

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.9: Integration

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Abstract

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

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

During Phase I the team identified the integration of the water produced in the F-T synthesis section with the gasification section as an area of potential synergy. By utilizing the F-T water in the petroleum coke slurry for the gasifier, the EECP can eliminate a potential waste stream and reduce capital costs. There is a low technical risk for this synergy, however, the economic risk, particularly in regards to the water, can be high. The economic costs include the costs of treating the water to meet the locally applicable environmental standards. This option may require expensive chemicals and treatment facilities.

EECP Phase II included tests conducted to confirm the viability of integrating F-T water in the slurry feed for the gasifier. Testing conducted at ChevronTexaco's Montebello Technology Center (MTC) included preparing slurries made using petroleum coke with F-T water collected at the LaPorte Alternative Fuels Development Unit (AFDU). The work included bench scale tests to determine the slurryability of the petroleum coke and F-T water. The results of the tests show that F-T water does not adversely affect slurries for the gasifier. There are a few cases where in fact the addition of F-T water caused favorable changes in viscosity of the slurries. This RD&T task was executed in Phase II and results are reported herein.

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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.

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Executive Summary

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

During Phase I the team identified the integration of the water produced in the Fischer-Tropsch (F-T) synthesis section with the gasification section as an area of potential synergy. The F-T water contains a variety of acids, alcohols, and other oxygenates. By utilizing the F-T water in the petroleum coke slurry for the gasifier the EECP can eliminate a potential waste stream and reduce capital costs. There is a low technical risk for this synergy, however, the economic risk, particularly in regards to the water, can be high since it can result in higher capital costs. Two options exist if the F-T water is not suitable for the slurry. First, the water could be pumped directly into the gasifier. This option would require a high-pressure pump. The second option is to dispose of the F-T water using conventional water treatment equipment. This option may require several separation columns and biotreatment units. Either option increases the capital and operating costs associated with the EECP.

Each of the EECP subsystems were assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified the use of the F-T water as a potential technical risk. In the Phase I Concept Design, the F-T water was pumped directly to the gasifier. This requires the use of a high pressure pump.

EECP Phase II included tests to be conducted to confirm the viability of integrating F-T water in the slurry feed for the gasifier. Testing to be conducted at Texaco's Montebello Technology Center (MTC) included preparing coke slurries made using PAR petroleum coke with the expected EECP F-T water. The work included bench scale tests to be conducted to determine the slurryability of the petroleum coke and F-T water. The results of the bench scale tests could allow larger batches of slurry for rheology testing. This RD&T task was executed in Phase II and results are reported herein.

Petroleum coke from Motiva's Port Arthur refinery and the two ChevronTexaco refineries yield water slurries that met the gasifier feed solids concentration, slurry pumpability, and other characteristics required for ChevronTexaco's proprietary gasification process with ChevronTexaco's proprietary additive.

The results of Rheology test loop showed that there was no observable adverse effect on pumpability and other related flow properties due to the use of F-T water (up to 7 %) as partial water source for coke slurring. In fact at lower slurry concentration, addition of F-T water may reduce the slurry viscosity. The results of the bench-scale tests confirmed the absence of detrimental effects by the addition of Fischer-Tropsch water (up to 20 %). There are few cases where in fact the addition caused favorable changes in viscosity. However, F-T water has the effect of lowering the slurry's pH. This may require the addition of an appropriate neutralizing chemical, such as ammonium hydroxide, to protect the slurry run tank and feed system from corrosion.

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

Background

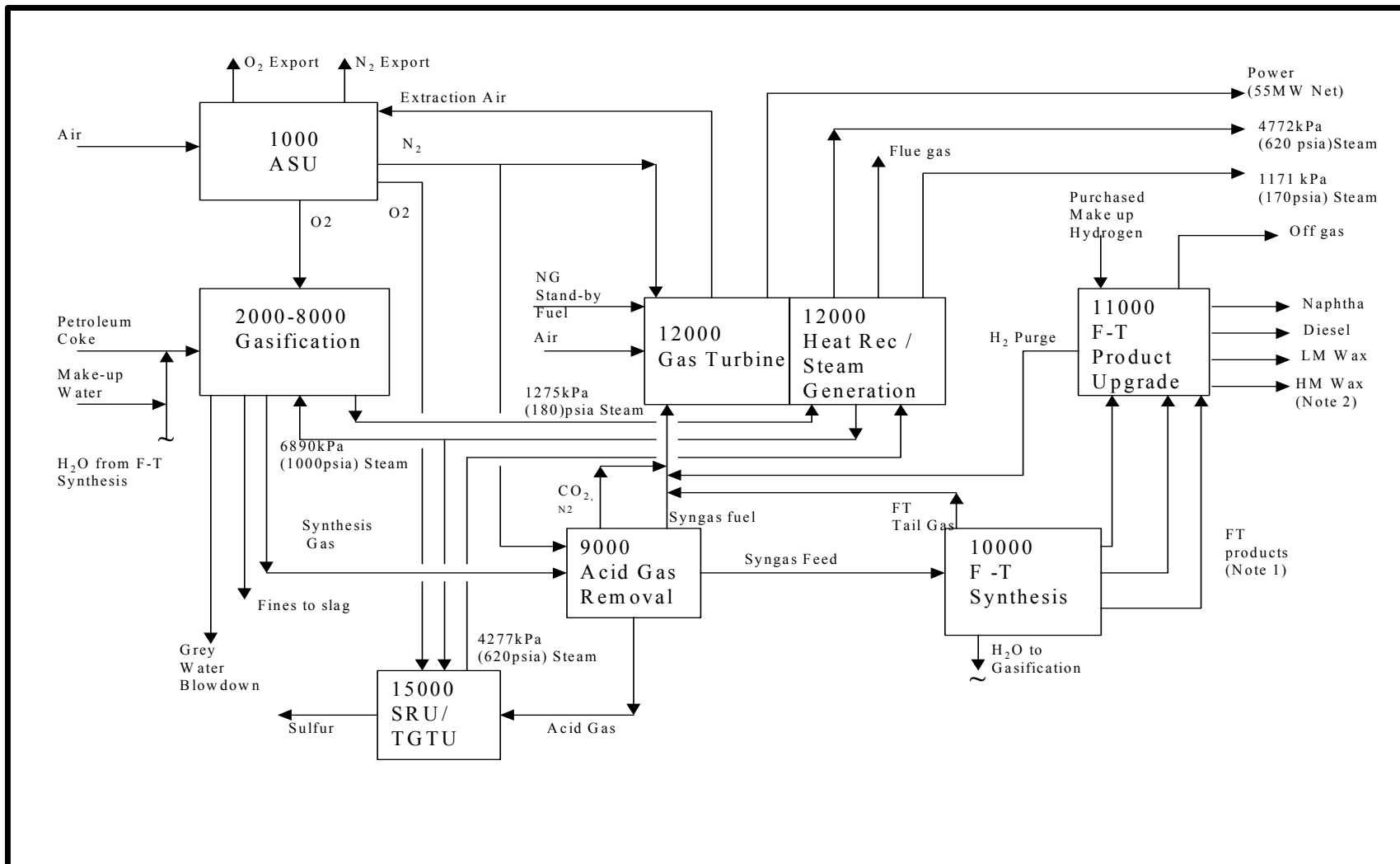
The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I was to determine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

The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and consume approximately 1,120 metric tons per day (1,235 short tons per day) of petroleum coke. During Phase I, the Motiva Port Arthur Refinery site was chosen for the EECP. The refinery site offered a ready source of petroleum coke as a feedstock.

EECP Concept

Petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen (H₂), carbon monoxide (CO), water vapor (H₂O), and carbon dioxide (CO₂) with small amounts of hydrogen sulfide (H₂S), methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. One portion of the stream is treated in the AGR to remove CO₂ and H₂S and then forwarded to the F-T Synthesis Unit. The other portion is treated in the AGR to remove the bulk of H₂S with minimal CO₂ removal and then forwarded as fuel to the GE frame 6FA gas turbine. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO₂. The resulting CO₂ and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides emissions. The bulk of the nitrogen is also sent to the gas turbine as a separate stream, where its mass flow also helps increase the power production and reduces nitrogen oxide emissions.

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



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NOTES:

1. Includes Light, Medium and Heavy FT Liquid product streams
2. LM = Low Melt
 HM = High Melt

**DOE EARLY ENTRANCE COPRODUCTION PLANT
 PORT ARTHUR REFINERY
 OVERALL BLOCK FLOW DIAGRAM**

DRAWN JSA	DATE 10/10/00	DOE AWARD NUMBER: DE-FC-99FT40658	REV.
DESIGNER	DATE	SUBCONTRACTOR PROJECT NO: 9202	0
CHECKED	DATE	TASK NO: 4.1.2	
APPROVED	DATE	DRAWING NO: KBR-P-BFD-0001	

carbon monoxide and hydrogen 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 and injected into the gasifier. The F-T tail gas and AGR off gas are sent to the gas turbine as fuel to increase electrical power production by 11%.

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

The power block consists of a GE PG6101 (FA) 60 Hz heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas as start-up and backup fuel, and primary fuel as a mixture of syngas from the gasifier, offgas from the AGR Unit, and tail gas from the F-T Synthesis Unit. Nitrogen gas for injection is supplied by the ASU for nitrous oxide (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 all of the EECP's requirements for nitrogen and instrument and compressed air. ASU nitrogen product applications within the EECP include its use as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NO_x emissions, and as an inert gas for purging and inerting. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor, hence oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums as they enter the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS gas, oxygen, and air to a burner. In the thermal reactor, the H₂S, a portion of which has been combusted to sulfur dioxide (SO₂), starts to recombine with the SO₂ to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser in which all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H₂S and SO₂ 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 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 SO₂ back to H₂S. 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. H₂S is removed from the quenched tail gas in an absorber by lean methyldiethanolamine (MDEA) solvent from the AGR Unit, and the tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

An important objective of the EECF project is to integrate and optimize the various subsystems of EECF with each other and with the selected host plant to minimize overall costs and environmental impact. During Phase I, each of the EECF subsystems were assessed for technical risks and barriers and a Phase II RD&T plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000).

The F-T water produced in the F-T synthesis reaction is separated from the F-T liquids in the Hot Separator and Cold Separator. The F-T water contains a variety of acids, alcohols, and other oxygenates. A potential integration risk identified by the RD&T plan is the use of Fischer-Tropsch (F-T) water in the petroleum coke slurry sent to the gasifier. In Phase I, the team proposed to use the F-T water in making the petroleum coke slurry for the gasifier. There is a low technical risk for this proposal. The economic risk, particularly in regards to the water, can be high. Two options exist if the F-T water is not suitable for the slurry. First, the water could be pumped directly into the gasifier. This option would require an expensive high-pressure pump. The second option is to dispose of the F-T water using conventional water treatment equipment. This option may require several separation columns and biotreatment units. Either option increases the capital and operating costs associated with the EECF.

EECF Phase II included tests to be conducted to confirm the viability of integrating F-T water in the slurry feed for the gasifier. Testing to be conducted at Texaco's Montebello Technology Center (MTC) included preparing coke slurries made using PAR petroleum coke with the expected EECF F-T water. The work included bench scale tests to be conducted to determine the slurriability of the petroleum coke and F-T water. The results of the bench scale tests could allow larger batches of slurry for rheology testing. This RD&T task was executed in Phase II and results are reported herein.

Task 2.9: Integration

The key issue with the petroleum coke slurry is the rheology of the slurry and the impact of F-T water. In the second (2nd) calendar quarter of 2001, samples of petroleum coke from Motiva Port Arthur and F-T water collected by ChevronTexaco at the LaPorte Alternate Fuels Development Unit (AFDU) outside of the EECF project were sent to ChevronTexaco's Montebello Technology Center (MTC) for testing on the Rheology Test Loop (RTL). RTL testing was completed by early third (3rd) calendar quarter of 2001. As a result of the merger between Texaco and Chevron in October 2001, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. To assess the possible impact of moving the proposed EECF host site to a ChevronTexaco refinery, samples of

petroleum coke from two ChevronTexaco refineries were sent to MTC for bench-scale testing with and without F-T water in the second (2nd) calendar quarter of 2002. ChevronTexaco had previously developed proprietary correlations between the RTL and bench-scale results.

Rheology Theory

Rheology is defined as the study of flow and deformation of matter. For laminar flow through straight smooth circular pipe, the viscosity of fluid at constant temperature is determined by plotting shear stress versus shear rate and the slope of the curve is viscosity, as shown in Figure 1. For a Newtonian fluid, the line should pass through the origin indicating that there is no yield stress. Coke (and coal) slurries used as feedstock for ChevronTexaco’s gasification process behave in a non-Newtonian manner, since they require an initial shear stress or force to make it flow, with any additional force producing a flow with a Newtonian relationship. This initial stress or force is known as Yield Stress and can be measured as the y-intercept.

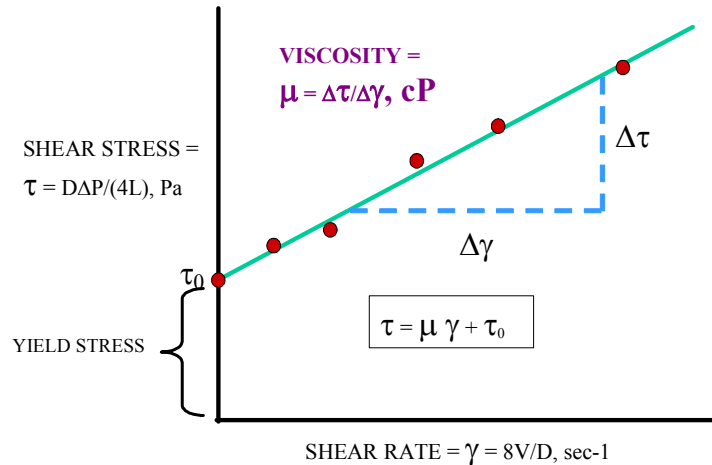


FIGURE 1: RHEOLOGY THEORY

Rheology Test Loop (RTL) Testing

During Phase I of the EECF project, the team identified the potential synergy of using water from the F-T synthesis section in the petroleum coke slurry of the gasification section. In the second (2nd) calendar quarter of 2001, F-T water collected by ChevronTexaco at the LaPorte Alternate Fuels Development Unit (AFDU) outside of the EECF project was sent to MTC along with petroleum coke from the Motiva Port Arthur Refinery. MTC conducted tests of the petroleum coke slurry on the RTL. The particle size, slurry concentration, and slurry additive are proprietary to the ChevronTexaco Gasification Process.

Rheology Test Loop

The RTL was constructed in 1996 at MTC to accurately measure the rheological properties of gasifier feedstocks, which are important for piping design and metallurgy specification. The process flow diagram of the RTL is shown in Figure 2. The flow rate, density, temperature, and pressure drop across the test loops were accurately measured. A Honeywell Distributed Control System (DCS) varies the slurry flow through the loop.

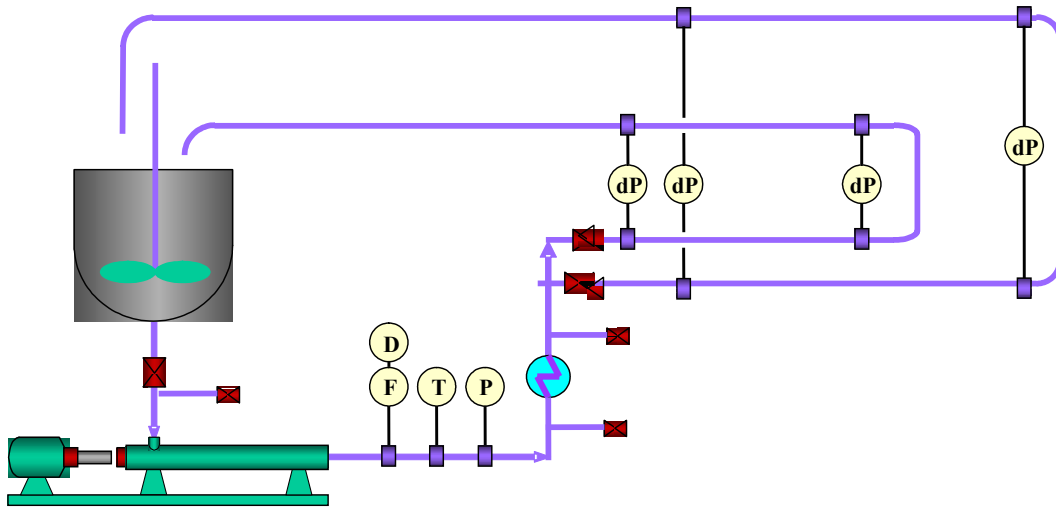


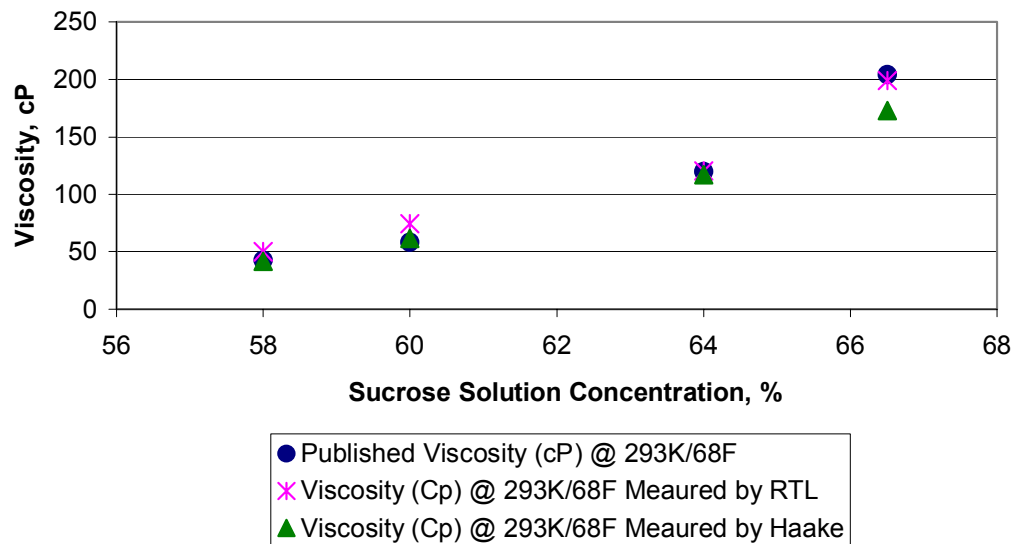
Figure 2: Rheology Test Loop Flow Diagram

RTL Validation Test

The performance of the RTL has been validated using four different concentrations of sucrose. Sucrose solution was selected as the validation fluid because of its Newtonian flow properties. Viscosity data at different concentrations have been published. The ASTM viscosity-temperature correlation was used to compare the RTL predicted viscosity to the published value.

Figure 3 shows that the viscosities measured with the RTL, in centipoises (cP), were in good agreement with the published viscosity and the results obtained in our laboratory using a Haake viscometer.

Figure 3: Comparison of MTC Viscosity Measurements vs. Published Data



Key Objectives

The key objectives and scope of this study are to:

1. Prepare petroleum coke slurry samples at two grind sizes and different solid concentrations for testing in the rheology test loop.
2. Measure flow properties of each slurry sample using different amounts of additive and FT-water.
3. Study the effect on slurry properties of using Fischer-Tropsch water as partial water source.
4. Study the effect of additive dosage on slurry properties. The additive is a key component of Texaco's proprietary gasification technology. In all cases the additive dosage was kept in ppm levels.

RTL Test Matrix

For the RTL test in the second (2nd) calendar quarter of 2001 the following test matrix was prepared.

I. Slurry Tests – Sample Set A:

Five batches of coke slurry were prepared at several solid concentrations within the range of +/- 6% of the ChevronTexaco commercial target, with plant water at a consistent particle size distribution determined by a set grinding mill speed. Using these batches of slurry a total of five segments were conducted to study the effect of 7% by weight Fischer-Tropsch (F-T) water and additive. The run conditions for these segments are shown below:

- **Segment-1:** No Additive; No F-T water
- **Segment-2:** Higher Level Additive; No F-T water
- **Segment-3:** No Additive; 7% F-T water
- **Segment-4:** Lower Level Additive; 7% F-T water
- **Segment-5:** Higher Level Additive; 7% F-T water

II. Slurry Tests – Sample Set B:

For grind size B, two batches of coke slurry with similar solid concentration range as mentioned in the Sample Set A were prepared with plant water at a finer grind size than Set A (higher grinding mill speed). With this batch, two segments were completed with 7% F-T water at 0 and higher level additive dosage. The run conditions for these two segments are shown below:

- **Segment-6:** No Additive; 7% F-T water (4 runs)
- **Segment-7:** Higher Level Additive; 7% F-T water (4 runs)

The indicated additive dosage is based on the weight of solids in the coke slurry. For all the above segments the amount of additive dosage was in ppm levels. The indicated wt% F-T water is based on the weight of the slurry water.

RTL Test Results and Discussion

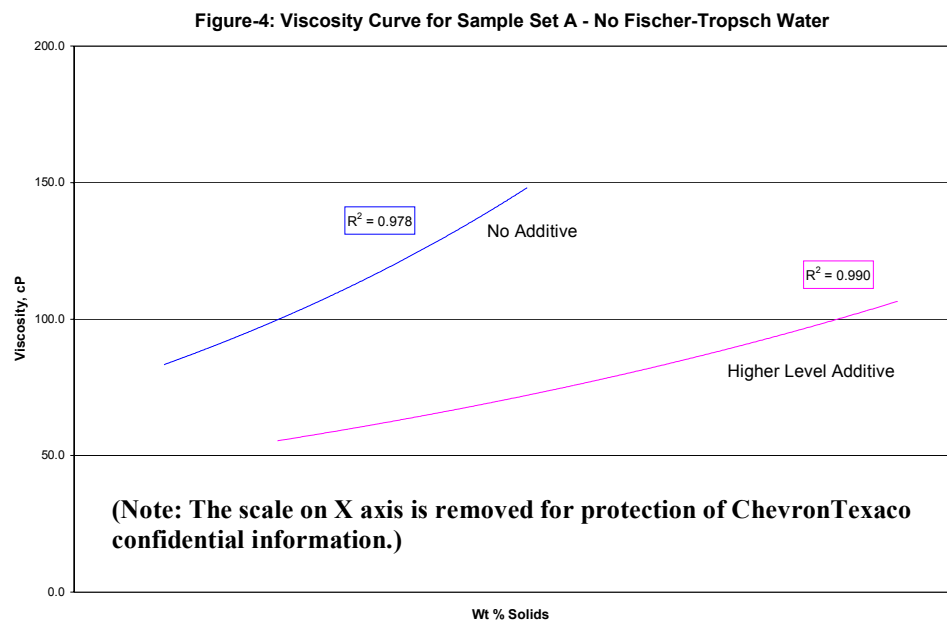
Using the flow model illustrated in Figure 1, the shear stress (τ) versus shear rate ($\dot{\gamma}$) was plotted for all the test runs in each segment and the viscosity (μ) and yield stress (τ_0) was determined. There was a very good curve fit for these calculations, as indicated by a R Square or regression coefficient close to 1.0.

For segments with the additive dosage, the solid concentrations where several percentage points above those segments without the additive. Slurry concentrations in segments without additive approximately reached the desired ChevronTexaco proprietary specification target within a +/- 1% accuracy. All runs were conducted with slurry at ambient temperature. The effect of temperature variation was not evaluated in this study, since based on ChevronTexaco's experience, these effects are found to be negligible relative to other measurements.

There was a significant reduction of viscosity and yield stress by the use of higher level additive dosage, irrespective of F-T water usage. F-T water did not have an adverse effect on the slurry pumpability and had a slightly positive effect on lowering the viscosity of slurry. Use of lower level additive dosage had negligible effect on the viscosity and yield stress. The pH value for runs without FT-water was around 7.5, whereas the pH value for runs with FT-water ranged from 4.5 to 5.5.

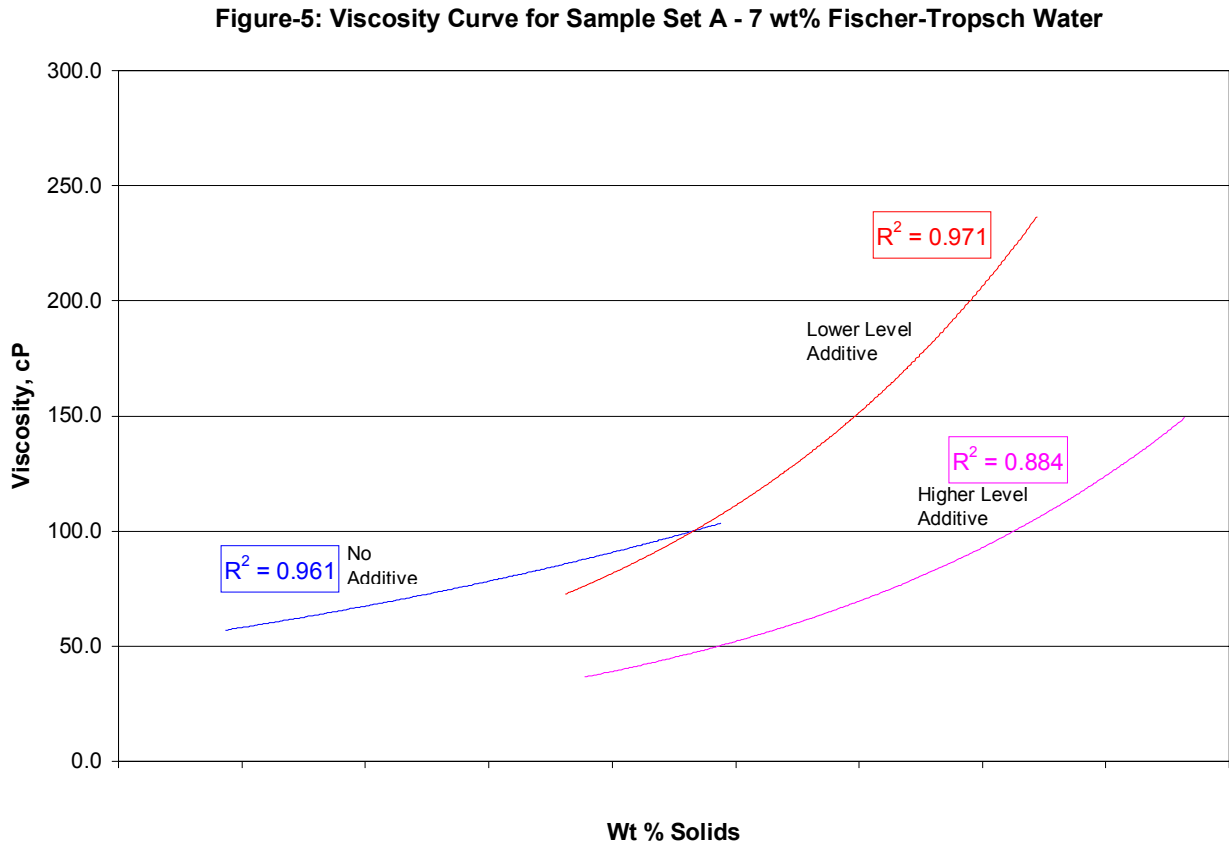
Effects of Additive Dosage, FT-Water, and Relative Grind Size

Figure 4 shows the viscosity curves for Segments 1 and 2 (Sample Set A) with 0% F-T water at no additive and higher level additive dosage, respectively. As shown, the viscosity is significantly reduced at higher level additive dosage compared to the



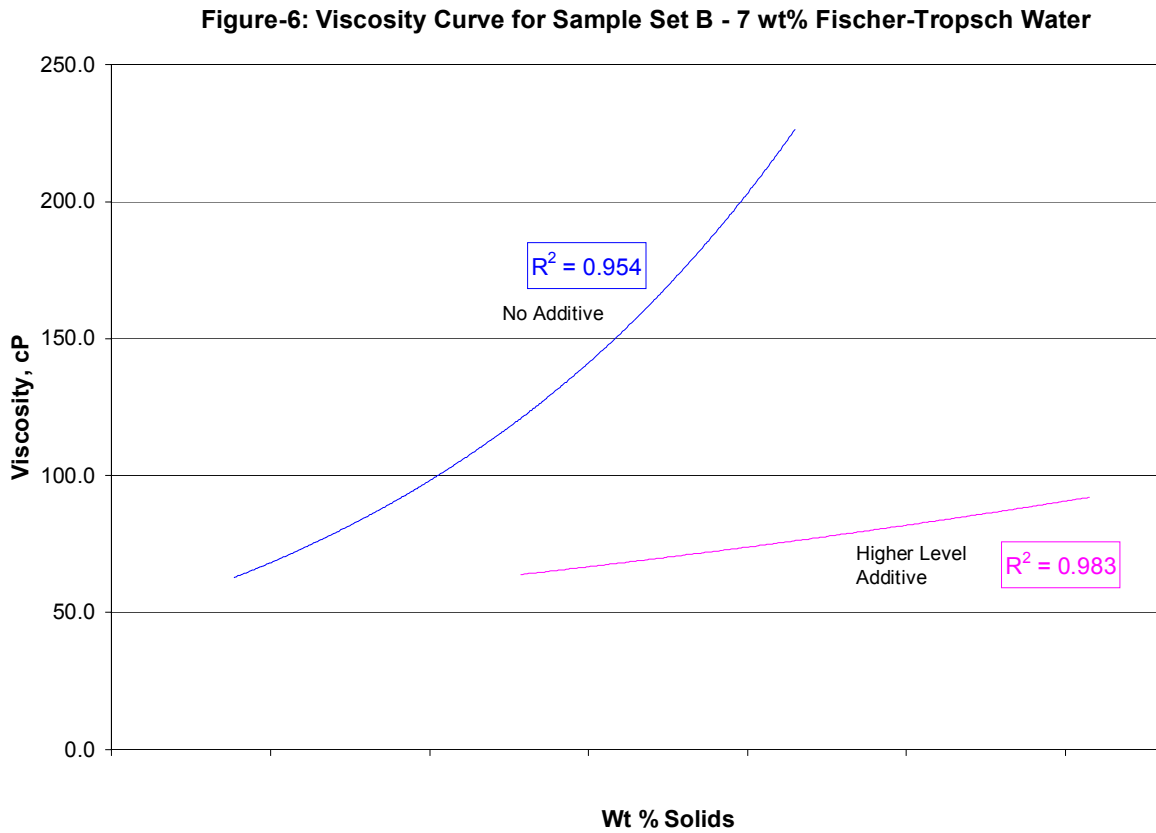
same solid concentration [weight percent (wt%)] without additive. The slurry was pumpable at a wide range of solid concentrations.

Similar behavior was observed for Segments 3, 4 & 5 (Sample Set A) with 7% F-T water and additive dosages of 0, lower level, and higher level, respectively. The results are shown in Figure 5. As shown, there is no significant difference between the viscosity curves for 0 and lower level additive. On the other hand, a significant drop in the viscosity and improved flow properties were observed at Higher Level additive dosage.



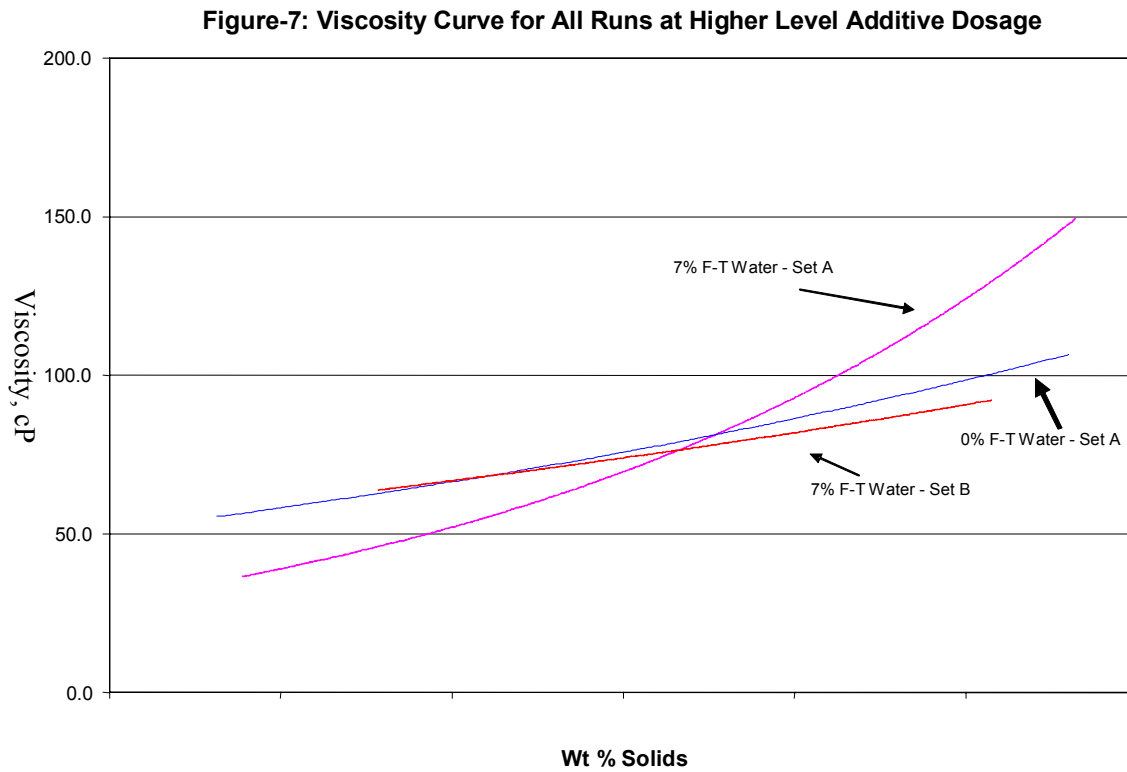
(Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

Figure 6 shows viscosity curves for segments 6 and 7 (Sample Set B). The effect of additive dosage on the viscosity is similar to that observed for segments 1 through 5, discussed above.



(Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

Figure 7 shows that the use of F-T water as partial slurry water source had no significant adverse effect on viscosity and slight positive effect at lower concentration of slurry. The only negative effect of the 7% F-T water use on slurry properties was the lowering of pH.



(Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

Additional Rheology Tests

The merger between Texaco and Chevron and the resulting sale of Texaco's interest in the Motiva Enterprises LLC joint venture introduced the possibility of moving the proposed EECF from Motiva Port Arthur to another refinery location. To assess the impact of this possibility on the integration of the F-T water in the petroleum coke slurry MTC conducted additional bench scale slurry tests on petroleum coke from two ChevronTexaco Refineries (designated Refinery A and Refinery B).

Test Matrix

The petroleum coke from refinery A and refinery B was ground with a lab rod mill in the presence of de-mineralized water and a selected amount of F-T water and the ChevronTexaco proprietary additive to prepare slurry with a predetermined amount of coke according to the sample matrix shown in Table 1. The slurry concentration and additive level are proprietary to the ChevronTexaco Gasification Process.

Table 1. Test Matrix for Bench-Scale Slurry Tests

F-T water %	Additive Concentration		
0	None	N/A	N/A
7	None	Lower Level	Higher Level
10	None	Lower Level	Higher Level
15	None	Lower Level	Higher Level
20	None	Lower Level	Higher Level

The viscosities of the samples were measured with a Stormer viscometer. The samples were diluted mainly with de-mineralized water while maintaining the F-T water concentration constant and subsequently measured for viscosity. The data collected were plotted to generate the solids percentage at 1000 centipoises (cP), 700 cP, 400 cP and 100 cP for each sample.

Test Results and Discussion

The solids percentage in each sample was then plotted as a function of the viscosity using different concentrations of F-T water and a fixed additive concentration. The graphs are shown in Figures 8 through Figure 13.

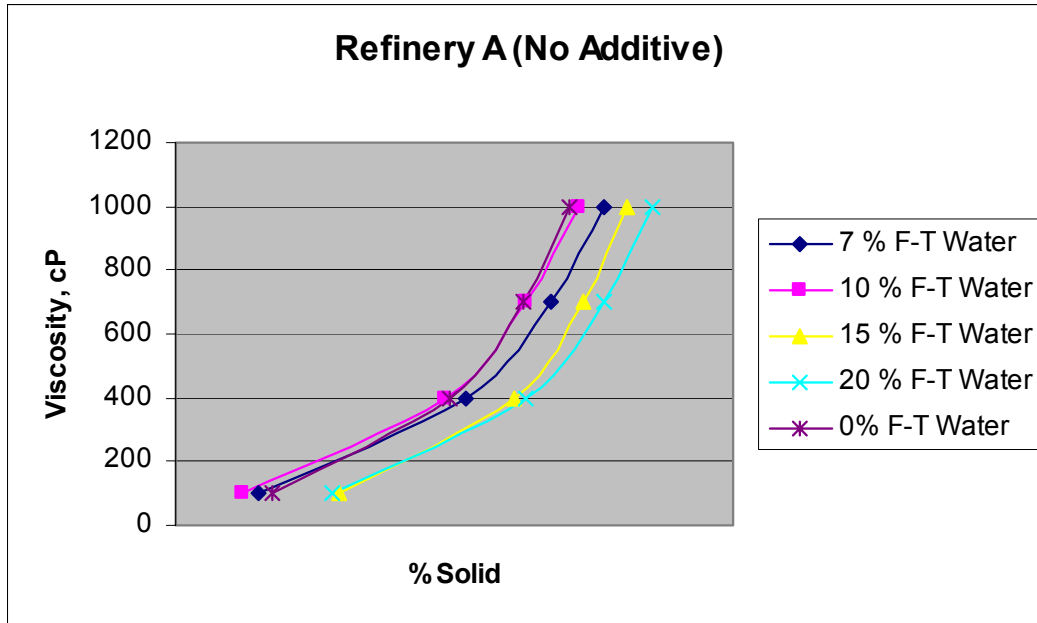


Figure-8: Viscosity Curves for Refinery A Petroleum Coke with No Additive
(Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

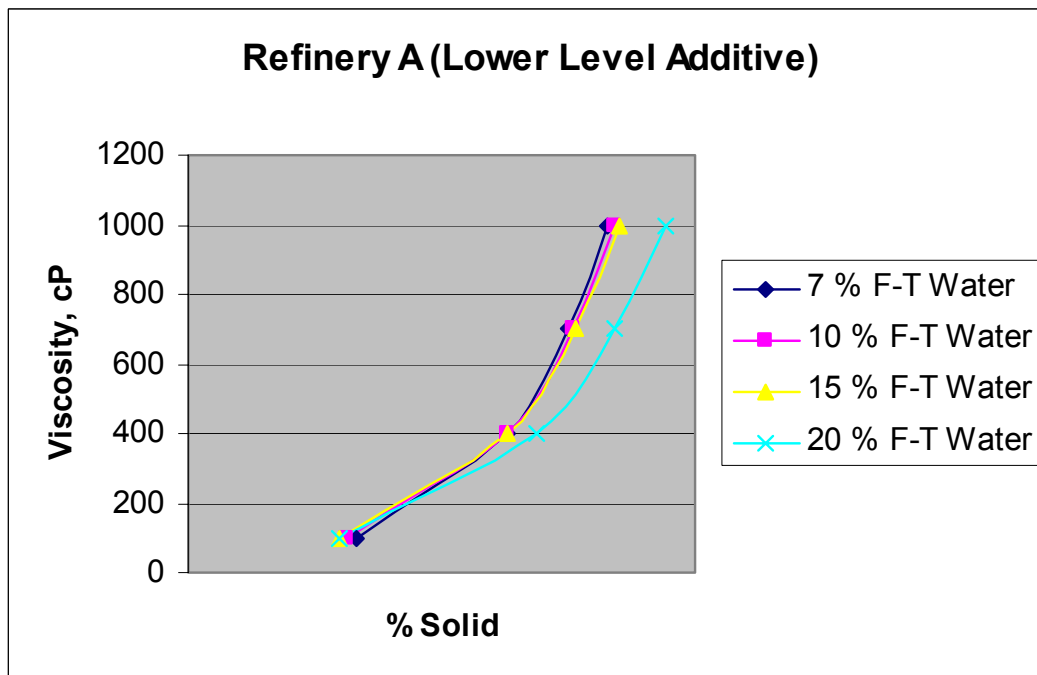


Figure-9: Viscosity Curves for Refinery A Petroleum Coke with Lower Level Additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

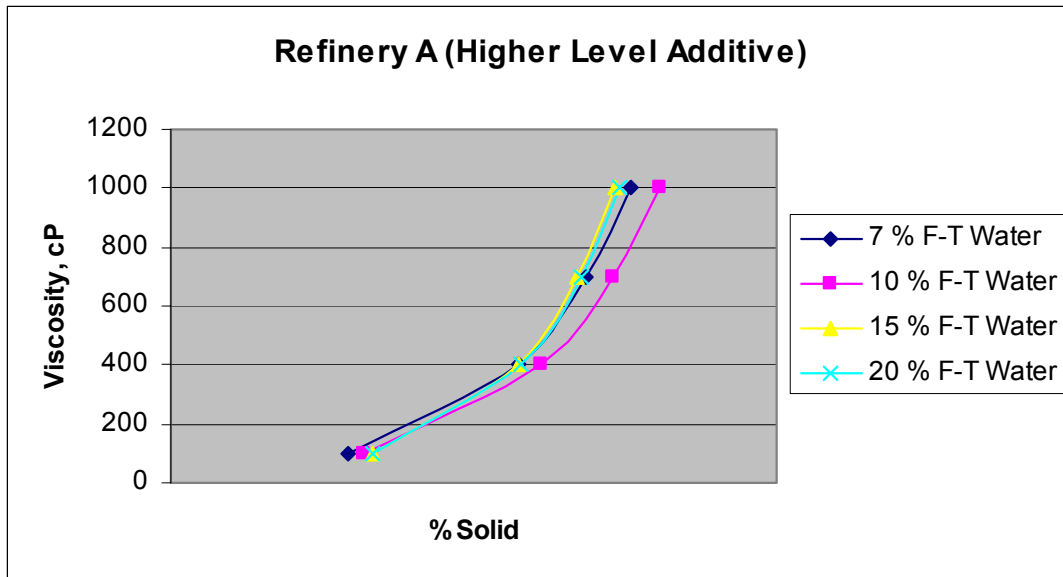


Figure-10: Viscosity Curves for Refinery A Petroleum Coke with Higher Level Additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

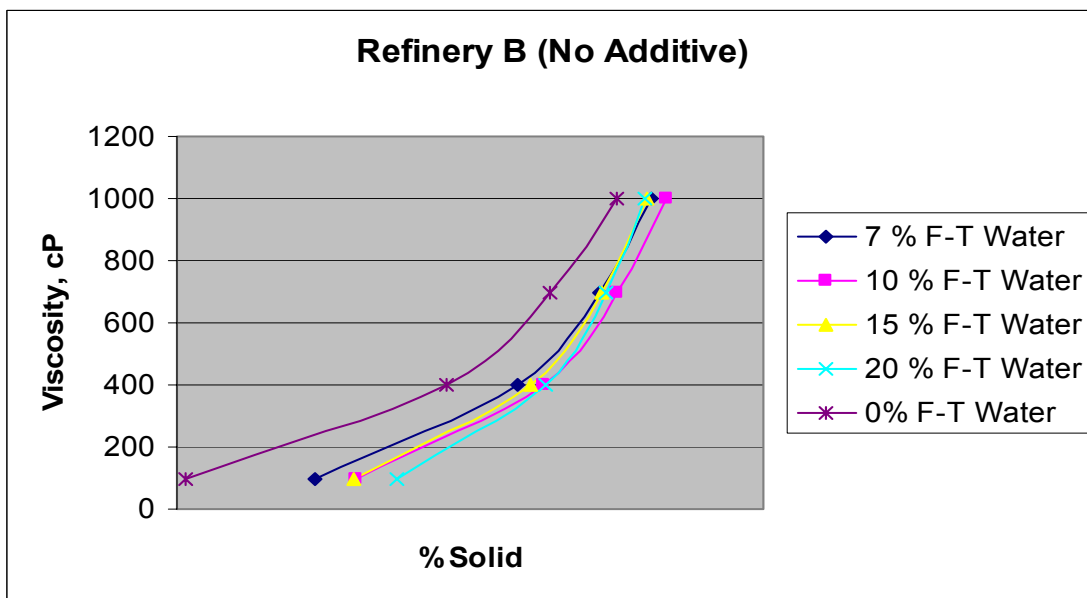


Figure-11: Viscosity Curves for Refinery B Petroleum Coke with no additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

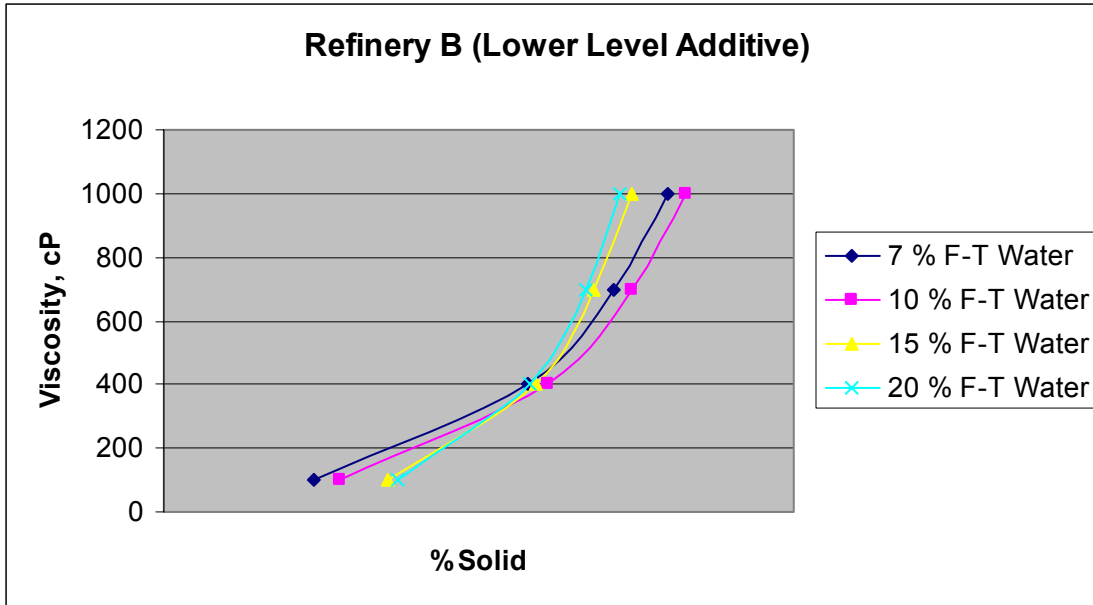


Figure-12: Viscosity Curves for Refinery B Petroleum Coke with Lower Level Additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

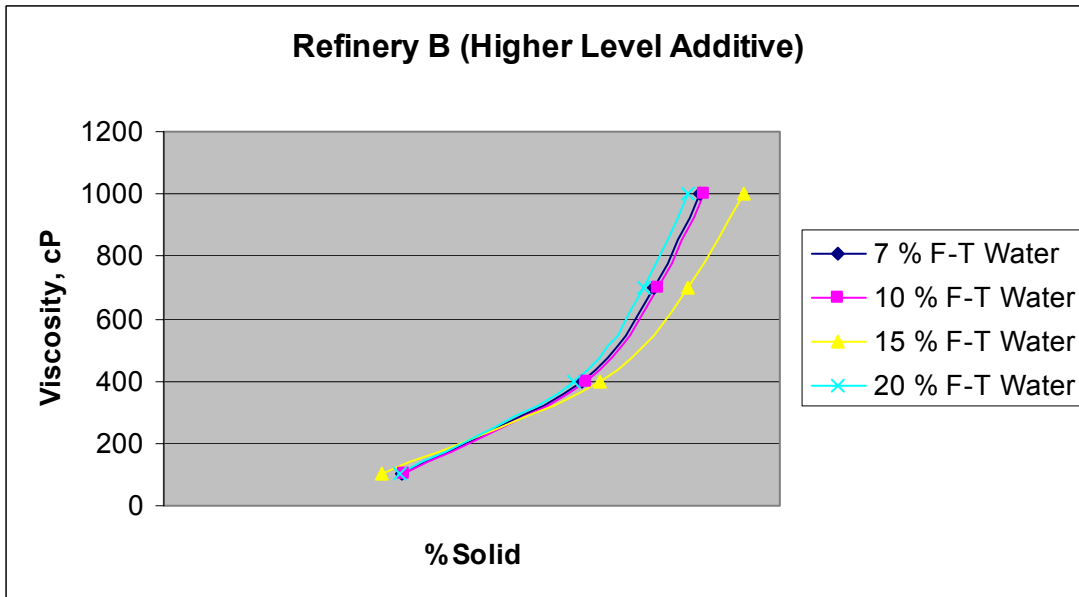


Figure-13: Viscosity Curves for Refinery B Petroleum Coke with Higher Level Additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

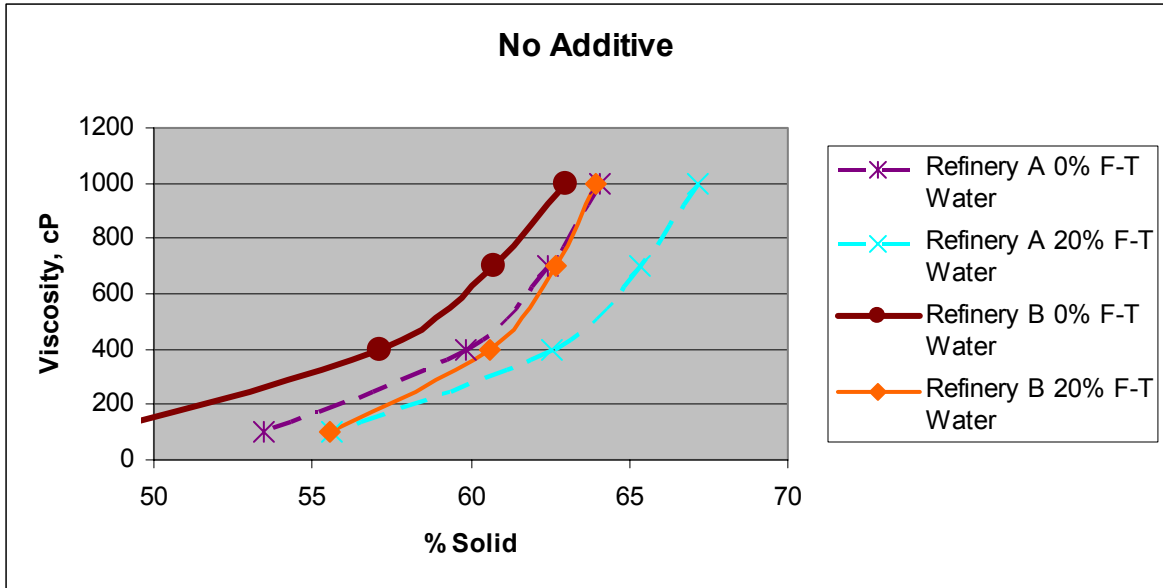


Figure 14: Potential Improvement In Viscosity With 20% F-T Water And No Additive
 (Note: The scale on X axis is removed for protection of ChevronTexaco confidential information.)

The results of the bench-scale tests confirm the absence of detrimental effects by the addition of Fischer-Tropsch water. There are a few cases where the addition caused favorable changes in viscosity particularly the refinery A petroleum coke at no additive and the higher additive levels. However, these effects are not clearly observed with refinery B petroleum coke. There is insufficient data to generalize any conclusion that the addition of F-T water always has a positive impact on the slurry. Additional rheology tests on coke from various sources would increase understanding of the effects of F-T water on slurry viscosity.

Conclusions

- Petroleum coke from Motiva's Port Arthur refinery yield water slurries that meet the solids concentration, pumpability, and other characteristics required for ChevronTexaco's proprietary gasification process with ChevronTexaco's proprietary additive.
- Petroleum coke from the two ChevronTexaco refineries yield water slurries that meet the solids concentration and other characteristics required for ChevronTexaco's proprietary gasification process with ChevronTexaco's proprietary additive.
- There was no observable adverse effect on pumpability and other related flow properties due to the use of including F-T water as a source of water for coke slurring. At lower slurry concentration, addition of F-T water may reduce the slurry viscosity. However, F-T 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 run tank and 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 slurries with and without F-T water.
- The results of the bench-scale tests confirm the absence of detrimental effects by the addition of Fischer-Tropsch water. There are few cases where in fact the addition caused favorable changes in viscosity, particularly the Refinery A petroleum coke at no additive and the higher additive levels, but these effects are not clearly observed in the Refinery B petroleum coke. There is insufficient data to generalize any conclusion that the addition of F-T water always has a positive impact on the slurry. Perhaps, more rheology tests on coke from various sources would shed more light on the effects of F-T water on slurry viscosity.

Bibliography

Anderson, J.H., Davis, W. K., Schrader, C.H., Shah L. S. “Early Entrance Coproduction Plant Phase I Concept Report”, May 2001.

ASTM test method D341-87.

Texaco Energy Systems Inc., Phase II RD&T Plan, October 2000

Weast, Robert, “CRC Handbook of Chemistry and Physics”, 58th edition p-D141.

List of Acronyms and Abbreviations

AFDU	Alternate Fuels Development Unit
AGR	Acid Gas Removal
ASTM	American Society for Testing and Materials
ASU	Air Separation Unit
CO	carbon monoxide
CO ₂	carbon dioxide
cP	centipoises
D	diameter (Figure 1); density meter (Figure 2)
dP	pressure drop
DCS	distributed control system
°F	Fahrenheit
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
GE	General Electric
H ₂ S	hydrogen sulfide
HRSG	heat recovery steam generator
K	Kelvin
KBR	Kellogg Brown & Root
MDEA	methyldiethanolamine
MTC	Montebello Technology Center
NO _x	nitrous oxides
P	pressure
RD&T	Research, Development, and Testing
RTL	Rheology Test Loop
SO ₂	sulfur dioxide
SRU	sulfur recovery unit
SWS	sour water stripper
T	temperature
TES	Texaco Energy Systems LLC
V	velocity
wt%	weight percent
Δ	change in
γ	Shear Rate
μ	Viscosity
τ	Shear Stress
τ_0	Yield Stress