EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Final Report

Reporting Period: January 2001 to June 2003

Contributors:

John Anderson (ChevronTexaco)
Charles Schrader (ChevronTexaco)
Fred D. Brent (ChevronTexaco)
Michael K. Porter (ChevronTexaco)
Steve Decanio (ChevronTexaco)
Govanon Nongbri (ChevronTexaco)
Ken Kwik (ChevronTexaco)
Danny A. Woodall (ChevronTexaco)
Kalapi Sheth (ChevronTexaco)
Peter Ricci (ChevronTexaco)
Michael Henley (ChevronTexaco)
Jimmy O. Y. Ong (ChevronTexaco)
Kenneth Yackly (GE)
Ashok Anand (GE)
Robert A. Battista (GE)
Chi M. Ho (GE)
Charles Benham (Rentech Inc.)
Mark Bohn (Rentech Inc.)
Belma Demirel (Rentech Inc.)
Mark Anselmo (Rentech Inc.)
Donald Todd (LCI)
Robert Schavey (LCI)
Roko Bujas (Gulftronic)
Don Wall (General Atomics)
Lalit Shah (ChevronTexaco)
Earl Berry (ChevronTexaco)
Ming He (ChevronTexaco)
Randy Roberts (ChevronTexaco)
David Storm (ChevronTexaco)
Jerome Mayer (ChevronTexaco)
Harry Tsang (ChevronTexaco)
Abdalla H. Ali (ChevronTexaco)
Raj Kamarthi (ChevronTexaco)
James F. Stevens (ChevronTexaco)
Centha A. Davis (ChevronTexaco)
Phyllis D. Hill (Kelly Services)
Chris Taylor (Kellogg Brown & Root)
Michael Tillman (Kellogg Brown & Root)
Jennifer Adams (Kellogg Brown & Root)
Robert F. Earhart (The Bechtel Corporation)
Marjan J. Roos (The Bechtel Corporation)
Jimell Erwin, Ph. D. (Southwest Research Institute)
Matthew G. Banks (Southwest Research Institute)
Terry L. Ullman (Southwest Research Institute)
T. D. Burchell (Oak Ridge National Laboratory)
O. O. Omatete (Oak Ridge National Laboratory)
Dennis Slater (Gulftronic)

Date Issued: September 22, 2003 (Preliminary)
December 16, 2003 (Final)
January 26, 2004 (Final – Revised)

DOE Cooperative Agreement No. DE-FC26-99FT40658

Texaco Energy Systems LLC
3901 Briarpark Drive
Houston, Texas 77042

Disclaimer

Abstract

In 1999, the U. S. Department of Energy (DOE) awarded a Cooperative Agreement to Texaco Energy Systems Inc. to provide a preliminary engineering design of an Early Entrance Coproduction Plant (EECP). Since the award, continuous and diligent work has been undertaken to achieve the design of an economical facility that makes strides toward attaining the goal of DOE's Vision 21 Program. The objective of the EECP is to convert coal and/or petroleum coke to power while coproducing transportation fuels, chemicals, and useful utilities such as steam. This objective is being pursued in a three-phase effort through the partnership of the DOE with prime contractor Texaco Energy Systems, LLC. (TES), the successor to Texaco Energy Systems, Inc. The key subcontractors to TES include General Electric (GE), Praxair, and Kellogg Brown and Root. ChevronTexaco provided gasification technology and Rentech Inc.'s Fischer-Tropsch (F-T) technology that has been developed for non-natural gas sources. GE provided gas turbine technology for the combustion of low energy content gas. Praxair provided air separation technology and KBR provided engineering to integrate the facility. A conceptual design was completed in Phase I and the report was accepted by the DOE in May 2001. The Phase I work identified risks and critical research, development, and testing that would improve the probability of technical success of the EECP. The objective of Phase II was to mitigate the risks by executing research, development, and testing. Results from the Phase II work are the subject of this report. As the work of Phase II concluded, it became evident that sufficient, but not necessarily complete, technical information and data would be available to begin Phase III - Preliminary Engineering Design. Work in Phase II requires additional technical development work to correctly apply technology 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 decision to proceed with Phase III centers on locating a new site and favorable commercial and economic factors.

Table of Contents

The Contractor can not confirm the authenticity of the information contained herein since this report is being submitted under the DOE requirement that the electronic files must be submitted without being write-protected.

List of Figures

List of Tables

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 was 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 was 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 with the U.S. Department of Energy (DOE) are Texaco Energy Systems, LLC (TES), a subsidiary of ChevronTexaco, General Electric (GE), Praxair, and Kellogg Brown & Root (KBR). In addition TES has provided gasification technology and Fischer-Tropsch (F-T) technology developed by Rentech Inc. (Rentech), GE has provided combustion turbine technology, Praxair has provided air separation technology, and KBR has provided engineering for integration.

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).

Multiple F-T catalyst regeneration and rejuvenation schemes were identified and tested. The study concluded that while technically feasible, the processes are uneconomical when compared to the cost of adding fresh F-T catalyst and disposing of the spent F-T catalyst. An F-T pilot test conducted in Rentech's bubble column reactor confirmed the F-T synthesis performance at the set design basis feed gas hydrogen to carbon monoxide ratio, temperature, pressure, and space velocity. The test also demonstrated that the presence of up to 5 volume % carbon monoxide in the feed gas does not adversely affect the performance of the F-T synthesis system.

An improved scheme for separating fine iron catalyst particles from F-T wax was identified and tested. This study successfully addressed one of the key technical and economic risks to maintain inventory of catalyst in the F-T synthesis reactor. Effective catalyst/wax separation is also required prior to upgrading the F-T product wax to finished products.

A combustion test was conducted to determine if the current GE 6FA gas turbine design would handle the range of fuel gas compositions representative of the EECP concept. The combustion test was successful for low-British thermal unit (Btu) gas (75

Btu/standard cubic feet). The test also showed that low nitrous oxide and carbon monoxide emission were possible with nitrogen injection.

Subsequently, an F-T diesel was successfully produced during a hydrocracking pilot plant test. In engine performance tests that were conducted to assess F-T diesel as a transportation fuel, the carbon monoxide, nitrogen oxide, hydrocarbon, and particulate matter emissions from the diesel engine were found to be lower than the equivalent emissions for a California Air Resources Board (CARB)-like reference diesel. Screening tests were also conducted to identify a catalyst that will produce a food-grade wax from the F-T wax. Coproduction options such as these help reduce business risk by offering plant configurations that best suits market demands and by producing goods that have the highest value.

Phase II testing showed that it is possible to utilize the spent F-T catalyst in the gasification fluxant and to capture carbon dioxide using electrical swing adsorption and desorption with a carbon fiber composite molecular sieve (CFCMS).

The decision to conclude the project at the end of Phase II or restructure the project at a new site is scheduled to be made in first or second calendar quarter of fiscal year 2004. In Phase I, a typical refinery site, Motiva Port Arthur, was identified as the potential EECP site. As a result of the merger between Texaco and Chevron, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. For Phase III of the EECP project, at the present time, TES has recommended to DOE that the EECP Cooperative Agreement be ended at the end of Phase II unless another project opportunity can be identified. Pending a favorable decision based on the identification of a new site and the availability of funds, preliminary engineering design of a demonstration-scale early entrance coproduction plant will be initiated.

Introduction

The Phase I Preliminary Concept Report for the Early Entrance Coproduction Plant (EECP) submitted to the U. S. Department of Energy (DOE) in 2000 identified technical risks that must be overcome to achieve a successful and economical facility that would convert coal and/or petroleum coke to power plus transportation fuel. The conceptual design, illustrated in **Figure 1**, is the result of the EECP partnership among Texaco Energy Systems Inc; now Texaco Energy Systems, LLC (TES), General Electric (GE), Praxair and Kellogg Brown and Root (KBR). In the concept, about 1200 tons per day (tpd) of coal and petroleum coke are processed through an integrated gasification combined cycle (IGCC) system, integrated with a Fischer-Tropsch (F-T) process and product upgrading to yield 55 megawatts (MW) of net power, steam, and 540 barrels per day (bpd) of F-T products. The IGCC system used in the conceptual design was the ChevronTexaco Gasification Process with a GE Frame 6FA combustion turbine. The F-T technology for the conceptual design was based on the Rentech Inc. (Rentech) precipitated iron-based catalyst. The wax upgrading process chosen for the conceptual design was Bechtel's Hy-Finishing^{SM} process. A successful and economical commercial application of the EECP concept would provide an important step toward attaining the goals of the DOE Vision 21 Program.

Petroleum coke is ground, mixed with water (H_2O) and pumped as a slurry to the Gasification Unit. This petroleum 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. Approximately 75% of the syngas is treated in the AGR to remove the bulk of H_2S with minimal CO_2 removal and is then forwarded as fuel to the 6FA gas turbine. The remaining 25% of the stream is treated in the AGR to remove CO_2 and H_2S and then passed through a zinc oxide guard bed to remove the remaining traces of sulfur before being forwarded to the F-T Synthesis Unit. 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 N_2 mixture (AGR offgas) is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides (NO_x) emissions. The bulk of the nitrogen from the air separation unit is sent to the gas turbine as a separate stream and combined in the combustion chamber with the syngas fuel to increase the power production and reduce NO_x emissions from the gas turbine.

In the F-T reactor, CO 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 while F-T water, a reaction byproduct, is returned to the Gasification Unit. The F-T tail gas and AGR offgas are fed to the gas turbine and mixed with syngas. This increases electrical power production by 11%.

In the F-T product upgrading unit (FTPU), the three F-T liquid streams can be combined and processed as a single feed or processed separately. In the presence of a hydrotreating catalyst, hydrogen reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracked light ends. The resulting four liquid product streams, naphtha, diesel, low-melt wax, and high-melt wax, leave the EECP facility via tank truck.

The power block consists of a GE PG6101 (6FA) 60 Hertz (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 a 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, offgas from the AGR, and tail gas from the F-T synthesis unit as the primary fuel. The ASU supplies N_2 gas for injection to the gas turbine for NO_x 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 to satisfy all of the EECP's requirements for N_2, instrument air, and compressed air. The ASU also produces N_2 for use within the EECP 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. 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 and oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) offgas from the gasification unit, are first routed to knockout drums and then to the Claus sulfur recovery unit (SRU). After entrained liquid is removed, the acid gas is preheated and fed along with the SWS offgas, 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 gas mixture then passes through a boiler to remove heat by 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. The H_2S is removed from the quenched tail gas in an absorber by using lean methyldiethanolamine (MDEA) solvent from the AGR. The tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR to be regenerated in the stripper.

Results and Discussion

During the conceptual design (Phase I), technical risks were identified and evaluated for their impact on the commercial plant. The technical risks that were identified in Phase I are listed **Table 1**. Table 1 also shows an assessment of each risk in terms of technical impact and economic impact to the commercial plant (H-high risk; M-medium risk; L-low risk). These assessments provided the basis for the preparation of a Research, Development, and Testing (RD&T) Plan that focused on mitigating the risks. The RD&T Plan was approved by the DOE in 2001.

Figure 1- EECP Conceptual Design

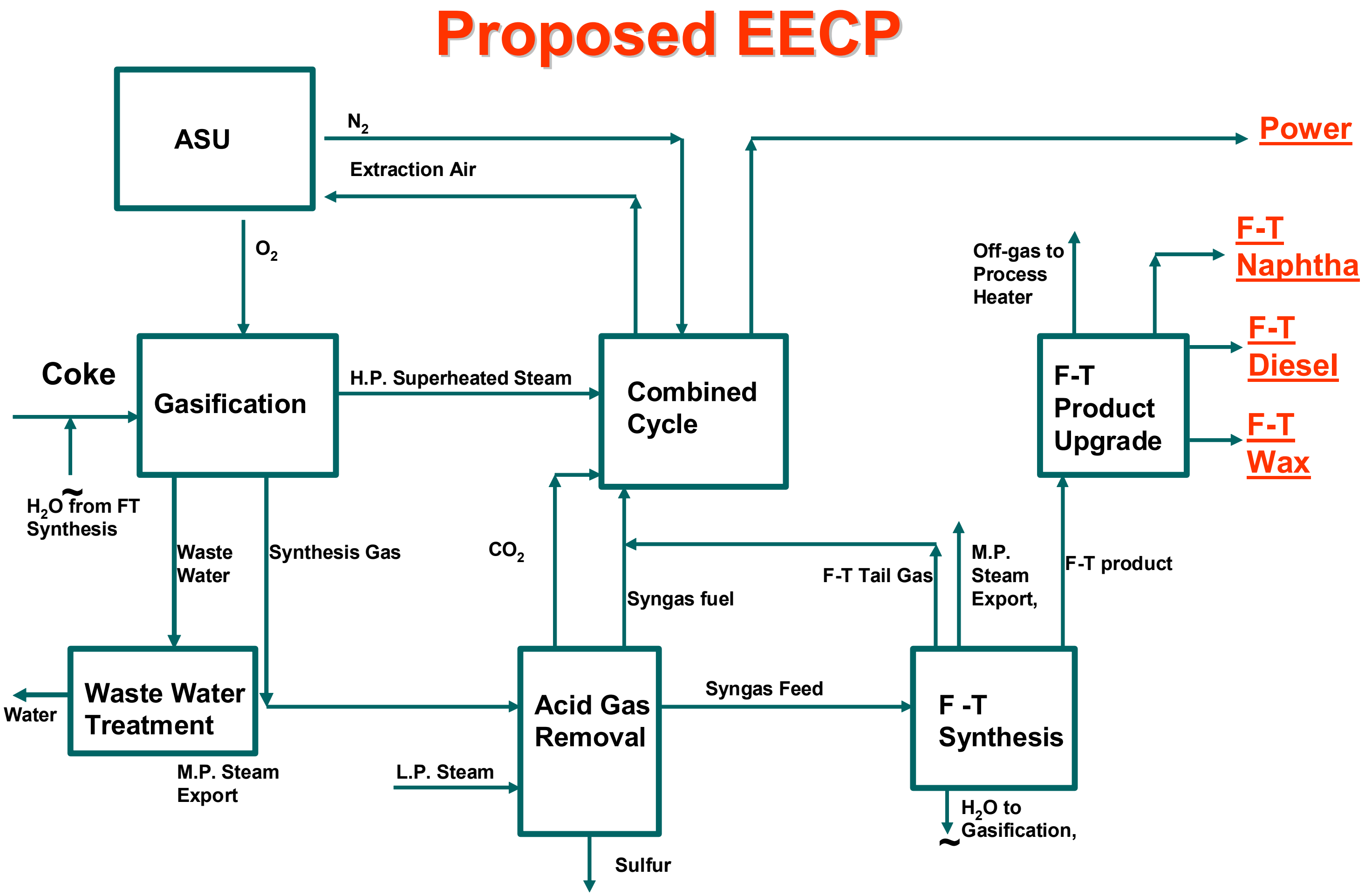


Table 1

Technical Risks and Design Deficiencies Identified in Phase I- Concept Design

Task Number	Subsystem	Technical Risk/Design Deficiency	Technical Risk	Economic Risk	Overall Risk
2.1.1	F-T	Catalyst Rejuvenation/ Regeneration	M-H	L	L
2.1.2	F-T	Catalyst Withdrawal/Addition	M	H	M
2.1.3	F-T	Temperature, Pressure, Space Velocity – conversion	M	H	M
2.1.3	F-T	% Catalyst in Reactor Slurry	H	H	M
2.1.3	F-T	Optimum H_2:CO ratio	L	M	M
2.1.3	F-T	Feed impurities (CO_2, sulfur, water)	M	H	M
2.1.3	F-T	Water-Gas Shift Activity	L	M	L
	F-T	Catalyst Deactivation Rate	L	H	M
	F-T	Catalyst/Wax Primary filtration	L	H	M
	F-T	Catalyst/Wax natural vs. forced slurry circulation	H	L	L
2.2.1	F-T	Scale up (hydrodynamics, kinetics)	H	H	M
2.3.1	F-T	Catalyst/Wax alternate filtration	M	H	M
2.3.2	F-T	Catalyst/Wax Second stage filtration	M	H	L
2.4.1	Gas Turbine	Low-Btu combustion	M	M	L
2.5.1	F-TPU	Confirmation of feed properties to upgrader	L	M	L
2.5.2 2.5.3 2.5.4	F-TPU	Pilot plant design confirmation run of licensor process	M	L	L
2.5.5	F-TPU	Determination of melt point grades of finished waxes	L	L	L
2.5.6	F-TPU	Determine cetane engine number volumetric blending factor for F-T diesel product streams	M	L	L
2.5.7.1	F-TPU	Naphtha products use in fuel cells	H	L	L
2.5.7.2	F-TPU	Naphtha product octane upgrade	L	L	L
2.5.7.3	F-TPU	Naphtha product ethylene cracker yields	L	L	L
2.5.8	F-TPU	Wax fractionation	L	L	L
2.6.2	F-TPU	Emissions testing F-T diesel product streams	M	L	L
2.7.1	Gasification	Petroleum coke characteristics	L	L	L
2.8.1	AGR	CO_2 stripper efficiency at high pressure	L	M	L
2.9.1	Integration	F-T water in slurry	L	H	L
2.10.1	Environmental	Slag & fines characterization	L	L	L
2.10.2	Environmental	Use of F-T catalyst in the fluxant	L	L	L
2.10.3	Environmental	F-T catalyst disposal	L	H	L
2.10.4	Environmental	CO_2 recovery from gas turbine	H	L	L
	ASU	None	-	-	-

As illustrated in **Table 2**, the work breakdown structure for executing the RD&T Plan have been extensive. The work of a large number of subcontractors, equipment vendors and laboratories has been coordinated and managed by the dedicated efforts of a team selected through the EECP partnership. Monthly and quarterly progress reports have been developed to monitor the progress of the RD&T. Two annual meetings were also conducted to review the results in detail.

TABLE 2

EECP Phase II - RD&T Work Breakdown Structure

Task 2.1: Pilot Plant Confirmation

Task 2.2: Fischer-Tropsch Mathematical Model and Reactor Scale-up Confirmation

Task 2.3: Catalyst/Wax Separation

Task 2.4: Low-Btu Gas Combustion Test

Task 2.5: F-T Product Upgrading

Task 2.6: Fuel/Engine Performance, Emissions

Task 2.7: Petroleum Coke Analysis

Task 2.8: CO_2 Stripping from MDEA at Medium Pressure

Task 2.9: Integration

Task 2.10: Environmental

Task3.0: Critical and Essential RD&T

Task4.0 Update Concept Basis of Design

Many of the tasks in the work breakdown structure were undertaken in parallel in order to schedule Phase II activities within a two-year period. Although most of the tasks were accomplished within the originally planned time, the schedule for processing the F-T wax was severely affected by delays in removing residual catalyst fines from the wax that was produced at the LaPorte, Texas DOE Alternative Fuels Development Unit (AFDU) in November 2000, The work was conducted without DOE funding. The original expectation for having clean wax was the spring of 2001. After a number of attempts to remove the catalyst fines, a clean wax was produced in the fall of 2002, a delay of about a year and a half. Although the schedule was delayed, the original budgeted cost was not exceeded.

The scope and major findings from each of the primary tasks will be briefly reviewed in this report. Individual Topical Reports were prepared and submitted previously.

Task 2.1: Fischer-Tropsch Pilot Plant Confirmation

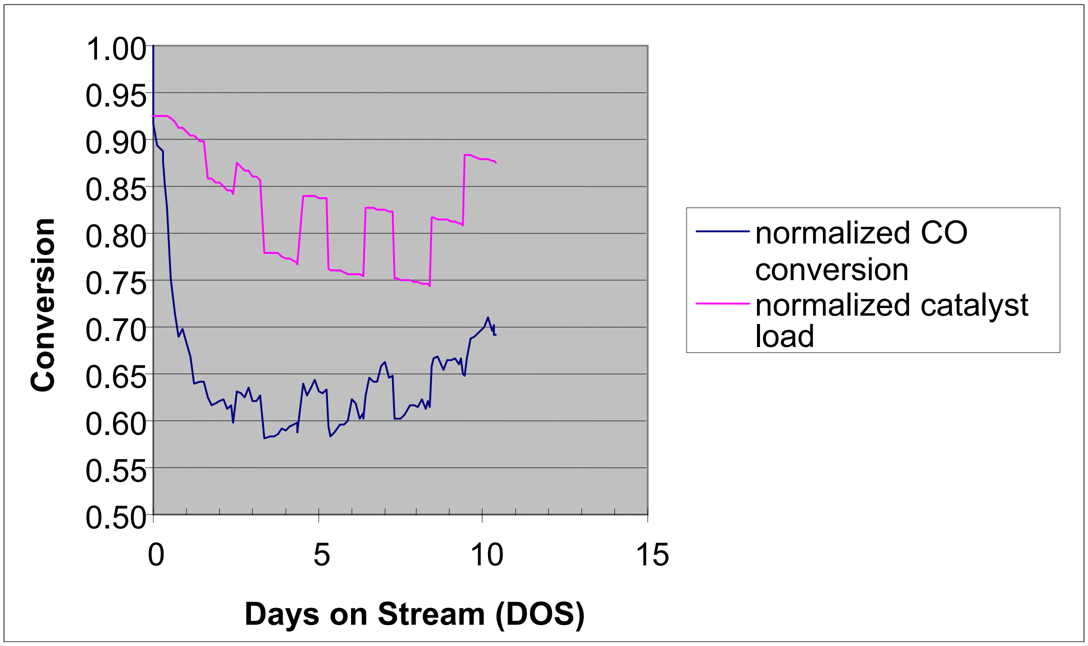
The scope of this task was to operate the Rentech bubble column reactor (BCR) at the reactor design conditions for a sufficient time to confirm that the estimated conversion and yields could be obtained and to investigate the feasibility of rejuvenation and regeneration of the catalyst.

The completion of this task required work with corporate funding outside of the EECP Project. The BCR was modified to allow withdrawal and addition of catalyst while in operation. The rate of catalyst replacement to offset deactivation was determined through experimental work conducted with autoclave reactors at the University of Kentucky Center for Applied Energy Research (CAER). The effect of CO_2 and the maximum amount of CO_2 in the feed gas was also determined through experimental work at CAER. Hydrodynamic and mass transfer studies conducted at the University of Pittsburgh were used to design the reactor geometry.

Several technical issues were identified for Phase II RD&T associated with the F-T synthesis reaction section. One of the issues is the handling and disposal of relatively large quantities of spent catalyst. It is important to obtain as much useful life from the catalyst as possible. If the catalyst is used on a once through basis, the operating cost of the F-T plant increases substantially. The operating cost can be reduced if the spent catalyst can be recycled. Loss of performance of the unsupported precipitated iron catalyst can be due to deposits, composition change, and attrition; therefore the, regeneration of spent F-T catalyst was considered. Experimental studies conducted by Rentech and TES included nitrogen stripping, hydrogen stripping, and oxidation plus reactivation. The program results confirmed that the deactivated catalyst did respond to the rejuvenation procedures. The in-situ regeneration treatment, however, did not significantly improve the deactivated catalyst performance. In the context of the Phase II RD&T, regeneration includes those steps that restore the activity and selectivity of the used catalyst, at least partially, to that of the active catalyst without the necessity of subjecting the catalyst to the activation procedure. Rejuvenation refers to a process that returns the catalyst to its original oxide state and therefore requires reactivation.

Operation of a commercial slurry F-T reactor will require periodic on-line catalyst withdrawal and addition. This is necessary to replace catalyst lost with product wax and to maintain reactor productivity as the catalyst deactivates. In Phase II RD&T, a catalyst withdrawal and addition system, outside of DOE funding, was successfully designed and implemented on Rentech's BCR. A test was conducted that demonstrated successful catalyst withdrawals and additions. As shown in **Figure 2**, the test demonstrated the successful manipulation of the reactor performance by catalyst additions and withdrawals. Results of the testing show that catalyst can be withdrawn and added to an operating F-T reactor safely and that the activity of the catalyst in the reactor responds in direct proportion to the mass of catalyst withdrawn or added. This suggests that a commercial reactor could be operated at a steady-state productivity and selectivity using methods demonstrated in this test.

Figure 2 – Catalyst Withdrawal and Addition

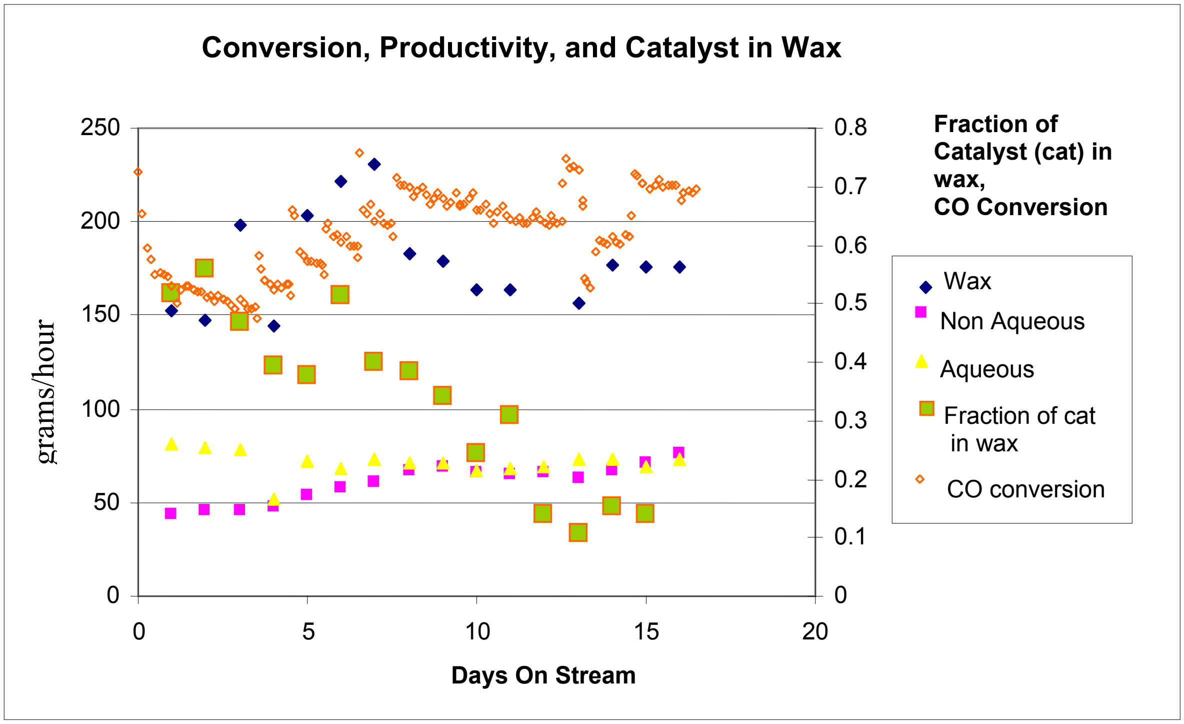


Another issue that was explored during the testing was whether unactivated catalyst added to the reactor will activate sufficiently under operating conditions. The elimination of a activation step would reduce the operational complexity of a commercial system substantially. Towards the end of the catalyst withdrawal and addition testing, unactivated catalyst was added to the reactor. Although the response was slower than that of the activated catalyst, unactivated catalyst added to the operating reactor became active within about 24 hours. These results show promise; however, it is important to note that the test was short and no long-term performance was ascertained.

The final issue addressed in this scope was the design basis confirmation test. The scope of this task was to operate the Rentech BCR at the design conditions for sufficient time to confirm that the estimated conversion and yields could be obtained. The main thrust of this work was to determine if a certain CO conversion can be achieved at a specific space velocity and feed synthesis gas feed ratio (H_2:CO) and if the expected F-T subsystem feed-gas CO_2 concentration of 5 volume % will damage the catalyst.

As shown in **Figure 3,** tests demonstrated a conversion of a 97% of the desired CO conversion at 111% of the space velocity. Based on that result and an understanding of how the catalyst and reactor respond to space velocity changes, it appears that the design basis proposed in Phase I conceptual design is feasible, but will require a slight modifications. In addition, it appears that 5% CO_2 in the feed (11.5 days to 12.5 days) gas is not detrimental to the catalyst.

Figure 3 – F-T Pilot Plant Confirmation Test



Major Findings: Catalyst Rejuvenation/Regeneration

Catalyst rejuvenation/regeneration is one possible way to address the catalyst disposal issue. If the catalyst can be effectively rejuvenated or regenerated, then the quantity of spent catalyst to be disposed can be reduced. This section presents the investigation effort in the area catalyst rejuvenation/regeneration. Most of the laboratory work for the catalyst rejuvenation was completed in Rentech's laboratory facility in Denver, Colorado. The majority of the catalyst regeneration work was done in ChevronTexaco's laboratory facility in Bellaire, Texas.

In the context of the task, rejuvenation includes those steps that restore the activity and selectivity of the used catalyst, at least partially, to that of the active catalyst without the necessity of subjecting the catalyst to the activation procedure. Regeneration refers to a process that returns the catalyst to its original oxide state and therefore requires reactivation.

In order to evaluate various candidate techniques, it was necessary to have a supply of deactivated catalyst. Catalyst produced by a commercial vendor (Vendor A) for the ChevronTexaco-funded LaPorte tests that had undergone 30 days of testing was available. Rentech also produced two batches from a second commercial vendor (Vendor B) of used catalyst for testing. In this manner, several hundred grams of catalyst were available for rejuvenation/regeneration work.

A literature search for work in this area was necessary to establish the current state of the art and to determine potential application of developed processes. The three-month literature search proceeded simultaneous to the laboratory work.

The process for rejuvenating spent catalyst involves several steps. Dewaxing is the first step that removes the wax from the spent catalyst. Supercritical fluid extraction with hexane was very effective. Tests with alkylation and reformate naphthas were also effective. These results indicate that there is potential to use F-T naphtha as the solvent for dewaxing. Additional testing may be required for confirmation. The second step in the catalyst rejuvenation process is to re-oxidize the catalyst back to iron oxide. Testing revealed that this is a delicate process. High temperature and high oxidation gas flow rates seem to sinter the catalysts. The optimized oxidation condition was determined to be 493K (220ºC) using 2 volume % O_2 in N_2 at the rate of 1.4 cubic meters per hour per kilogram of catalyst ($m^3h^{-1}kg\ cat^{-1}$). The third step is to reactivate the catalyst. This was completed with a proprietary Rentech activation method. Testing with this rejuvenated catalyst showed significant improvement in activity compared to the deactivated catalyst. Testing of rejuvenated catalyst showed a reduced alpha. This was contributed to the loss of potassium from the catalyst. Addition of potassium significantly improved the alpha. The results from this catalyst rejuvenation shows promise that spent F-T catalysts can be rejuvenated.

Catalyst regeneration involves in-situ treatment of the spent catalyst in order to restore its activity. Nitrogen stripping and hydrogen reduction were the two methods tested in this task. Nitrogen stripping was found to be effective in one case on one catalyst. The hydrogen treatment tests did not show any improvements. Literature surveys indicate that the hydrogen reductions may have been too harsh for effective regeneration of these catalysts. Further investigations might utilize nitrogen stripping followed by CO or syngas regeneration.

In evaluating the cost of such regeneration and rejuvenation techniques, it was determined that the processes would not be economical compared to the cost of the addition of fresh F-T catalyst and disposal of spent catalyst since the rate of deactivation of the catalyst is less than that predicted in Phase I. The impact of disposing the spent F-T catalyst is discussed later in this report under Task 2.10.

Major Findings: Catalyst Withdrawal/Addition

Development of an online catalyst withdrawal/addition system is critical in maintaining reactor productivity. Over time, as the catalyst in the reactor ages and becomes less productive; it will need to be removed from the reactor and replaced with fresh catalyst. In this task, a system for catalyst withdrawal and addition was designed, fabricated and tested on the Rentech BCR. The system was designed to allow online catalyst withdrawal and addition without interrupting reactor operations. During the test, unactivated catalyst was also added to the BCR to determine if it would activate sufficiently under typical operating conditions

Safe withdrawals and additions of catalyst from an operating reactor were demonstrated in this test. The reactor activity responded accordingly. This suggests that a commercial reactor could be operated at steady-state productivity and selectivity using methods demonstrated in this test. Addition of un-activated catalyst to the operating reactor appeared to become active. Further investigations are required to demonstrate if there are any the long-term effects of the addition of un-activated catalyst.

Major Findings: Pilot Test in a Bubble Column Reactor

Since Phase I, TES and Rentech have done much testing outside of Cooperative Agreement for the EECP Project with corporate funds to investigate the kinetic effects of the feed gas on the F-T reaction. Based on those experiences and the mathematical model discussed in Task 2.2, the F-T synthesis section design basis was revised. In the revised design basis, the feed gas required testing to confirm that the H_2:CO ratio and the CO_2 concentration in the feed was technically feasible. This test was done at Rentech's BCR in Denver, Colorado.

The test confirmed the F-T synthesis performance at the set design basis feed gas H_2:CO ratio (0.76), temperature (322K/120^{o}F), pressure (3,737 kPa/542 psia) and space velocity. The test also demonstrated that the presence of up to 5 volume % CO_2 in the feed gas does not adversely affect the performance. Since the design basis and performance were developed with the mathematical model (Task 2.2), the results of this test give confidence to the model as a design and scale-up tool.

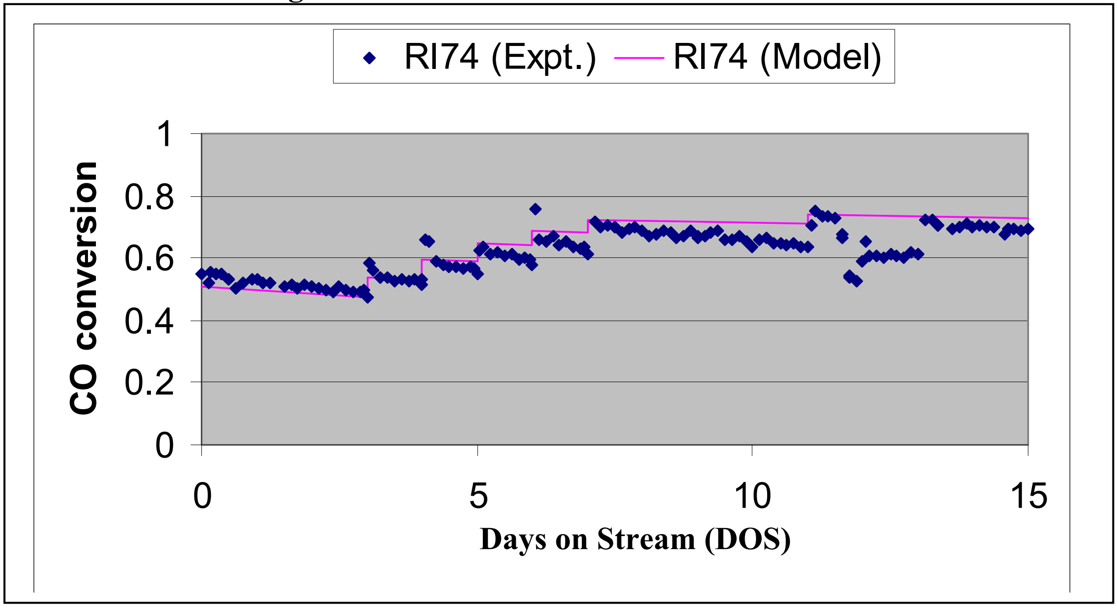
Task 2.2: F-T Mathematical Model and Reactor Scale-up Confirmation

The ChevronTexaco proprietary mathematical model is a multi-component numerical model that includes detailed kinetics to predict reactor performance for F-T synthesis in a slurry bubble column reactor. The model assumes that the gas phase travels in plug flow, the liquid phase is completely back-mixed, the mass transfer resistance is in the liquid phase, the catalyst is evenly distributed throughout the column, intraparticle resistances are negligible, hydrodynamic and physicochemical properties are spatially independent, and the reactor operates in an isothermal, isobaric and steady-state regime. The gas phase equation for each component is solved using a fourth order Runge-Kutta method, and a secant method is used as an iterative procedure to obtain closure for the liquid phase concentrations.

The scope of this task was to compare the mathematical model to experimental data obtained from an extended test on Rentech's BCR.

Figure 4 shows the comparison between the predicted results (Model) and the experimental (Expt.) data for CO conversion as a function of days on stream (DOS). During the F-T confirmation test, catalyst was added to the reactor to increase slurry concentration to the EECP design basis point. The model compares quite closely to the magnitude of the conversions and is able to account for increases in catalyst concentration and average reactor temperature (Day 11). However, the model is unable to predict the response of conversion after each addition is made – the slopes of the lines are much less than the experimental data. This difference could be attributed to the large uncertainty in calculating the amount of catalyst within the reactor for any given period of time.

Figure 4 – F-T Mathematical Model Results



Major Findings: F-T Mathematical Model

The scale-up of the EECP F-T reactor from the 1.5-inch (38 millimeter) inside diameter (id) Rentech bench-scale reactor to an 8-foot (2.4 meter) id or larger demonstration-scale reactor presents a major technical challenge. ChevronTexaco's proprietary model compares closely to experimental data acquired from Rentech's BCR. The model was also successfully used outside of the EECP Project in the F-T demonstration at the LaPorte AFDU (22 inch/0.56 meter id reactor). Based on the test results, the team believes the risk in the EECP F-T reactor scale-up has been reduced and the mathematical model is planned to be used for the design of the EECP F-T reactor.

Task 2.3: Fischer-Tropsch Catalyst/ Wax Separation

The scope of this task was to determine if a filtration scheme could be developed that would provide an F-T product free of iron catalyst. This would allow the upgrading of the raw F-T product into finished F-T wax products. It also allows for the retention of the iron catalyst within the slurry reactor system.

The general consensus for F-T operations using an iron catalyst has been that the separation of catalyst fines from the F-T heavy wax product is very difficult and may be a fatal flaw with current available technology. There have been many attempts to simply and efficiently separate the catalyst from the liquid wax including modification of the F-T product recovery system. Work under this task also proved to be very difficult. The conceptual design of Phase I F-T catalyst/wax separation system consisted of a two stage process to achieve an F-T wax having less than 10 ppm by weight of catalyst. The two stages are defined as primary and secondary.

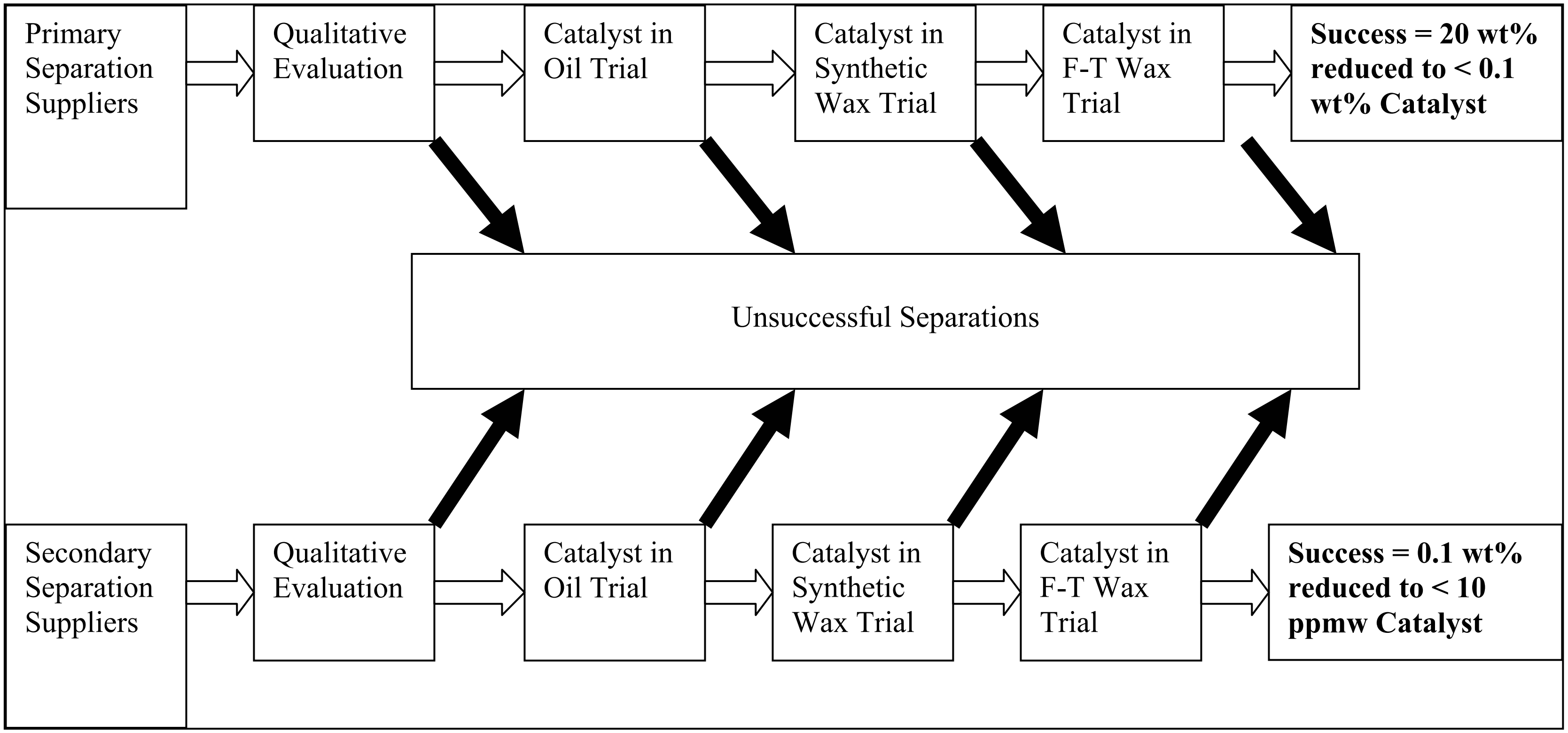
A large number of vendors and licensors were identified as potential suppliers of the technology to prepare the F-T product wax for upgrading. The 24 identified vendors and licensors could be broadly classified into the following categories:

Barrier filtration
Crossflow filtration
Magnetic separation
Electrostatic separation

The objective of the primary separation stage was to reduce the catalyst concentration from the reactor concentration to less than 0.1 weight % (wt%). The catalyst concentration of the raw product is assumed to be 20 wt%. Only two potential suppliers were identified who could perform this initial separation. These two suppliers were Rentech using their propriety Dynamic Settler technology, and another company, using magnetic separation technology.

The potential suppliers of the secondary separation were evaluated through a series of tests designed to identify the ability and capability of each supplier to meet the objective of providing a wax with less than 10 parts-per-million-weight (ppmw) of catalyst. The sequence of testing is shown in **Figure 5**. A critical criteria from the testing sequence appeared as suppliers needed to test the actual F-T wax. The F-T wax had a melting point of about 394K (250°F). This high melting point wax required separation process equipment that could be safely operated at 450K (350°F) or higher in order to obtain a fluid with a viscosity that is low enough to filter without excessive pressure drops.

Figure 5 - Catalyst / Wax Separation Test Sequence

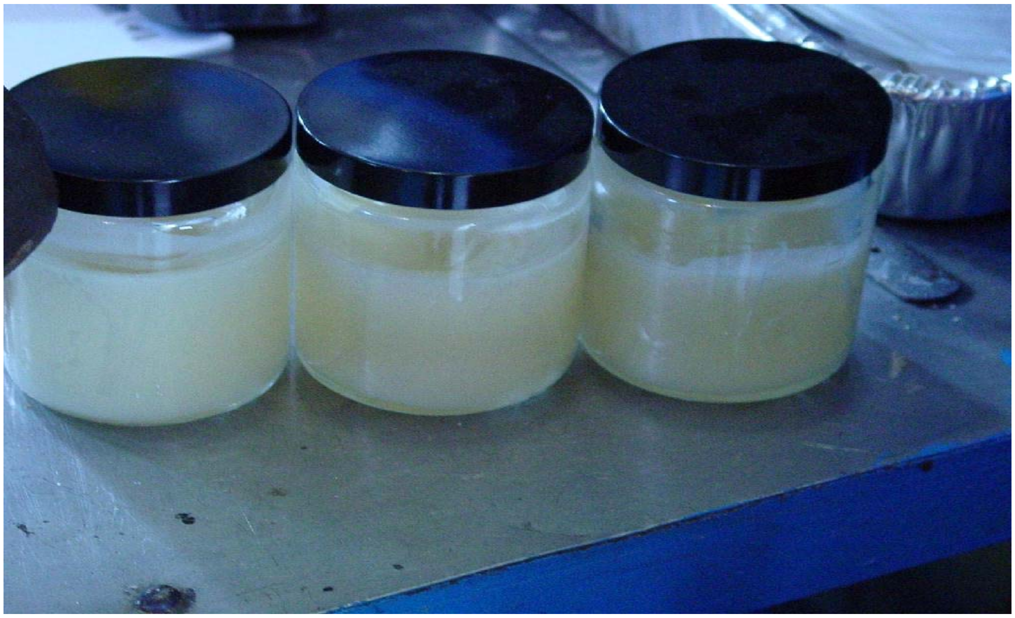


Major Findings: F-T Catalyst/Wax Separation

The final recommended filtration scheme for the EECP concept is the combination of the Rentech Dynamic Settler technology as the primary separation and cross flow filtration as the secondary separation using the LCI Scepter® Micro-filtration system. The Rentech Dynamic Settler technology was selected based on testing outside of DOE funding.

The results of the secondary separation testing identified crossflow filtration using the LCI Scepter® Micro-filtration system to be best suited for producing a filtrate that met the EECP secondary catalyst/wax separation standards of less than 10 ppmw (see **Figure 6** below). Other technologies, magnetic separation and electrostatic separation, were promising and were able to reduce the solids concentrations in the filtrate; however additional RD&T will be needed for these technologies to obtain 10 ppmw filtrate required for the EECP concept.

Figure 6 – Cleaned Wax Produced By LCI Scepter® Micro-Filtration System



Task 2.4: Low-British Thermal Unit (Btu) Gas Combustion Test

The scope of this task was to develop and to conduct a combustion test to determine if the current GE 6FA gas turbine combustor design would handle the range of fuel gas compositions representative of the EECP concept based on different operating scenarios.

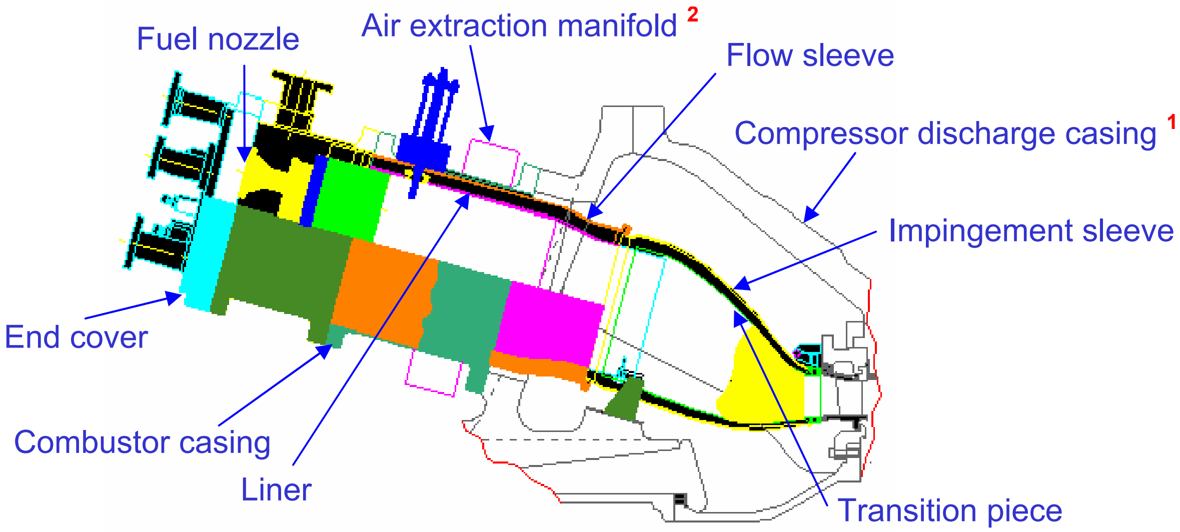
The syngas available from the gasification process typically has a heating value of about 300 Btu per standard cubic feet (SCF). The heating value of the syngas is made up primarily from the constituents that include H_2 and CO that are present with some contribution from minor constituents such as light hydrocarbons that include methane and ethane. The conversion of CO and H_2 to F-T products, including CO_2, causes the heating value of the F-T tail gas to become significantly lower than the syngas. The heating value of the F-T tail gas may be as low as 75 Btu/SCF. Because the EECP F-T design uses only about 25 vol % of the available syngas, the effect of an F-T outage on the total economics of the EECP is minimized. As a result, the F-T tail gas combined with the remaining syngas that is fed to the combustion turbine will have a heating value that is well within the operating range for combustion turbine design. However, a commercial coproduction plant would process all of the available syngas through the F-T reactor, the F-T tail gas would be the sole feed gas to the combustion turbine. Foresight to a commercial coproduction plant resulted in a combustion test of low Btu gas (75 Btu/SCF) at the GE Combustion Turbine facility in Greenville, South Carolina.

The EECP team studied a total of 12 cases of gas turbine feed gas mixtures based on different operating scenarios of EECP plant. However, only two cases, based on the lowest and the highest heating values, were selected for testing. The lower heating value (LHV) of the primary fuel, however, is lower than the value that has been demonstrated in the current 6FA gas turbine combustor design. Another potential technical risk is the fuel composition variation. When the EECP F-T reactor is not operating, the primary fuel consists only of syngas and AGR offgas. A combustion test is therefore required to verify that the current gas turbine combustor design can handle the fuel and its variation. Since nitrogen from the ASU will be used as diluent for NO_x abatement, its effect should also be evaluated. In summary, the test was planned with focus on the following three objectives:

1) To verify GE gas turbine combustor design for EECP fuel composition variances
2) To evaluate the effect of fuel composition
3) To determine the effectiveness of nitrogen diluent injection for NO_x abatement

For testing purposes, only a single gas turbine combustor was utilized. The combustor is mounted on a test stand designed for simulating the inlet (compressor discharge) and outlet (turbine inlet) conditions for the combustor. A schematic of the combuster is shown in **Figure 7**. The test stand provides an interface with a single combustor and simulates the upstream and downstream conditions of the combustor. The combustion air, typically supplied by two compressors, passes through flow sections at which the flow rate is controlled and measured.

Figure 7 - Combustion Laboratory Test Stand Schematic



[1] Test stand simulates the compressor discharge casing with a pressurized enclosure.
[2] Test stand has no provision for air extraction piping. To simulate effect of air extraction, amount of air flow into the combustor is reduced.

Table 3 and 4 present the comparisons between “measured” and “planned” test point conditions for the low Btu gas mixtures. Each measured test point was compared to a corresponding planned test point The ratio between the measured and the planned is also shown for some parameters. Test point (Tp) 5a was intended to repeat test point Tp5 with better settings for the test point conditions. Test point Tp7 was an additional test point that was taken as an intermediate point between 50 vol % and 100 vol % N_2/fuel ratio.

The blowout point, test point Tp14, was attempted but not recorded during the test. During the process of blowing out the combustor, the flame went out before test conditions were held steady enough to record an official test point. However, all the test parameters were continuously scanned every two seconds and were recorded.

During this test, a CO flow measurement error was not discovered until the flow measurement section was inspected after the test. A plastic cap was found partially blocking the flow orifice. As a result, the actual CO flow rate was considerably lower than what the measurement indicated. Between test point Tp9 and Tp13, another flow measurement problem occurred. The boiler of the CO_2 vaporizing system tripped. The trip remained unnoticed until the CO_2 temperature dropped below its dew point.

These facility problems caused the actual fuel composition and fuel flow rate to deviate considerably from what was planned. Consequently, other parameters including combustor exit temperature, main chamber pressure (simulating compressor discharge pressure), diluent-to-fuel ratio, equivalent fuel flow rate (defined as the sum of blended test points), and the temperature for fuel and diluent were lower than expected. A substantial amount of heat from the fluids was lost to in the pipes between the heater exit and the test stand. Later in the test, fuel and diluent temperatures were closer to their planned values as the heat losses to the pipes were adequately compensated.

The blended fuel flow measurements were also found to be inaccurate. The fuel composition was measured independently by mass spectrometer and was used in conjunction with the measured combustor exit temperature to back calculate the equivalent fuel-to-air ratio. Trace amounts of O_2, ethane, propane, and argon were recorded by the mass spectrometer but were discarded as measurement noise in the calculations.

The natural gas test points were closely simulated to the planned conditions. Most of the measured parameters were within a few percent of their respective planned values. However, the measured natural gas fuel flow rate was consistently 8-12% higher than planned.

Table 3
Comparison of Low Btu Gas Test Point Conditions Between Measured and Planned

	Test point	Fuel type	Load condition	Equivalent fuel/air ratio [1]	Diluent/Low-Btu fuel ratio [2]	Low-Btu fuel temperature, deg F	Diluent (N_2) temperature, deg F
Measured	Tp5	-	-	0.2906	0.00	210.1	-
Planned	5	Case 5b	100%	-	0.00	400.0	-
Ratio					1.00	0.53	
Measured	Tp5a	-	-	0.2905	0.00	217.9	-
Planned	5	Case 5b	100%	-	0.00	400.0	-
Ratio					1.00	0.54	
Measured	Tp6	-	-	0.4423	0.54	253.7	223.9
Planned	6	Case 5b	100%	-	0.50	400.0	550.0
Ratio					1.08	0.63	0.41
Measured	Tp7	-	-	0.4752	0.74	270.1	393.5
Planned[3]	-	-	-	-	-	-	-
Ratio					-	-	-
Measured	Tp8	-	-	0.5238	1.19	416.5	465.2
Planned	7	Case 5b	100%	-	0.93	400.0	550.0
Ratio					1.28	1.04	0.85
Measured	Tp9	-	-	0.5347	1.05	402.1	454.5
Planned	9	Case 2	100%	-	1.03	400.0	550.0
Ratio					1.02	1.01	0.83
Measured	Tp10	-	-	0.4473	0.74	400.4	489.8
Planned	8	Case 2	100%	-	0.94	400.0	550.0
Ratio					0.79	1.00	0.89
Measured	Tp11	-	-	0.5354	0.60	400.0	515.0
Planned	12	Case 5b	50%	-	0.97	400.0	550.0
Ratio					0.62	1.00	0.94
Measured	Tp12	-	-	0.3297	0.00	402.1	-
Planned	10	Case 5b	50%	-	0.00	400.0	-
Ratio					1.00	1.01	
Measured	Tp13	-	-	0.0528	0.00	383.5	-
Planned	11	Case 5b	FSNL	-	0.00	400.0	-
Ratio					1.00	0.96	

Note 1: Due to blended fuel flow stream measurement error, Equivalent fuel / Air ratio was back calculated based on fuel composition measured by mass spectrometer and combustor exit temperature

Note 2: Calculated based on back calculated Low Btu fuel flow

Note 3: Test Point not planned.

FSNL: Full-Speed-No-Load

Table 4

Comparison of Low Btu Gas Fuel Compositions Between Measured and Planned

	Test point	Fuel type	Mass Spec H2,%mole dry	Mass Spec C0,%mole dry	Mass Spec N2,%mole dry	Mass Spec CH4,%mole dry	Mass Spec CO2,%mole dry
Measured	Tp5	-	27.6	19.7	28.1	1.0	23.2
Planned	5	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.15	0.70	1.13	1.05	1.05
Measured	Tp5a	-	29.9	20.3	27.4	1.0	21.1
Planned	5	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.25	0.72	1.10	1.05	0.96
Measured	Tp6	-	31.9	19.9	27.4	1.1	19.3
Planned	6	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.33	0.71	1.10	1.07	0.88
Measured	Tp7	-	28.2	19.0	27.3	1.1	24.1
Planned[1]	-						
Ratio			1.18	0.68	1.09	1.07	1.10
Measured	Tp8	-	30.6	19.7	27.5	1.1	20.8
Planned	7	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.28	0.70	1.10	1.07	0.95
Measured	Tp9	-	28.6	19.7	28.8	0.0	22.5
Planned	9	Case 2	24.0	32.0	27.0	0.0	17.0
Ratio			1.19	0.62	1.07	1.00	1.33
Measured	Tp10	-	28.5	21.5	29.1	0.0	20.6
Planned	8	Case 2	24.0	32.0	27.0	0.0	17.0
Ratio			1.19	0.67	1.08	1.00	1.21
Measured	Tp11	-	26.0	16.6	24.5	0.9	31.7
Planned	12	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.08	0.59	0.98	0.87	1.44
Measured	Tp12	-	26.5	18.9	26.2	1.0	27.0
Planned	10	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.11	0.68	1.05	1.00	1.23
Measured	Tp13	-	27.3	22.1	25.4	1.1	23.8
Planned	11	Case 5b	24.0	28.0	25.0	1.0	22.0
Ratio			1.14	0.79	1.02	1.13	1.08

Note 1: Test point not planned.

Major Findings: Low-Btu Gas Combustion Test

The following general conclusions were drawn from this test program evaluation:

1. Low-Btu EECP fuels are viable for GE gas turbine applications.
2. All test points attempted showed no sign of combustion related problems that may produce excessive emissions or adversely impact the normal life of component parts.
3. Low-NO_x and low-CO emissions are possible with N_2 injection for 6FA application.
4. Less than 10 ppmw of NO_x and CO emissions at 6FA full-load conditions appear feasible with an appropriate amount of nitrogen injection as in the proposed EECP concept.

Although a number of test facility issues related to the blended fuel flow control and measurement system prevented the precise setting of the test point conditions as planned, the overall test was considered successful. The specific findings of the test included the following:

1. Issues on simulating the test conditions for the low-Btu gas portion of the test have been identified through data reduction and facility inspection, and were accounted for in the evaluation of the data.
    - Volumetric LHV of the low-Btu blended fuel and the equivalent fuel (diluent injection included) was lower than what was originally planned.
    - H_2:CO ratio of the blended fuel was higher than its planned value.
    - Combustor exit temperature was lower than its planned value.
2. Test point conditions for the natural gas portion of the test were successfully simulated.
3. All the test points attempted show no sign of any combustion related problem.
4. The effect of diluent injection was demonstrated in the NO_x correlation, which is consistent with previous experience. The measured NO_x also compared well with cycle deck predictions based on actual test conditions.
5. The higher than expected H_2:CO ratio should have increased the flammability range of the equivalent fuel. However, the lower than expected volumetric LHV reduced flammability. As a result, the upper-to-lower flammability ratio (U/L FLR) of the equivalent fuel was kept within 18% of the planned value, with majority of the test points within a few percent. The lowest value for U/L FLR originally planned was 3.2. Lowest U/L FLR successfully tested was 3.37. Both sets of numbers are well within the past experience for satisfactory low-Btu fuel combustion.
6. Highest overall equivalence ratio planned was about 0.6 and was applicable to the two test points with Case 2 gas. The highest overall equivalence ratio tested was 0.5. For high overall equivalence ratio (ratio between the actual fuel air ratio and the fuel air ratio at stoichiometric condition), there is a concern that the primary zone may be too rich for CO and unburned hydrocarbon (UHC) burn out. However, the combustor exit temperatures for the Case 2 gas test points are within the range where CO and UHC were measured at 10 ppm or less.

7. Equivalent fuel with LHV as low as 75 Btu/SCF (16% below the planned value) found to burn successfully. However, combustor exit temperature in this case was 16% lower than planned value. The blended fuel flow rate was lower than what it should be for simulating the combustor exit temperature as planned and the overall equivalence ratio was only 0.37. It is not clear if this fuel can still burn without any CO emission problem if the overall equivalence ratio has to be raised to attain a higher combustor exit temperature.
8. Combustion dynamics were within the acceptable limits.
9. The gas turbine combustor liner temperature and flow distribution were satisfactory.
10. Combustor pressure drop was consistent with design requirements.
11. The combustor operated satisfactorily with performance as designed.

The results of the combustion test showed that F-T tail gas with a low-Btu or heating value could be used as fuel to a GE Frame 6FA gas turbine combustor.

Task 2.5: F-T Product Upgrading

The scope of studies for upgrading the F-T products was extensive. The unique and contaminant-free properties of F-T products allow consideration of a number of upgrading processes. A summary of the upgrading processes considered in Phase II of the EECP is shown in **Figure 8**. The F-T liquid streams from the LaPorte AFDU test conducted in November 2000 were the feedstocks for the upgrading. These streams included a wide boiling point range of light hydrocarbons and waxes that were fractionated and blended into naphtha, diesel, and wax products. These products were processed by the following technologies:

- Naphtha hydrotreating
- Steam pyrolysis of the hydrotreated naphtha
- Diesel hydrotreating
- Wax finishing to obtain wax for food and pharmaceutical applications
- Wax hydrocracking to convert wax to naphtha and diesel

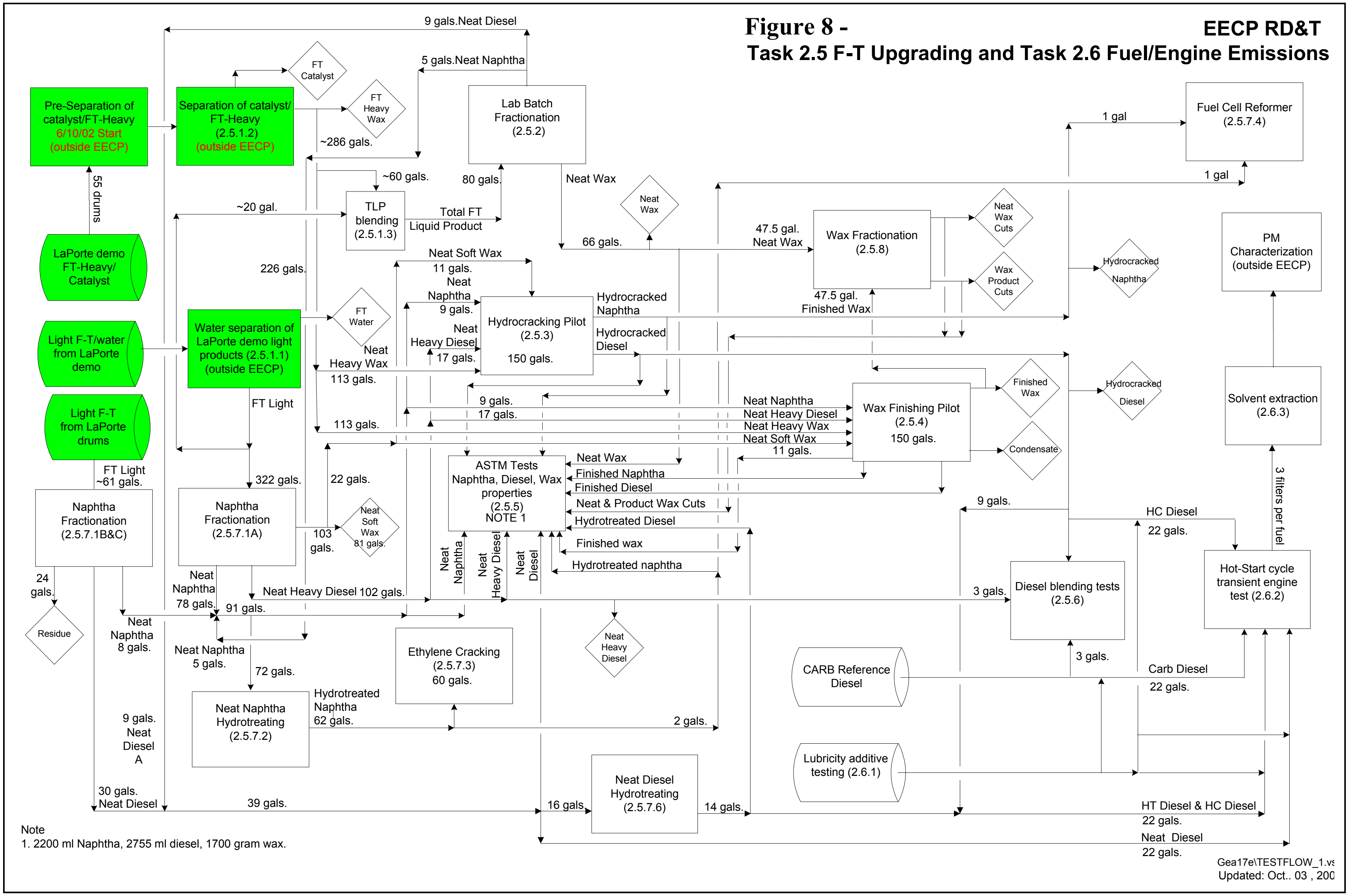


Figure 8 -

EECP RD&T

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

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

Gea17e\TESTFLOW_1.vs
Updated: Oct.. 03 , 200

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks. 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 EECP Task 2.5 and Task 2.6 risks were mitigated by demonstrating that the products derived from the upgrading of the total F-T synthesis liquid product can meet or exceed current product specifications. The EECP Phase II F-T naphtha feedstock component to produce ethylene and propylene or hydrogen fuel from a fuel cell reformer, diesel transportation fuels, and specialty food-grade wax products all meet the appropriate standards.

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 demonstration used the primary filtration system developed by Rentech and TES. The F-T heavy product (wax) from this demonstration filter system contained more than the ten ppmw of the F-T iron catalyst that the pilot plants are designed to handle. The presence of catalyst in a concentration greater than ten 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 RD&T Subtask 2.5.3 entitled "Hydrocracking Pilot" and the Phase II RD&T Subtask 2.5.4 entitled "Wax Finishing Pilot". The presence of greater than ten ppmw catalyst in the feed slates to these pilot plants can cause the termination of these pilot plant operations due to pressure drop problems, flow maldistribution 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 RD&T Subtask 2.5.4 entitled "Wax Finishing Pilot" catalyst carry over from feed into the finished wax product could result in failure to attain the Saybolt color specification for the food grade wax.

Major Findings: F-T Product Upgrading

Testing during Phase II RD&T Task 2.5 determined 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 showing 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 RD&T Task 2.5 are illustrated in **Figure 8**.

One objective of the 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 to overcome is that the EECP have a favorable economic return on investment. In order to achieve favorable economics, the finished product lines 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 contents, low aromatic contents, and high hydrogen contents. 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 may be difficult to achieve a premium value or a large market share for the neat transportation fuels produced from the EECP. However, the F-T fuels can serve as blend stocks to meet or improve diesel quality or, when blended as supplemental supply to refinery cracked diesel, to increase diesel supply.

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 demonstration F-T heavy product stream, into a high cetane quality transportation diesel since the specialty waxes market is very small. 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 hydrocracked F-T naphtha product is expected to be a desired feed component for thermal or ethylene crackers in a chemical plant for the production of ethylene and propylene and as a hydrogen reformer feed for 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 is 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, which is considered to be similar in composition, is commercially proven.

Neat and hydrocracked F-T diesel blending tests with a CARB-like diesel fuel were conducted in Subtask 2.5.6 as shown in **Figure 9**. The hydrocracked F-T diesel performed well in diesel blending test product evaluations as a direct blending component in transportation diesel. The two test fuels, the neat F-T diesel and the hydrocracked 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 the cetane number response shown in **Figure 10**, pour point as shown in **Figure 11**, cloud point as shown in **Figure 12**, lubricity as shown in **Figures 13 and 14**, viscosity as shown in **Figure 15**, and storage stability as shown in **Figure 16**. The results of the Subtask 2.5.6 product evaluations were considered to mitigate the technical and economic risks initially identified with direct blending of F-T diesels into transportation fuels.

Figure 9 – Flow of Work for Subtask 2.5.6 Diesel Blending Testing

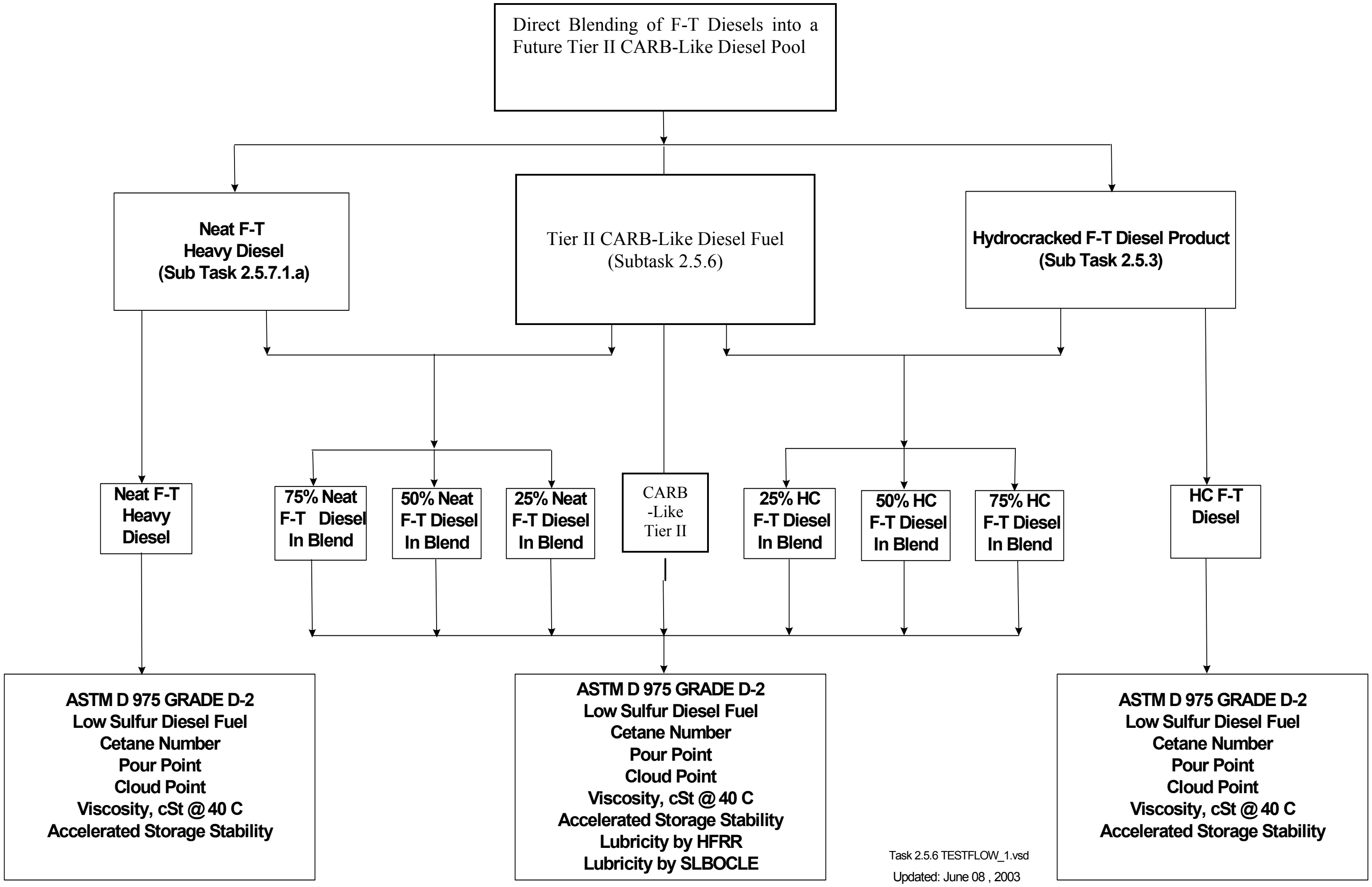


Figure 10 – Cetane Number Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

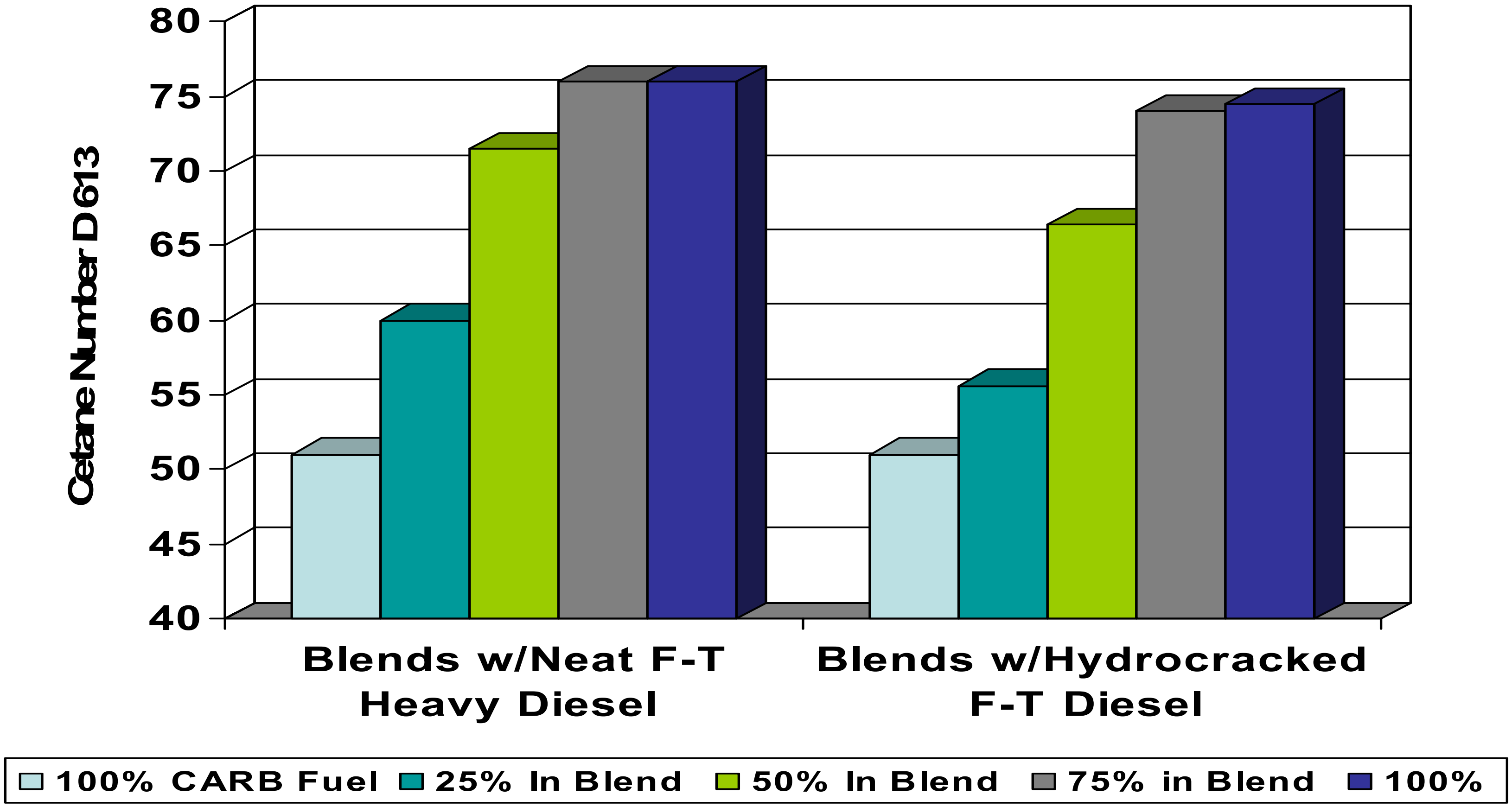


Figure 11 – Pour Point Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

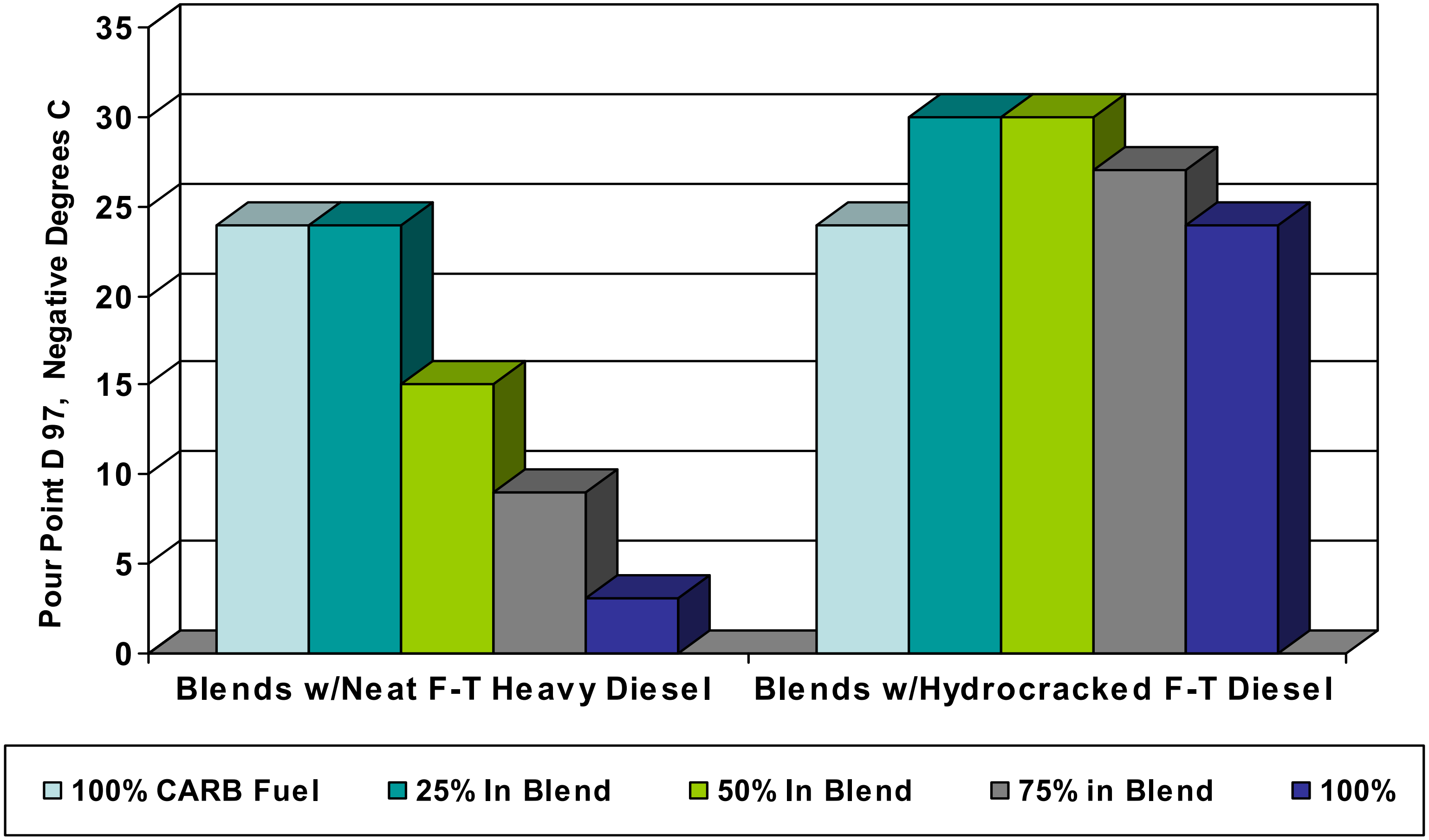


Figure 12 – Cloud Point Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

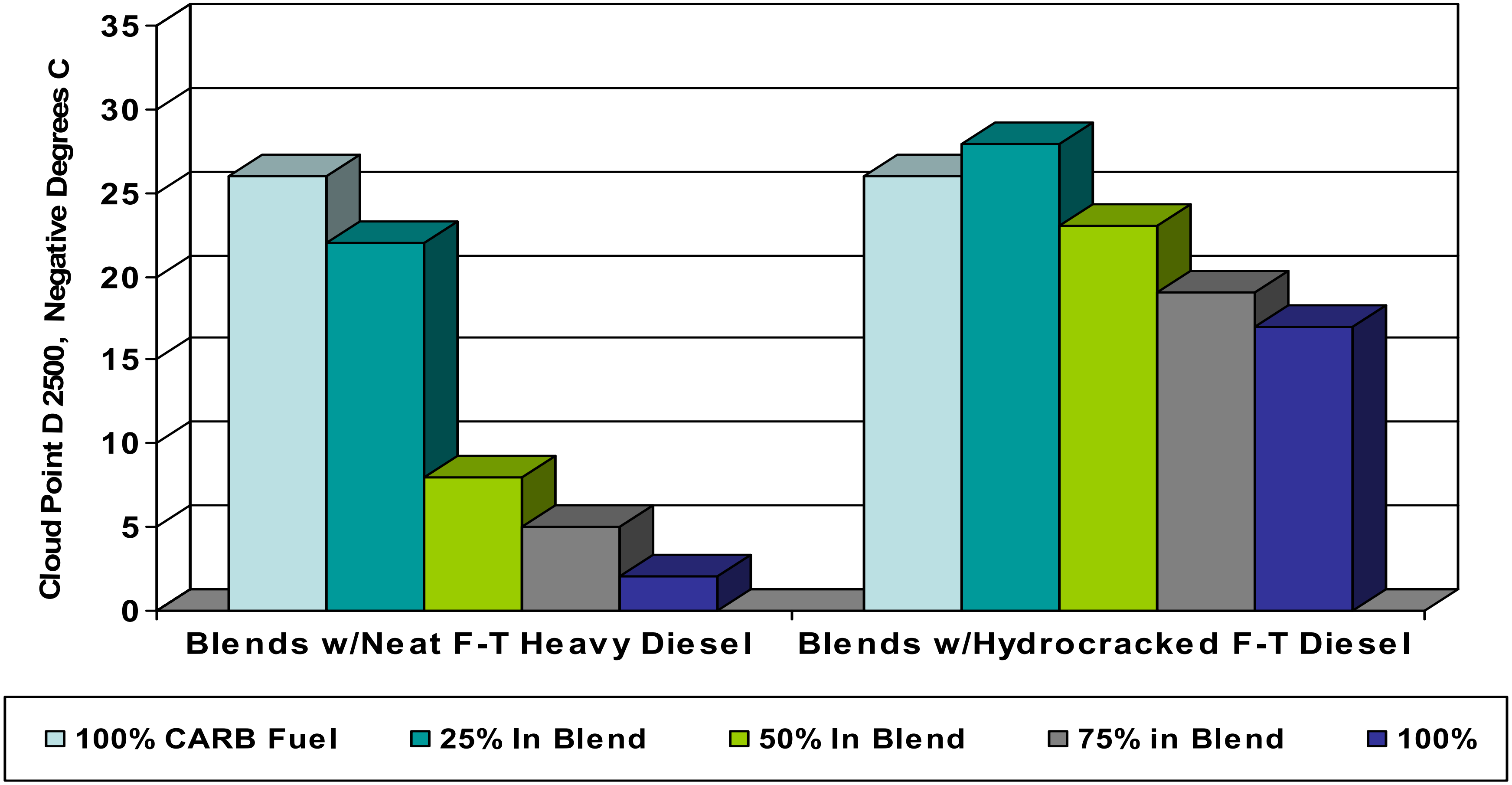


Figure 13 – High Frequency Reciprocating Rig (HFRR) Lubricity Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

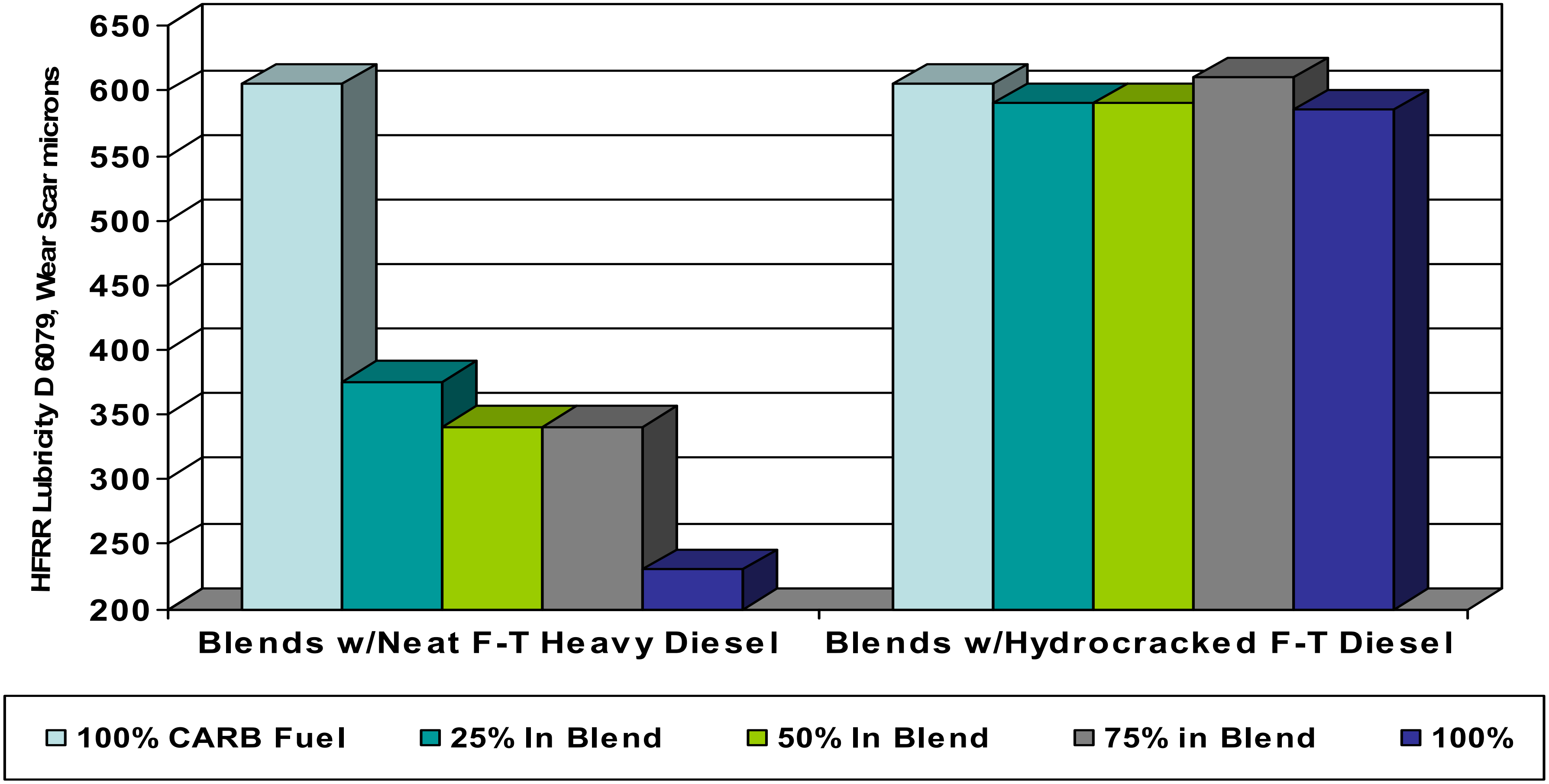


Figure 14 – Scuffing Load Ball On Cylinder Lubricity Evaluator (SOBOCLE) Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

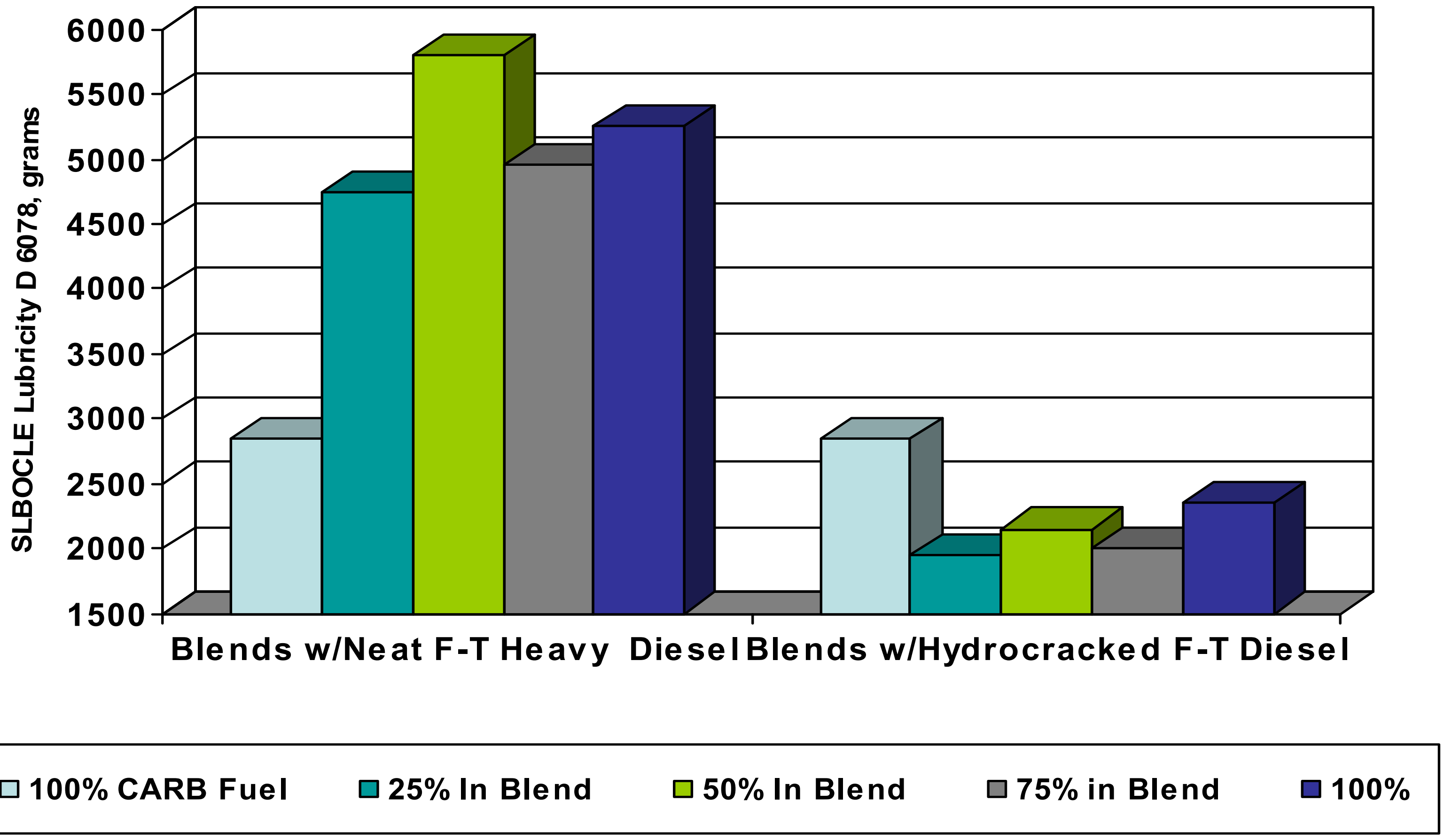


Figure 15 – Viscosity at 313K (40^{o}C/104^{o}F) Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

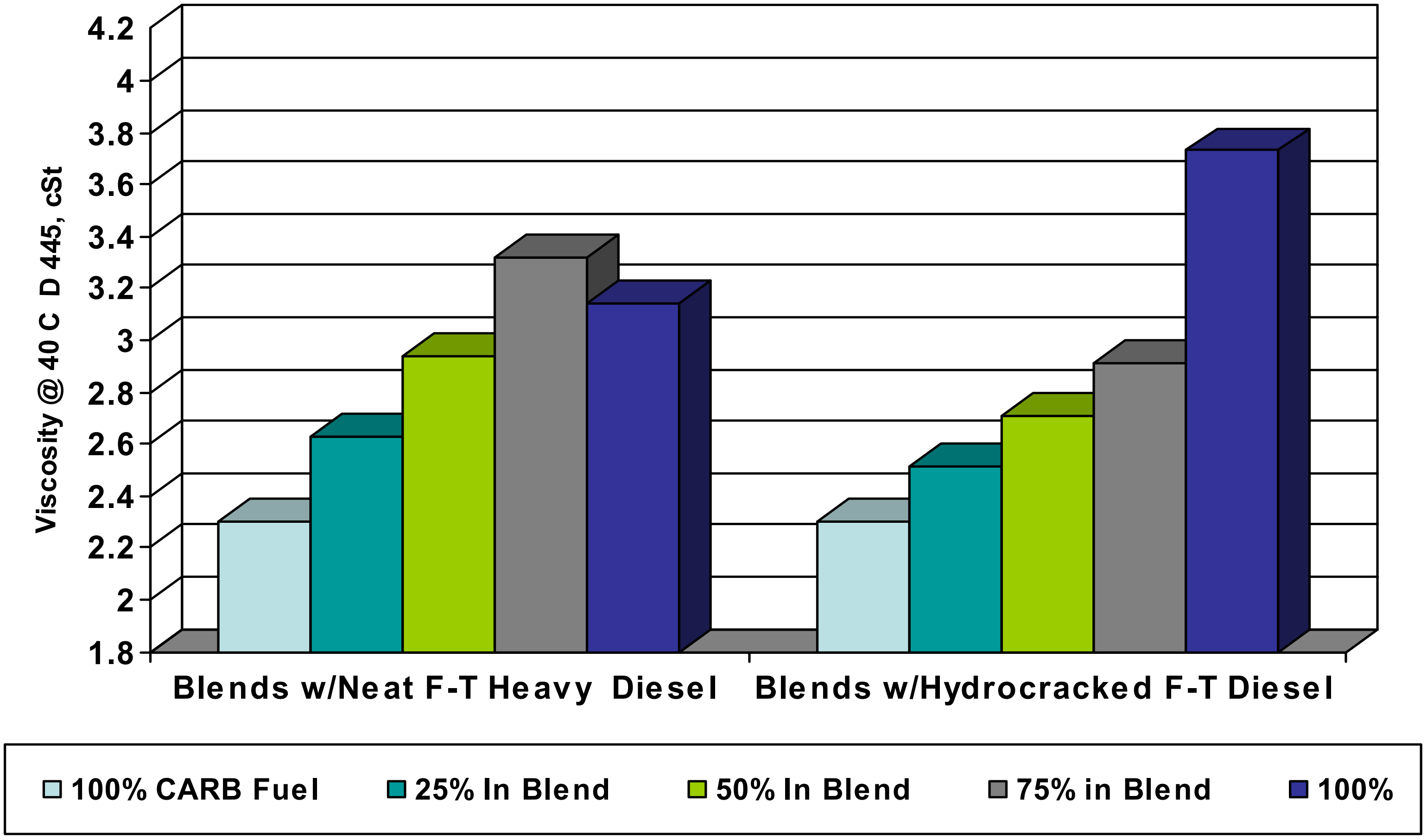
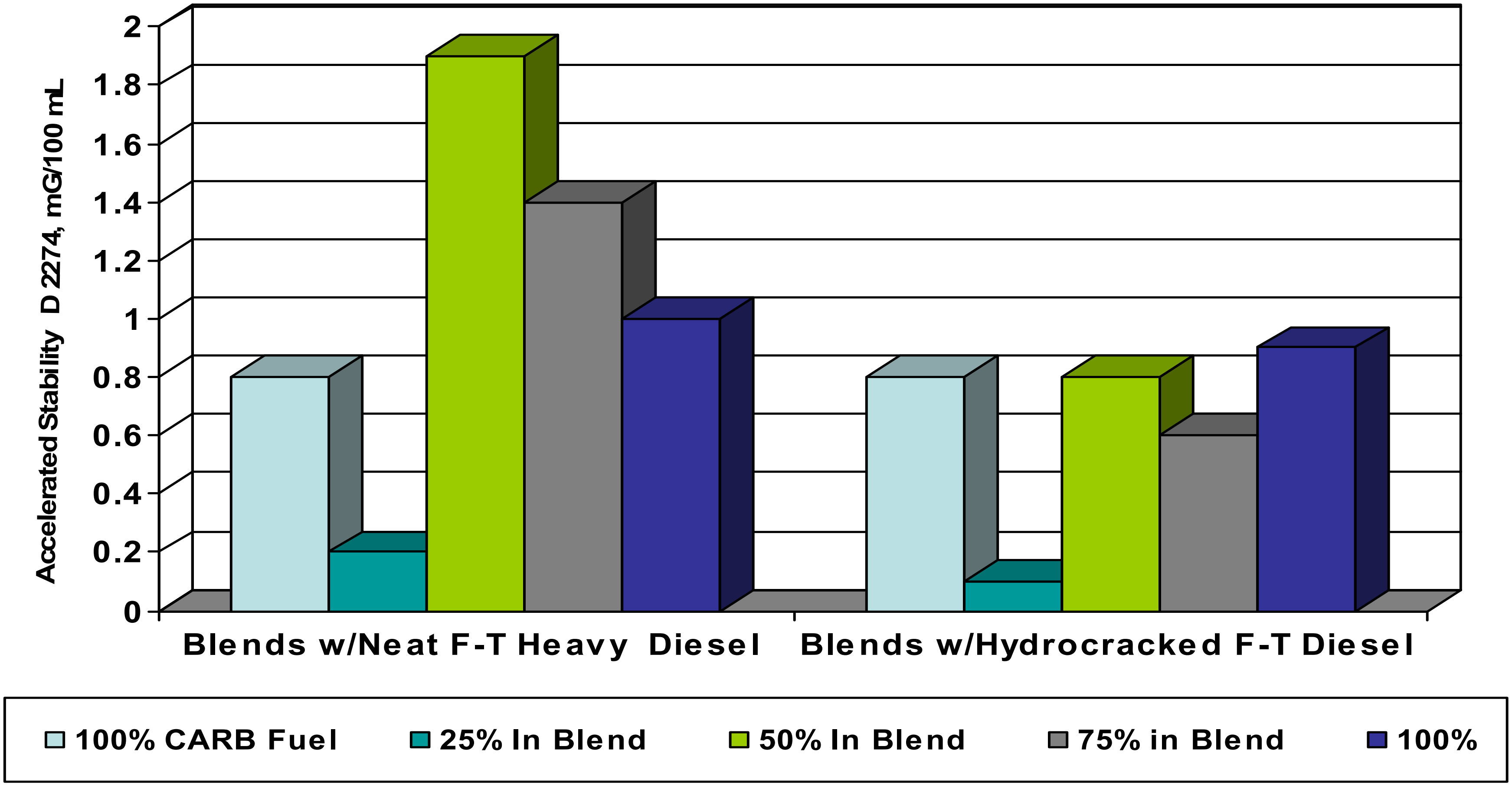


Figure 16 – Accelerated Stability Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



The hydrocracked F-T diesel performed well as a test fuel and as a blend component in a test fuel prepared with hydrotreated F-T diesel in the product. The hydrocracked F-T naphtha product did not perform to expectations as a fuel cell reformer feed for the generation of hydrogen fuel.

The refined EECP F-T synthetic paraffinic high-melt wax product obtained after wax finishing is expected to be similar to petroleum-based paraffin wax in chemical composition, but exhibits a higher melting point and hardness as a result its anticipated higher molecular weight. 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, cable compounds, graphic arts applications, printing inks, plastics lubrication, color concentrates, and as a component for many wax blends. The high-melt characteristics of the wax product obtained from wax finishing will target U.S. Food and Drug Administration (FDA) regulations for food-grade applications.

The wax finishing pilot plant test program demonstrated that it is not possible to simultaneously process the naphtha/diesel and the wax feeds 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 wax product from the distillation bottoms. 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 that is equipped with a vacuum distillation column provided that the vacuum is deep enough to enable separation of products at approximately 436K (325°F). 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 – 13,891 kilopascals (kPa) (2,000 pounds per square inch-gauge [psig])
Hydrogen Treat Gas Rate - 674 Nm^3/m^3 (4,000 scf/bbl) H_2/oil
Liquid Hourly Space Velocity (LHSV) – 0.5

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. The desired quantity of hydrotreated F-T naphtha was generated for end-use that was found to perform well as a fuel cell reformer feed generating the highest yield of hydrogen fuel among the four feeds tested. The hydrotreated F-T naphtha also performed well as an ethylene cracker feed generating commercial ethylene and propylene with yield predictions from the licensor model tuned with pilot plant data that were in agreement with its feed composition.

Task 2.6: F-T Diesel Fuel/Engine Performance and Emissions

The scope of Task 2.6 consisted of fuel lubricity property testing, fuel response to lubricity additives, and hot-start transient emission testing using a neat F-T diesel product, a hydrocracked F-T diesel product, a blend of hydrotreated and hydrocracked F-T diesel products, and a Tier II CARB-like diesel reference fuel. Testing was done to specifically demonstrate that the F-T diesel fuels produced through upgrading will have superior emission characteristics compared to conventional fuels.

The risks to the EECP from F-T product upgrading and fuel/engine performance, and emissions were mitigated by conducting extensive experimental studies. These studies demonstrated that the following products, derived from the upgrading of the total F-T synthesis liquid product, can meet or exceed current specifications:

- An acceptable naphtha feedstock component for a chemical plant steam cracker to produce ethylene and propylene
- A naphtha feedstock component for hydrogen fuel generation for a fuel cell reformer
- Finished diesel as a transportation fuel
- Specialty food-grade wax products

Major Findings: F-T Lubricity Testing

The lubricity additive testing mitigated the potential risk of engine failure from the use of F-T diesels. The American Society for Testing and Materials (ASTM) D6079 lubricity test (Lubricity of Diesel Fuel by HFRR) was conducted on four fuels (neat F-T diesel product, a hydrocracked (HC) F-T diesel product, a blend of hdyrocracked (HC) and hydrotreated (HT) F-T diesel products, and a Tier II CARB like diesel). Fuel candidate lubricity property testing was performed first to confirm the need for additive use. Southwest Research Institute (SwRI) then conducted trials with two commercial lubricity additives on each of the four diesels at target additive concentrations of 15 parts-per-million (volume) [ppmv], 100 ppmv, and 200 ppmv. Two commercial lubricity additives designated as Additive 1 and Additive 2 for the Subtask 2.6.1 test program were utilized in these Task 2.6 product evaluations.

The HFRR wear scar width data presented in **Figure 17** show the results of the initial lubricity inspection done on the neat F-T diesel product, the HC F-T diesel product, the blend of HC and HT F-T diesel products, and the Tier II CARB-like diesel. The data in Figure 17 confirm that the neat F-T diesel passes lubricity inspection without additive treatment with an HFRR 230 micron wear scar width that is well below the HFRR wear scar width of less than 450 microns considered acceptable by United States and European standards. The HC F-T diesel product, the blend of HC and HT F-T diesel products, and the Tier II CARB-like diesel all exhibited failing HFRR wear scar widths in the 600 micron to 640 micron range. The HFRR wear scar width data presented in Figure 17 show the response of the neat F-T diesel product, the hydrocracked F-T diesel product, and the blend of HC and HT F-T diesel products to treatments with the commercial lubricity Additive 1 at target concentrations of 15 ppmv, 100 ppmv, and 200 ppmv. The HFRR wear scar width was reduced for each of the three F-T diesels as the Additive 1 concentration was increased. The 640 HFRR wear scar width without additive for the HC F-T diesel product decreased from 450 micron to 220 micron as the Additive 1 concentration was increased from a target concentration of 100 ppmv to 200 ppmv. The 600 HFRR wear scar width without additive for the blend of HC and HT F-T diesel products decreased from 570 micron to 280 micron as the Additive 1 concentration was increased from a target concentration of 100 ppmv to 200 ppmv. Base on the HFRR wear scar width data presented in Figure 17 from the Additive 1 trials with the HC F-T diesel product and the blend of HC and HT F-T diesel products, an Additive 1 treatment at 175 ppm concentration was selected for qualifying these two F-T diesels as test fuel candidates for the product evaluations. The data presented in **Figure 18** shows the fuel candidates passing lubricity. The neat F-T diesel product passed with an HFRR wear scar width of 230 microns without additive. A passing HFRR wear scar width of 415 microns was obtained on the HC F-T diesel product at an Additive 1 concentration of 175 ppmv. A passing HFRR wear scar width of 400 microns was obtained on the blend of HC and HT F-T diesel products at an Additive 1 concentration of 175 ppm. A passing HFRR wear scar width of 385 microns was obtained on the Tier II CARB-like diesel at an Additive 1 concentration of 175 ppm.

HFRR wear scar widths obtained with each of the three F-T diesels during the commercial lubricity Additive 2 trials at target concentrations of 15 ppmv, 100 ppmv, and 200 ppmv are not discussed here but the work is documented in the Task 2.6. Topical Report. The HC F-T diesel product and the blend of HC and HT F-T diesel products which failed lubricity without additive treatment did not have a significant response to treatment with the commercial lubricity Additive 2. A passing HFRR wear scar of less than 450 microns could not be obtained with Additive 2 treatment of the F-T diesels in the 15 ppm to 200 ppm concentration range.

Figure 17 – F-T Diesel Response to Additive

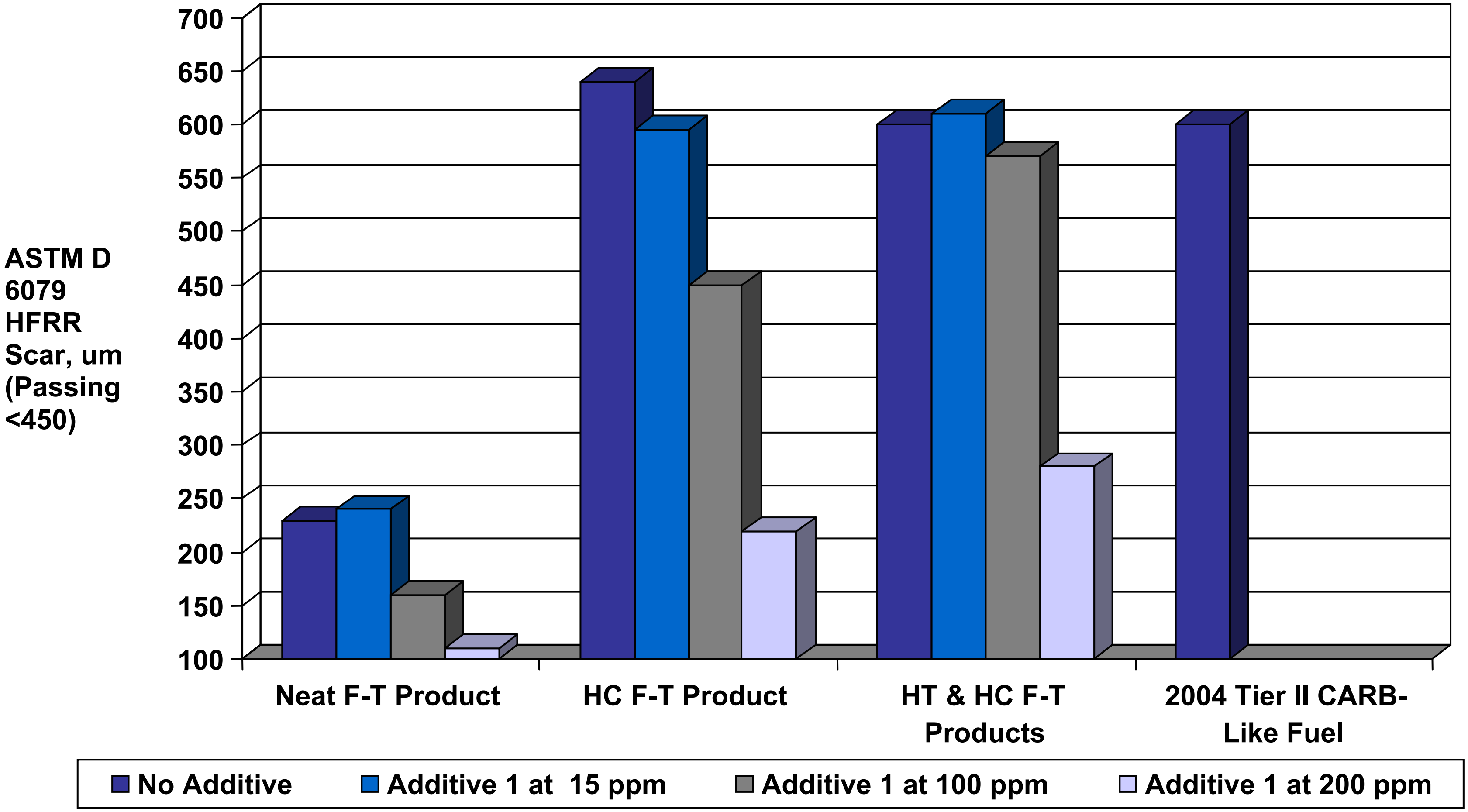
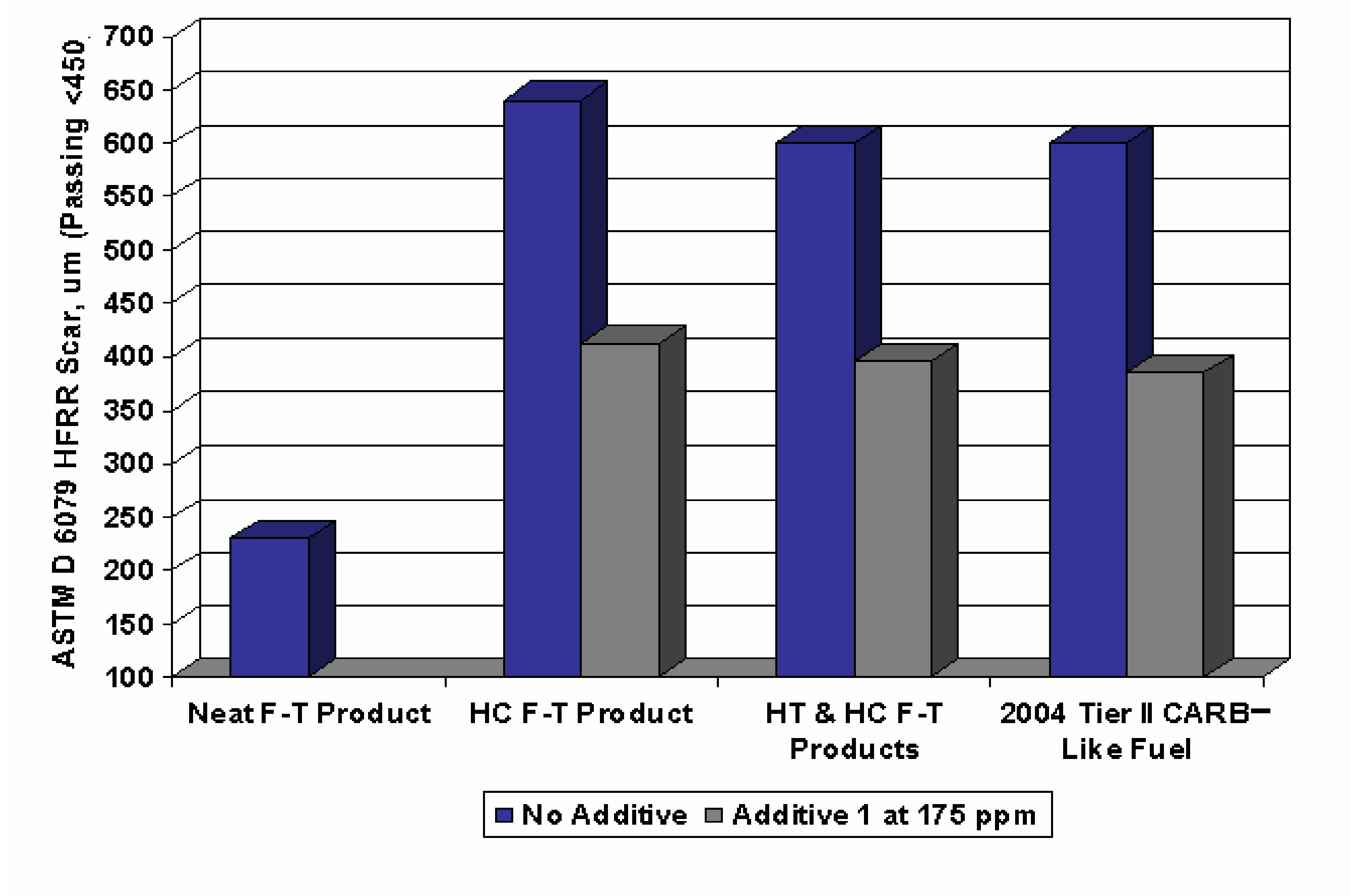


Figure 18 –Test Fuel Candidates Passing Lubricity



Major Findings: Hot-Start Cycle Transient Engine Test

The hot-start cycle transient engine test mitigated the potential economic risks identified in the Phase II RD&T Plan dealing with obtaining a premium price in the market place for the anticipated superior performance of these F-T diesel fuels. Work conducted under Subtask 2.6.2 determined whether the superior properties of low sulfur, low aromatics, and high cetane exhibited by the F-T diesels produced hot-start cycle transient engine test performances that yield lower fuel emissions than conventional diesel fuels. The results of thee tests yielded sufficient emissions information to verify that the F-T diesels provide significant reductions in emissions.

The hot-start transient emission data (see **Figure 19**) shows the neat F-T diesel reduced NO_x, particulate matter (PM), hydrocarbons (HC), CO, and the Soluble Organic Fraction (SOF) from total PM by 4.5 %, 31 %, 50 %, 29 % and 35%, respectively, when compared to a Tier II CARB-like diesel. The HC F-T diesel product also reduced NO_x, PM, HC, CO and SOF by 13%, 16%, 38%, 17% and 21%, respectively, when compared to the Tier II CARB-like diesel. The blend of HC and HT F-T diesel products also reduced NO_x, PM, HC, CO and SOF by 13%, 17%, 63%, 21% and 39%, respectively, when compared to a Tier II CARB-like diesel. The fuel/engine performance and emissions of the three F-T diesels exceeded the performance of a Tier II CARB-like diesel fuel.

Major Findings: Solvent Extraction of Particulate Matter

The solvent extraction of particulate matter tests were conducted to extract the soluble organic fraction (SOF) from the PM collected during the three hot-start transient cycles conducted each day on each diesel test fuel candidate. SwRI used solvent extraction laboratory procedures to quantify the amount of SOF present in the diesel total PM for each of the four diesel fuel candidates. The solvent extraction procedure was performed on three hot-start transient cycle filters per one-day testing of each diesel test fuel candidate. The SOF from total PM was determined for the three F-T diesel fuels and the Tier II CARB-like diesel reference fuel. The data presented in Figure 19 shows the percent reduction in the SOF from total particulate for each of the three F-T diesels compared to the Tier II CARB-like diesel.

Major Findings: Ethylene Cracking

The hydrotreated naphtha was steam cracked using a pyrolysis pilot unit at the KBR Technology Center in Houston, Texas. KBR has made commercial predictions of cracking HT F-T naphtha that were compared to KBR reference petroleum naphtha feedstock. **Figure 20** shows that F-T naphtha is an excellent feedstock for ethylene production.

Figure 19 –Hot-Start Transient Emissions Results

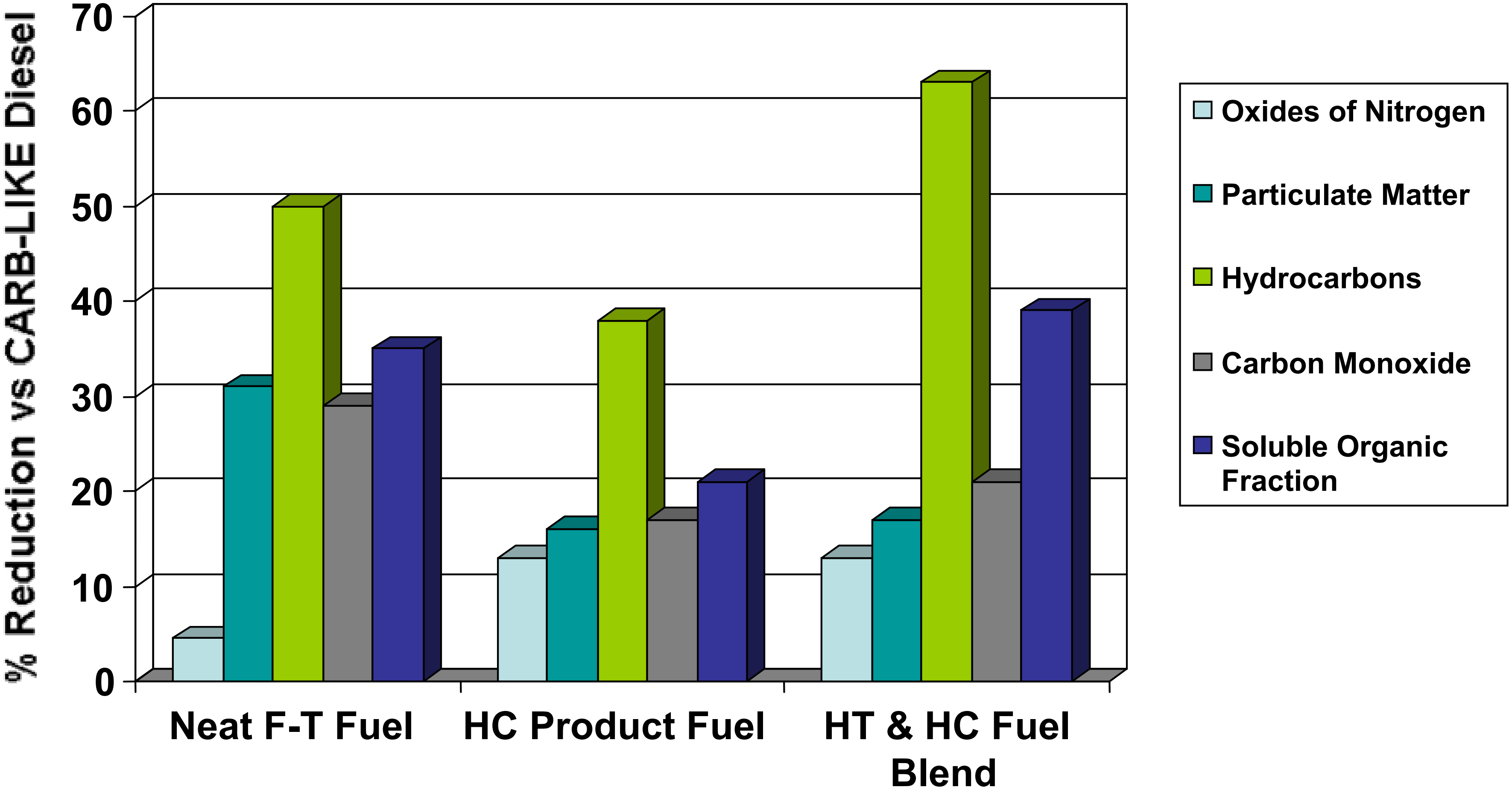
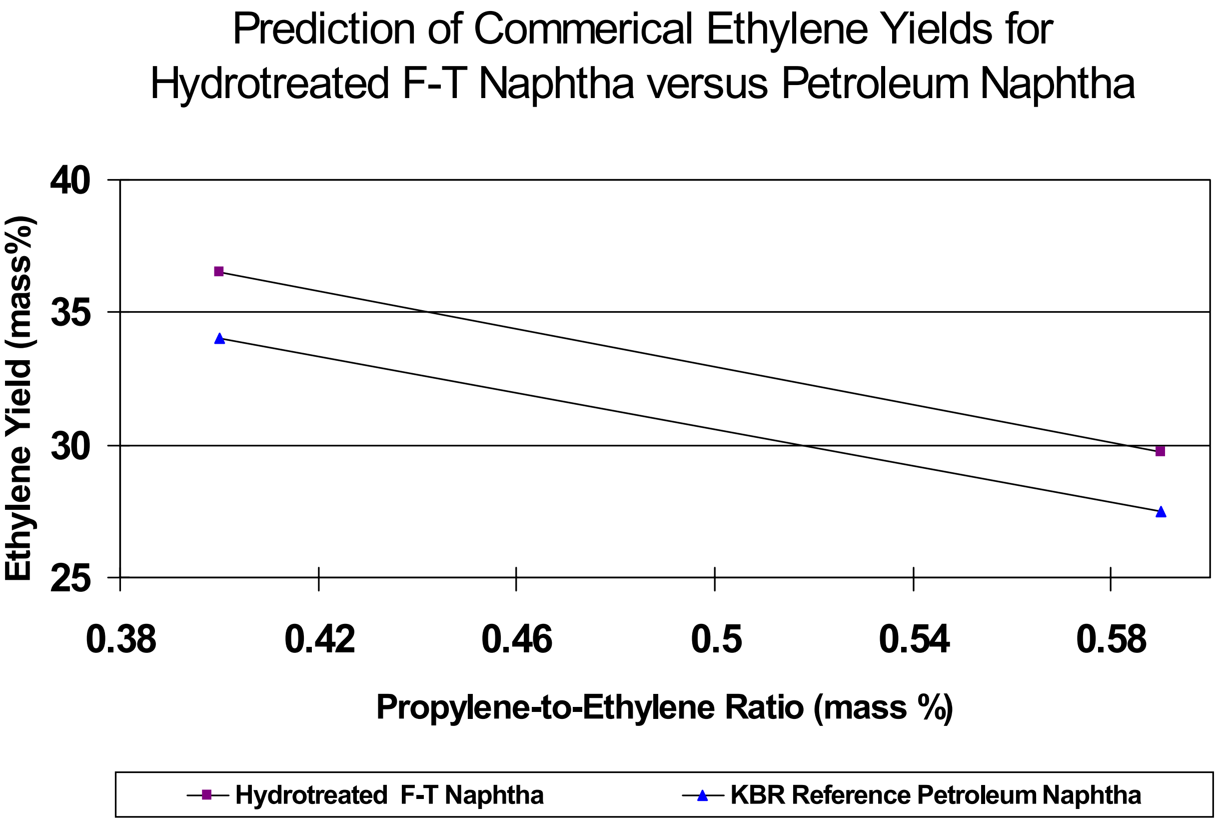


Figure 20 -


Prediction of Commerical Ethylene Yields for
Hydrotreated F-T Naphtha versus Petroleum Naphtha
Ethylene Yield (mass%)
40
35
30
25
0.38
0.42
0.46
0.5
0.54
0.58
Propylene-to-Ethylene Ratio (mass %)
Hydrotreated F-T Naphtha
KBR Reference Petroleum Naphtha

Task 2.7: Petroleum Coke Analysis

This scope of this task was to analyze typical refinery petroleum coke samples to determine the applicability of the EECP concept to the refinery industry.

Petroleum coke samples were analyzed at ChevronTexaco's Montebello Technology Center (MTC) in Montebello, California. **Table 5** summarizes the differences between the three samples. Samples from the two ChevronTexaco refineries, identified as Refinery A and Refinery B, have higher carbon and hydrogen and lower sulfur amounts by weight percent (wt%) basis compared to the Motiva Port Arthur petroleum coke. Also, the gross heating value of the Motiva Port Arthur petroleum coke is less than that of the two ChevronTexaco Refineries.

In Phase I, a typical refinery site, Motiva Port Arthur, was identified as the potential EECP site. As a result of the merger between Texaco and Chevron, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. No new site as been identified for the proposed EECP. Therefore, it was decided to compare the Motive Port Arthur petroleum coke to petroleum coke samples from two ChevronTexaco refineries.

Table 5

Petroleum Coke Characteristics

Charge to Gasifier	**EECP Phase I Design Conditions**	**Motiva Port Arthur (Typical)**	**ChevronTexaco Refinery A**	**ChevronTexaco Refinery B**
Ultimate Analysis, wt%, dry basis				
Carbon	88.61	88.61	89.43	89.74
Hydrogen	2.80	2.80	4.14	4.29
Nitrogen	1.10	1.06	1.05	1.08
Sulfur	8.00 Max	7.30	5.08	4.60
Oxygen	0.00	0.00	0.00	0.00
Ash	0.40 Max	0.23	0.39	0.29
Moisture as Received, wt%	9	8.37	10.07	9.31
Chloride Content, parts per million (ppm) by weight, dry basis	50 max	20	<5	23
Gross Heating Value, KJ/KG (Btu/lb), Dry Basis	34536 (14,848)	34536 (14,848)	35,504 (15,264)	35,658 (15,330)

Major Findings: Petroleum Coke Analysis

The differences in the petroleum coke samples will result in the team updating the EECP gasification design conditions. For example, the lower sulfur content of the petroleum coke samples from the two ChevronTexaco refineries can lead to a reduction in the capital costs of the sulfur recovery unit. The higher hydrogen to carbon ratio of the two ChevronTexaco refinery petroleum coke samples should result in slightly higher hydrogen to carbon monoxide ratio in the synthesis gas. This could improve the yield from the F-T synthesis reactor. The lower sulfur content and higher hydrogen content could improve the overall EECP economics. However, any update of the design conditions must be site specific. After a suitable site has been selected, the team will initiate an update of the concept design basis. The location for the proposed EECP will be based on the availability of a low cost feedstock such as petroleum coke or coal and integration potential with the proposed EECP. The gasification process should handle any refinery petroleum coke; however, each refinery site will require an up date of the design basis due to varying yields of specific components and the quantity of sulfur contained in the petroleum coke.

Task 2.8: Carbon Dioxide Stripping From Methyldiethanolamine (MDEA)

The scope of this task was to validate design assumptions and performance projections used for the Phase I conceptual design for N_2 stripping of CO_2 from MDEA.

Various methods were evaluated to develop the data necessary to properly design a commercial stripping column using nitrogen at medium pressure to remove CO_2 from MDEA at medium pressures. The most cost effective approach was determined to be the development of equilibrium data.

DB Robinson & Associates Ltd. (DBR) was selected to collect equilibrium data to verify or validate an existing commercially available computer simulation model. If required, the new equilibrium data could be incorporated into the computer simulation package.

The experimental procedure for each data point was carried out according to the following steps:

1. An MDEA solution was prepared using a balance. A sample, titrated with 0.1 N standard hydrogen chloride (HCl), was used to check the concentration of the amine.
2. Nitrogen was added into the cell to bring the pressure to 101.4 kPa (14.7 psia). The nitrogen was circulated for 5 minutes using the magnetic pump to reduce the oxygen content in the charged MDEA solution.
3. Nitrogen was added into the cell again to 101.4 kPa (14.7 psia). A 0.5 g liquid sample was withdrawn for titration with 0.1 N HCl. The resulting amine solution was verified to within 0.1 wt% of the required value.
4. After establishing the correct amine solution in the cell, CO_2 and/or H_2S gases were charged into the cell. The gas was circulated for 10 minutes. The cell was

then heated to the desired temperature. The pressure was adjusted with nitrogen to about 2,413 kPa (350 psia).

5. The system was equilibrated at a pressure of 2,413 kPa (350 psia) and the specified temperature by vapor circulation for at least 10 hours.

After equilibration, samples of vapor were taken and injected directly into the gas chromatograph (GC) for N_2, H_2S, and/or CO_2 concentration determination. The GC was calibrated at concentrations close to the experimental value for each system. Samples of 2 to 3 grams of the liquid phase were charged to a sample bomb that had been loaded with a known amount of monoethanolamine (MEA) solution. The MEA solution was used to fix the acid gases in the withdrawn liquid sample at ambient conditions. The acid gas concentrations in the amine solution were determined by GC as well as by the titration method.

Major Findings: Carbon Dioxide Stripping From MDEA

The following general conclusions were drawn from this test program evaluation:

1) The EECP design point for H_2S had a partial pressure error of –21 % when comparing DBR data to the computer simulator estimates. If equipment design is based on computer simulations, additional H_2S is predicted to evolve from the rich MDEA in the nitrogen stripper which results in the need for additional re-absorption of H_2S downstream. Thus, the down stream equipment will be slightly oversized to handle this additional acid gas. This is a conservative and generally accepted approach. The EECP design point for CO_2 has a CO_2 partial pressure error of – 4 % when comparing DBR data to the computer simulator estimates. This means that there will be slightly less CO_2 in the overhead stream from the nitrogen stripper and subsequently less going to the combustion turbines. This difference is judged as relatively insignificant and may be easily handled by normal process design margins.

The difference between the DBR data and the computer simulation estimate was judged acceptable, and the current AGR design is considered reasonable.

2) There appears to be close agreement between DBR data and the computer simulation package results. For the CO_2 only system, computer simulation over-predicts vapor phase CO_2 partial pressures at relatively high CO_2 loading in MDEA, and under-predicts vapor phase CO_2 partial pressures at low loadings of CO_2 in MDEA.

3) The computer simulation package over-predicts vapor phase H_2S partial pressure at relatively high H_2S loading in MDEA, but under-predicts vapor phase H_2S partial pressures at low H_2S loadings in MDEA.

4) The trend for CO_2 vapor phase concentration shows a closer agreement between experimental values with computer simulations.

5) H_2S partial pressure deviations are mostly positive for combined H_2S and CO_2 systems. The trend implies that the use of computer simulator predictions would lead to higher quantities of H_2S in the gas phase than actually expected. Similarly, CO_2 partial pressure deviations are mostly negative which would lead to lower CO_2 quantities in the gas phase than actually expected.

In summary, computer simulations for nitrogen stripping of MDEA aqueous solutions for a combined H_2S and CO_2 system predicts higher H_2S and lower CO_2 vapor phase compositions at relatively high acid gas MDEA loadings, but low H_2S and CO_2 vapor phase compositions at lower acid gas MDEA loadings when compared to DBR experimental data.

For the nitrogen stripper design proposed for the conceptual EECP MDEA AGR Unit, H_2S vapor phase composition error between DBR data and computer simulation is less than 21% in magnitude. The computer simulation package predicts higher H_2S removal in the nitrogen stripper than actually occurs. This makes downstream re-absorption equipment oversized to handle the increased amine circulation required to meet the H_2S content in the re-absorber overhead stream that goes to the combustion turbine. This is generally conservative from an equipment design standpoint and an accepted design practice.

The magnitude of CO_2 vapor phase composition error is less than 5% and judged within normal design margins. The flow rates for the stripping nitrogen should remain relatively unchanged from what is predicted by the simulation model.

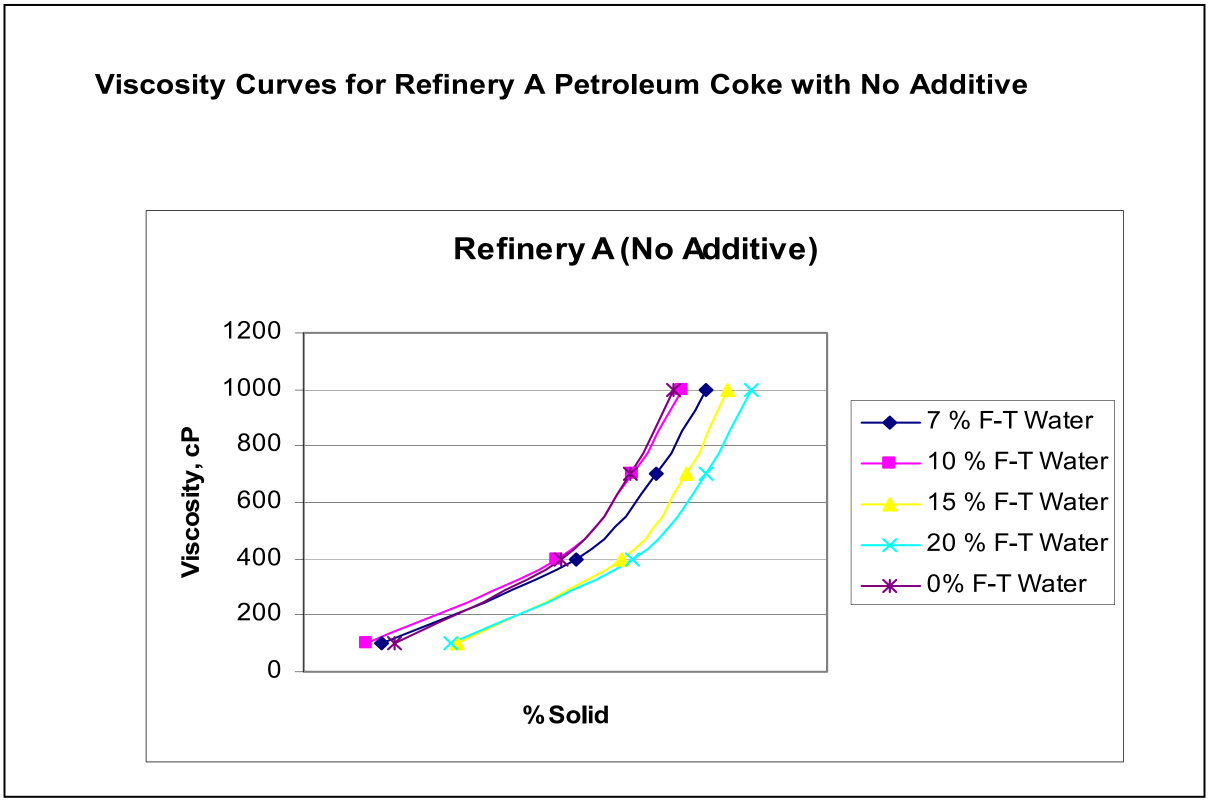
Task 2.9: Integration

Integration within the EECP was considered to be very important to achieve an economical design concept. The inclusion of F-T offers an additional integration opportunity to increase efficiency and reduce cost. The incremental cost of F-T is much less than the base cost of a gasification-based power generation facility. However, there are some characteristics of F-T that can reduce the total cost of an integrated gasification Fischer-Tropsch plant. Two integration aspects that were studied were (1) the use of the F-T by-product water to replace a portion of the water required to make the slurry feed to the gasifier and (2) the use of the F-T spent catalyst as a portion of the fluxant fed to the gasifier.

The scope of this task was to conduct tests to determine if various potential integration aspects developed in Phase I could be incorporated into the EECP concept to increase efficiency and reduce capital and operating costs.

Experimental work was conducted at the ChevronTexaco's MTC to determine the effect of the F-T by-product water on solids concentration in the slurry. As shown in **Figure 21,** F-T by-product water can be used to increase the solids content of the slurry. Increasing the solids content of the slurry directionally improves the thermal efficiency of the gasifier. In addition, successful reuse of the F-T by-product water will reduce the cost of water treatment.

Figure 21 - Slurry Concentration with F-T Water



Major Findings: Petroleum Coke Slurry with F-T Water

The following general conclusions were drawn from this test program evaluation:

- Petroleum coke from the Motiva Port Arthur refinery or the two ChevronTexaco refineries can be used to prepare slurries that meet the solids concentration, pumpability, and other characteristics required for ChevronTexaco's proprietary gasification process. In some cases, ChevronTexaco's proprietary additive may be required to meet the solids concentration and pumpability requirements.

- Petroleum coke from either of the two ChevronTexaco refineries can be used to prepare slurries that meet the solids concentration and other characteristics required for ChevronTexaco's proprietary gasification process. In some cases, ChevronTexaco's proprietary additive may be required to meet the solids concentration and pumpability requirements.

- There was no observable adverse effect on pumpability and other related flow properties due to the use of including F-T by-product water as a source of water for petroleum coke slurrying. At lower slurry concentration, addition of F-T by-product water may reduce the slurry viscosity. However, F-T by-product water has the effect of lowering the slurry's pH. The lower pH may require the addition of an appropriate neutralizing chemical, such as ammonium hydroxide, to protect the slurry tank and slurry feed system from corrosion.

- Solid concentrations can be improved by the use of a ChevronTexaco proprietary viscosity-enhancing additive while maintaining good pumpability and improved flow properties.

- The enhancement effect on slurry properties due to additive dosage was observed for petroleum coke slurries prepared with and without F-T by-product water.

- The results of the bench-scale tests confirm the absence of detrimental effects by the addition of F-T by-product water. There are few cases where the addition resulted in a favorable change in viscosity, particularly the Refinery A petroleum coke with no additive. At higher additive levels, these effects are not clearly observed with the Refinery B petroleum coke. There is insufficient data to generalize any conclusion that the addition of F-T by-product water always has a positive impact on the characteristics of the slurry. Perhaps, more rheology tests using petroleum coke from various sources would shed more light on the effects that F-T by-product water have on slurry viscosity.

Major Findings: Spent F-T Catalyst in Fluxant

The use of F-T spent catalyst as a portion of fluxant to the gasifier was also studied. The results of that study suggest that the spent catalyst, after proper preparation, could be included with the fluxant. According to a number of patents, the iron components in the gasifier feed may reduce unwanted emissions. Additionally, the inclusion of the F-T spent catalyst in the fluxant would reduce the EECP waste streams and eliminate the need for landfilling the spent catalyst.

Sending the spent F-T catalyst to the ChevronTexaco gasifier in the proposed EECP provides another option to dispose the F-T catalyst other than landfill. The small amount of spent catalyst (in relation to the amount of petroleum coke) should not negatively affect the performance of the gasification section.

Task 2.10: Environmental

Two environmental subtasks were investigated. One was the impact of disposing spent F-T catalyst. The second was the capture of CO_2 from the combustion turbine exhaust.

Disposal of F-T catalyst became more important when regeneration, rejuvenation, and reuse of the catalyst appeared to be uneconomical. One option for disposal that was considered was landfill. The landfill option is not desired because complete removal of the hydrocarbon from the catalyst renders the catalyst pyrophoric, and the retention of hydrocarbon on the catalyst represents a loss of valuable product that affects the economics of the project. However, in the event landfill is required, testing of an F-T catalyst/wax mixture was undertaken. Tests on the spent F-T catalyst/wax mixture indicated that the catalyst met specifications required for non-hazardous landfilling under current EPA ("Toxic Characteristic Leaching Procedure" [TCLP]) and the more stringent California (CA) ("Waste Extraction Test" [WET]) rules governing landfill disposal. A summary of the testing is shown in **Table 6**. A more unique option for disposal of the spent catalyst is integration with the gasifier. This integration option was discussed previously.

TABLE 6

Spent F-T Catalyst Disposal

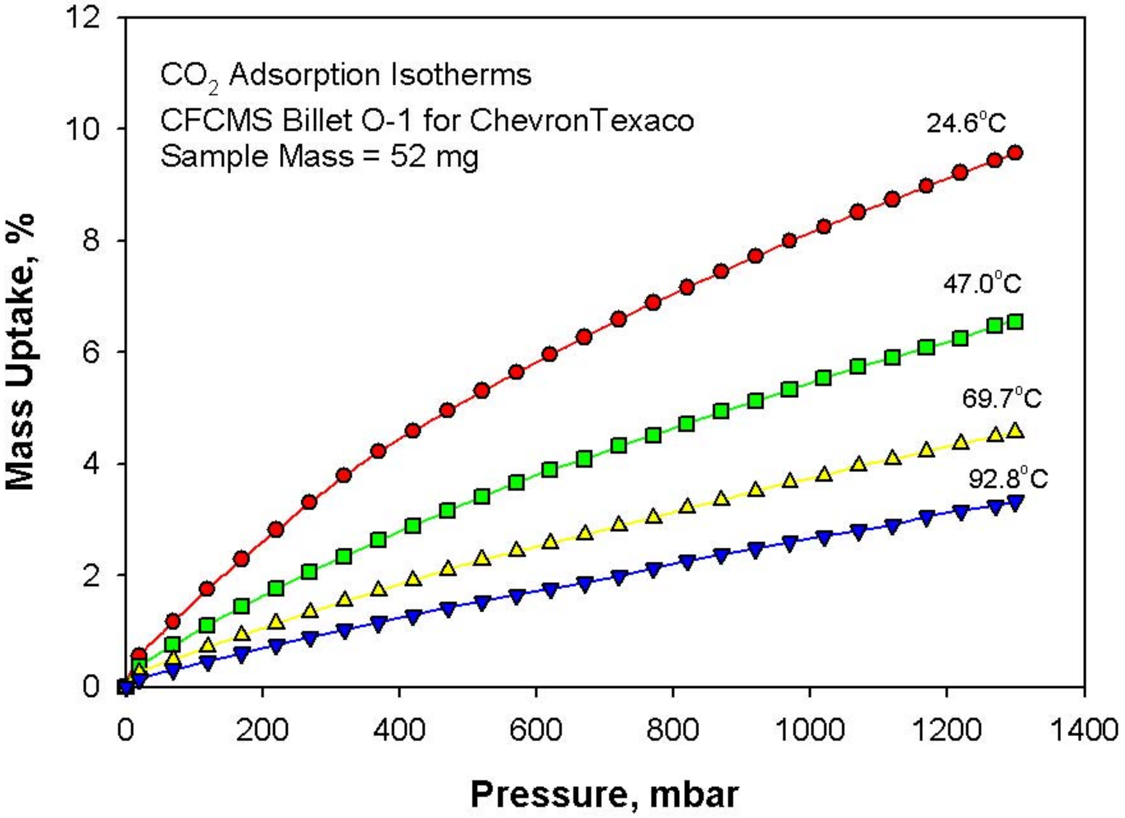
F-T Spent Catalyst Disposal Tests

Analyte	TCLP	WET	CA LIMIT
Benzene, mg/l	Not Detected	Not Detected	0.5
Toluene, mg/l	0.0037	0.018	---
Ethylbenzene, mg/l	Not Detected	Not Detected	---
Total xylenes, mg/l	Not Detected	0.011	---
Copper, mg/l	0.64	5.0	25.0 (STLC)

STLC - Soluble Threshold Limit Concentration
Tests by Del Mar Labs.

The capture of CO_2 for the combustion turbine exhaust would be an important milestone toward sequestering and reducing global emissions of carbon that would be desirable under DOE's Vision 21 Program. **Figure 22** shows some of the results from experimental work conducted by Oak Ridge National Laboratory using a proprietary electrical swing adsorption and desorption with carbon fiber composite molecular sieves (CFCMS). The results shown in Figure 22 indicate that the CFCMS is very effective at capturing CO_2 at lower temperatures and higher pressures. However, the combustion turbine exhaust gas is at a lower pressure and at a temperature high enough to avoid condensation.

Figure 22: Carbon Dioxide Capture from Combustion Turbine Exhaust



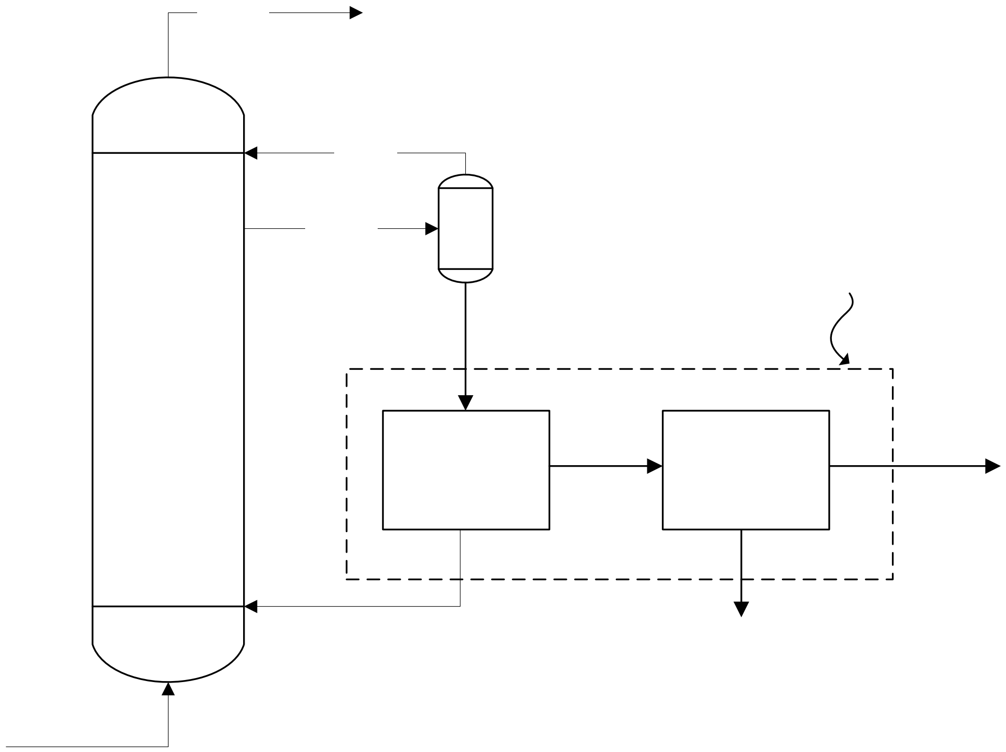
The removal of the captured CO_2 from the CFCMS requires some advances also. While electrically assisted desorption appears to be successful, the removal of the desorbed CO_2 from the carbon fibers must be accomplished so that the final gas has a concentration of CO_2 that is sufficient to economically use for reinjection and sequestration.

Based on the testing, the CFCMS has met the preliminary objectives of the task. However, additional development and configuration design is required to optimize the CFCMS system before it can be incorporated into an EECP or Commercial Coproduction Plant.

Task3.0: Additional RD&T

Rentech and TES screened and tested multiple technologies to meet the EECP secondary catalyst/wax separation system objective of removing the remaining catalyst solids from the filtrate prior to F-T product upgrading. Based on using the Rentech primary separation device – the Dynamic Settler – the filtrate solids content from the primary catalyst/wax separation system is expected to be less than 0.1 wt %. To account for operational upsets and swings in the secondary catalyst/wax separation feed, 0.5 to 1 wt % slurry was assumed as a design feed for the secondary catalyst/wax separation. The secondary catalyst/wax separation system must remove the solids to the 10 ppmw level. The proposed EECP catalyst/wax separation is shown in **Figure 23**.

Figure 23 – EECP Catalyst/Wax Separation



The initial work conducted under Task 2.3: Fischer-Tropsch Catalyst/Wax Separation identified the LCI Scepter® technology as the secondary step for producing an F-T wax having a solids content of less than 10 ppmw. However, for a successful implementation of EECP concept, the team felt that additional testing was necessary to validate the performance of the secondary catalyst/wax separation system based on the EECP design capacity. The additional testing was initiated to obtain data in an extended range of concentration for use in the scale-up design of the secondary catalyst/wax separation system operating at EECP capacity and consisted of the following testing program:

- Generate flux and separation data using a new, 26-nanometer Scepter filter module.
- Allow comparison with data from the tests conducted under Task 2.3: Fischer-Tropsch Catalyst/wax Separation.
- Apply LCI proprietary additive powder to the LCI Scepter® filter surface prior to operation to possibly increase separation efficiency and facilitate cleaning.
- Extend the range of data from approximately 8:1 concentration factor achieved in previous tests, to approximately 10:1 in this test series.
- Investigate flux decline over a 24-hour period at low concentration.
- Obtain additional operating experience with LaPorte AFDU catalyst/wax slurry.
- Obtain additional axial fluid velocity at the filtering surface, temperature, and pressure data sufficient to propose a design based on the capacity of the EECP.
- Test for hysterisis with concentration.

Major Findings: Filter Performance

Pre-treating the filter element with the LCI proprietary additive powder in a water suspension prior to exposure to the feed appeared to reduce the time required to achieve acceptable rejection of the suspended material. While this pretreatment had no measurable effect on the flux to pressure drop (J/P) ratio, the bubble point changed from 13 psi to 24 psi. This is consistent with previous observations that the LCI proprietary additive powder serves to block or reduce the size of the largest pores while having little effect on the smaller ones.

Initial J/P ratios measured in Durasyn 164, hexane and water were typical values expected for unused filters. Measurements following testing showed 1-2 orders of magnitude reduction at the same conditions indicating that a significant resistance layer had developed on the filter surface during testing. Performance during testing showed little hysterisis and steady performance with time, which leads to the conclusion that the resistance layer was formed quickly and then, became stable with little time-related decline during testing. Sometimes a specific feed component present in small quantities causes the majority of the time-dependent fouling. When feed supplies are limited, as was the case in this test, the specific component that causes fouling can also be limited leading to a false conclusion about the extent of fouling. Additional performance data gathered from actual operation of the system will be needed to determine the long term fouling effects.

Data from this design test were regular, predictable and conformed to expected mathematical forms.

The results of the washing study were mixed. The cleaning regimen used following the first, aborted test with these materials showed encouraging results. The same regimen after this test yielded very little improvement in standard J/P ratios. Additional work is needed to fine-tune the cleaning procedures to recover fouled filters.

Long-term flux decline information needs to be developed from operation with an adequate supply of fresh feed. Best practice dictates best design data are obtained when tests with fresh feed are scaled to the filter area.

Overall, this test program reduced the risk in the secondary catalyst/wax separation section of the F-T Synthesis Section of the proposed EECP. Task 2.3: Fischer-Tropsch Catalyst/wax Separation identified a successful method for cleaning the F-T wax to less than 10 ppmw solids. The RD&T performed for Task 2.3 was a major step in advancing the Rentech F-T Synthesis technology. Based on the results of this task (Task 3.0), LCI will be able provide the necessary design of a second stage of F-T Catalyst/wax separation system for the EECP.

Task 4.0: Design Basis Update

The scope of this task was to incorporate the results from Phase II RD&T activities and modify the design basis for the technologies that will require design basis changes. These design basis changes, which are not site dependent, have been identified as the F-T synthesis and the F-T product upgrading.

The Phase I design concept was based on making assumptions for the design of various technologies such as the ASU, gasification unit, AGR, SRU, tail gas treating unit (TGTU), F-T synthesis, FTPU, gas turbine (GT), steam system, and off-sites. The Phase I work identified the risks and critical research, development and testing (RD&T) that would improve the probability of the economic and technical success of the EECP. The results of RD&T efforts for Phase II improved the quality of the assumptions made in Phase I for the basis of design for the EECP concept.

As the RD&T work of Phase II concluded, it became evident that sufficient, but not necessarily complete, technical information and data would be available to begin Phase III - Basic Engineering Design. Also due to the merger of Chevron and Texaco, the proposed refinery site for the EECP was not available. It was apparent that some technical development work would be needed to correctly apply technology at another site. Specifically, additional technical information is required on the feedstock characteristics and product upgrading system design.

The objective of Task 4 of Phase II is to update the concept basis of design produced during Phase I. As part of this task, technologies that will require design basis changes and are not site dependent have been identified as F-T synthesis and F-T product upgrading. The design basis for both above technologies has been modified to incorporate those changes.

The design basis changes for those components of the EECP that are site and feedstock dependent have been identified as the gasification unit and its associated units such as ASU, AGR, SRU, TGTU, GT, and steam system. The update to the design basis for these units will be done as part of Phase III, once a new site for the EECP has been selected.

As per the agreed scope of work for Phase II, heat and material balances, equipment sizing, process flow sketches, process descriptions, utility/catalyst/ chemical summaries, plot plan, emission and effluent summary, cost estimate, and proforma calculations have not be done in this task. Instead, these activities will be part of Phase III, once a new site for the EECP has been selected.

Major Findings: Design Basis Update

The F-T synthesis section design basis has been revised using the information ascertained from the development work carried out since Phase I. The body of work used in the revision of the design basis includes both Phase II RD&T and efforts outside the scope of the EECP.

The F-T synthesis section is designed to convert syngas produced in the Gasification section to liquid hydrocarbons using Rentech technology. The syngas is produced by the gasification of petroleum coke. Part of the syngas, after H_2S removal, is delivered to the F-T synthesis section. The syngas is first treated with zinc oxide to remove the remaining H_2S and then sent to the F-T reactor. The F-T reactor is a slurry bubble column reactor. The F-T liquid products from the F-T synthesis section are sent to the product upgrading section for further treatment. The F-T catalyst handling section maintains the reactor catalyst activity by daily removal of spent and addition of fresh catalyst.

Tables 7 through 9 summarize feed, product, and effluent streams in relation to the F-T synthesis plant.

Table 7

Feed Streams Entering F-T Synthesis Section

Feeds	From	Pressure, kPa (psia)	Temperature, K (°F)
F-T Syngas Feed	AGR	3737 (542)	322 (120)
GT Syngas Feed	AGR	2206 (320)	307 (93)
High Pressure Purge Gas	FTPU	12,617 (1830)	322 (120)
F-T Fresh Catalyst	Offsite		

Table 8

Products Streams Leaving F-T Synthesis Plant

Products	From	Destination	Pressure, kPa (psia)	Temperature, K (°F)
GT Syngas Feed	Preheater	Gas Turbine	2413 (350)	478 (400)
F-T Light Liquid	Cold Separator	Product Upgrading	2661 (386)	322 (120)
F-T Medium Liquid	Hot Separator	Product Upgrading	2723 (395)	355 (180)
F-T Wax	Filtered Wax Pump	Product Upgrading	621 (90)	538 (509)
430 psia Steam	Combined Gas Preheater	Offsite	2965 (430)	505 (450)

Table 9

Effluent Streams

Effluent	From	Destination	Pressure, kPa (psia)	Temperature K (°F)
F-T Water/Alcohol	F-T Water Pump	Gasification	5170 (750)	344 (160)
1st Wax Surge Drum Offgas	1st Wax Surge Drum	Offsite	207 (30)	538 (509)
2nd Wax Surge Drum Offgas	2nd Wax Surge Drum	Offsite	138 (20)	
Water Surge Drum Offgas	Water Surge Drum	Offsite		
F-T Catalyst Fines	Wax Filtration System, FT Water Surge Drum	Offsite		
F-T Spent Catalyst	Wax Filtration System	Offsite		

A cursory evaluation of the modifications to the design basis do not show any major changes required for the capital investment for the EECP concept. An assessment of the impact from minor changes on the plant economics was not made because of a new site has not been selected. The selection of a new site is expected to have a greater impact than any noted modifications.

Conclusion

The work of a large number of subcontractors, equipment vendors, and laboratories has been coordinated and managed by the dedicated efforts of a team selected through the EECP partnership. Monthly and quarterly progress reports have been developed to monitor the progress of the RD&T Program. Two annual meetings were also held to review the results in detail. In addition, Topical Reports have issued and approved by DOE following the completion of each Phase II task.

Work conducted under Phase II has shown the following:

- Confirmation that the F-T reactor can obtain CO conversion and yields equal to the original concept presented in Phase I.
- Identified potential suppliers who can successfully separate F-T catalyst from product wax.
- Confirmed combustion turbine performance using a simulated, low-Btu content F-T tail gas.
- Identified operating conditions as well as product qualities for wax finishing, wax hydrocracking, naphtha pyrolysis, and fuel cell reforming.
- Determined the superior quality of the F-T diesel over CARB-like diesel as a transportation fuel with lower CO, NO_x, hydrocarbon, and particulate matter diesel engine emissions than the CARB-like reference diesel.
- Identified integration of F-T synthesis with gasification by using the F-T water in preparing slurry for gasifier feed and using F-T spent catalyst as part of the fluxant to the gasifier.
- Confirmed that the F-T catalyst/wax mixture meets specifications for non-hazardous landfill, if required.

Cursory evaluations of the modifications to the design basis do not indicate that there will be any major changes required for the capital investment for the EECP concept. The results obtained in Phase II will improve and reduce the risks of the preliminary engineering design that will be developed in Phase III of the project, if a new site is selected.

An impact from the modifications on the plant economics was not made because of a new site has not been selected at this time and the site will have a greater impact on the plant economics than any noted modifications.

List of Acronyms and Abbreviations

^oC	degrees Celsius
^oF	degrees Fahrenheit
AFDU	Alternative Fuels Development Unit
AGR	Acid Gas Removal
ASU	Air Separation Unit
BCR	bubble column reactor
BPD	barrels per day
BTU	British thermal unit
CAER	University of Kentucky Center for Applied Energy Research
CARB	California Air Resources Board
CFCMS	carbon fiber composite molecular sieves
CO	carbon monoxide
CO_2	carbon dioxide
DOE	U.S. Department of Energy
DOS	days on stream
DBR	DB Robinson & Associates Ltd.
EECP	Early Entry Coproduction Plant
expt.	experimental
FCC	Fluid Catalytic Cracking
FDA	U.S. Food and Drug Administration
F-T	Fischer-Tropsch
FTPU	Fischer-Tropsch Product Upgrading
GC	gas chromatograph
GE	General Electric
H2	hydrogen
H2S	hydrogen sulfide
HC	Hydrocarbons or Hydrocracked
HCl	hydrogen chloride
HT	Hydrotreated
HFRR	High Frequency Reciprocating Rig
LHSV	Liquid Hourly Space Velocity
H_2	hydrogen
H_2:CO	hydrogen to carbon monoxide ratio
H_2O	water
H_2S	hydrogen sulfide
HRSG	Heat Recovery Steam Generator
Hz	Hertz
IGCC	Integrated Gasification Combined Cycle
K	Kelvin
KBR	Kellogg Brown & Root
LHV	Lower Heating Value
MTC	Montebello Technology Center
MDEA	Methyldiethanolamine

N2	nitrogen
NOx	nitrogen oxides
O2	oxygen
PM	total particulate
ppmv	parts per million (volume)
ppmw	parts per million (weight)
Psia	pounds force per square inch absolute
Psig	pounds force per square inch gauge
RD&T	Research, Development, and Testing
SCF	standard cubic feet
SOBOCLE	Scuffing Load Ball on Cylinder Lubricity Evaluator
SO_2	Sulfur Dioxide
SOF	Soluble Organic Fraction
SRU	Sulfur recovery unit
STLC	Soluble Threshold Limit Concentration
SwRI	Southwest Research Institute
SWS	Sour Water Stripper
TCLP	Toxic Characteristic Leaching Procedure
U/L FLR	the upper-to-lower flammability ratio
TES	Texaco Energy Systems LLC
TGTU	tail gas treating unit
Tp	test point
WET	Waste Extraction Test
wt%	weight percent