674
	95%	694									689
	EP	700									701

Conclusions

A total of 0.053 cubic meter (14 gallons) of the neat Fischer-Tropsch diesel was hydrotreated. The TAN decreased from 3.7 mg KOH/g to less than 0.05 mg KOH/g which was the product specification target. The diesel hydrotreating produced around 15% naphtha range material. The naphtha range material was most likely generated by the saturation of oxygenates. A total of 0.0397 cubic meter (10.5 gallons) of diesel range material was collected. Since this was short of the 0.0833 cubic meter (22 gallons) of material required for the Hot Start Cycle Transient Engine Test and the Solvent Extraction, hydrocracked diesel material was blended with the hydrotreated diesel to make up the difference.

List of Acronyms and Abbreviations

°API	degree(s) API
°C	degrees Celsius
°F	degrees Fahrenheit
AED	
AFDU	Alternative Fuels Demonstration Unit
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
C#	hydrocarbons with # number of carbons
C#-	hydrocarbons with less than # number of carbons
C#+	hydrocarbons with more than # number of carbons
cSt	centistokes
EECP	Early Entrance Co-Production
EP	End Point
F-T	Fischer-Tropsch
g	gram
gal	gallons
H_2	Hydrogen
H_2O	Water
HPS	high pressure separator
IBP	Initial Boiling Point
IC#	iso-ydrocarbon with # number of carbons
ID	Identification
ILT	ChevronTexaco Integrated Laboratory Technologies
K	kelvin(s)
KOH	potassium hydroxide
LV%	liquid volume percent
m^3	cubic meter(s)
mg	milligram(s)
NAA	Neutron Activation Analysis
NC#	normal hydrocarbon with # (number) carbons
NH_3	ammonia
ppm	parts per million
Prod.	Product
RD&T	Research, Development and Testing
SCF/B	standard cubic feet per barrel
SWRI	Southwest Research Institute
TAN	Total Acid Number
TEMA	ChevronTexaco Technology Marketing
TX	Texas
vol%	volume percent
wt	Weight
wt%	Weight percent