EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.5: Fischer-Tropsch Product Upgrading

Reporting Period: January 2001 to August 2003

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Date Issued:
September 16, 2003 (Preliminary)
November 10, 2003 (Final)
January 27, 2004 (Final – Revised)

DOE Cooperative Agreement
No. DE-FC26-99FT40658
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Abstract

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

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

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

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Executive Summary

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

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

Background

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

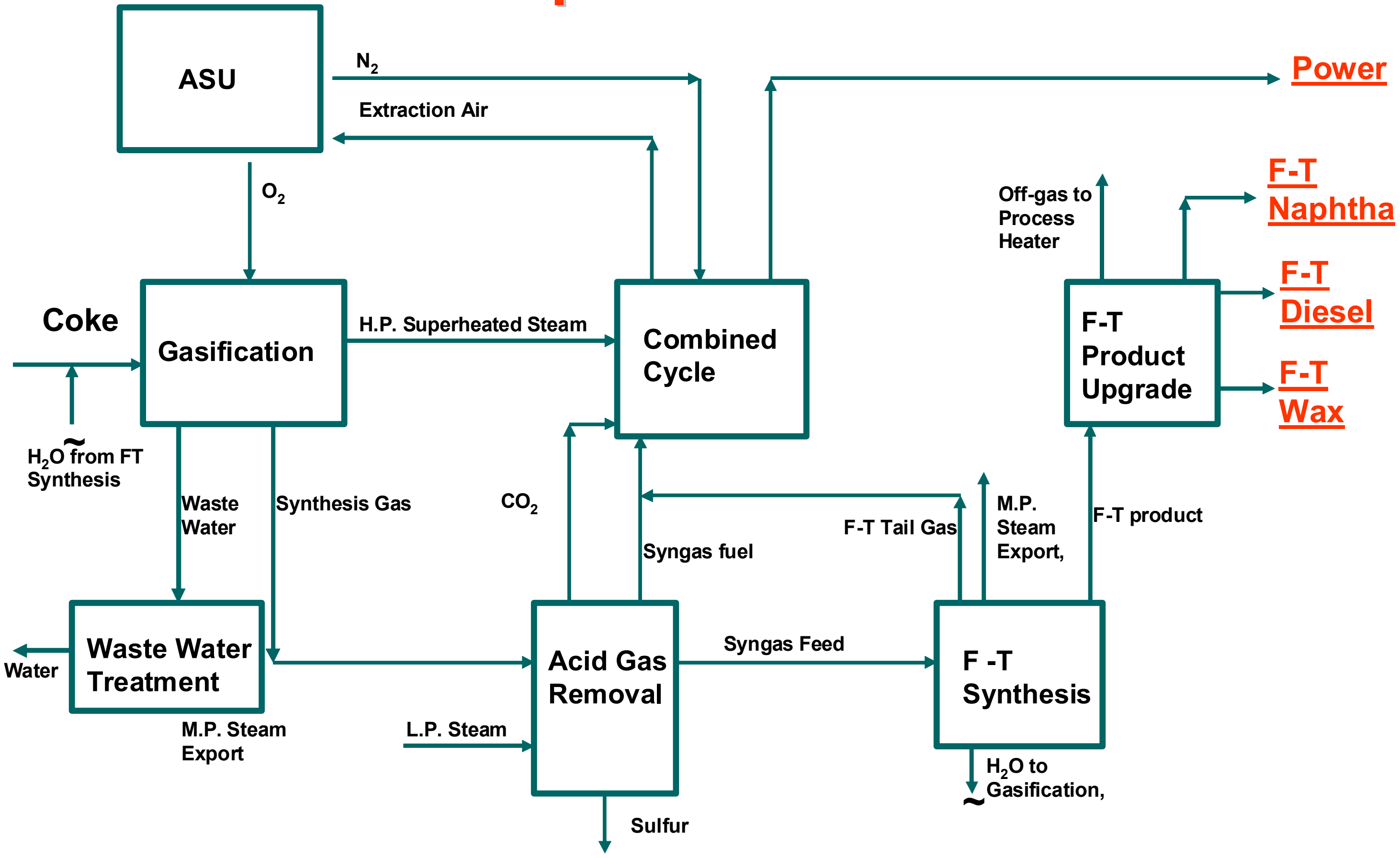
The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and will consume approximately 1,235 short tons per day of petroleum coke. The EECP Concept is illustrated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

EECP Concept

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

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

Proposed EECP



Schematic 1 - EECP Concept

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

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

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

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

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

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

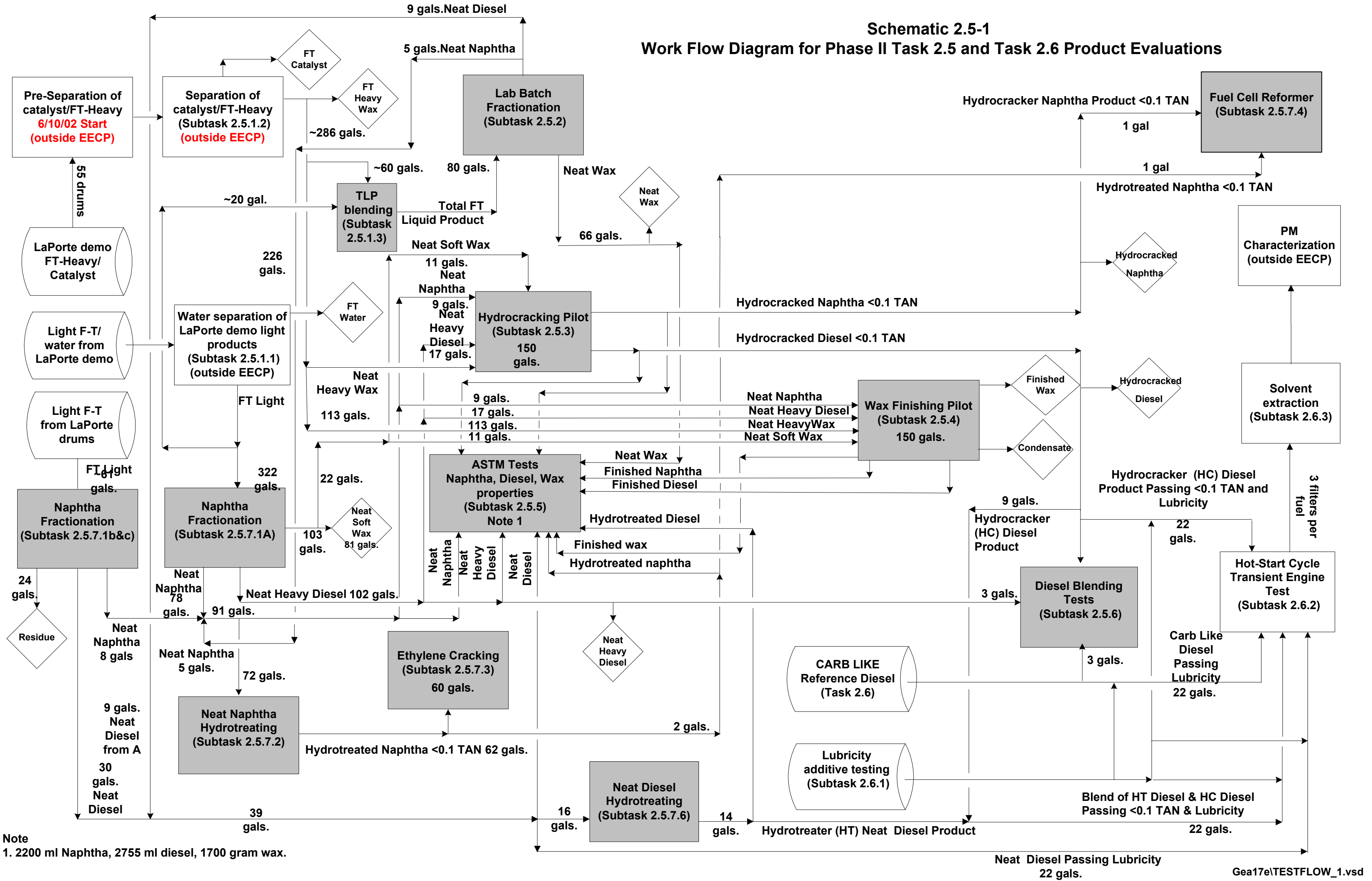
The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO_2 back to H_2S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along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

Subtask Product Evaluations Performed for Task 2.5 Outside DOE Funding

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

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

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



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

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

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Subtask 2.5.1 Preparation of LaPorte AFDU Products

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

Experimental

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

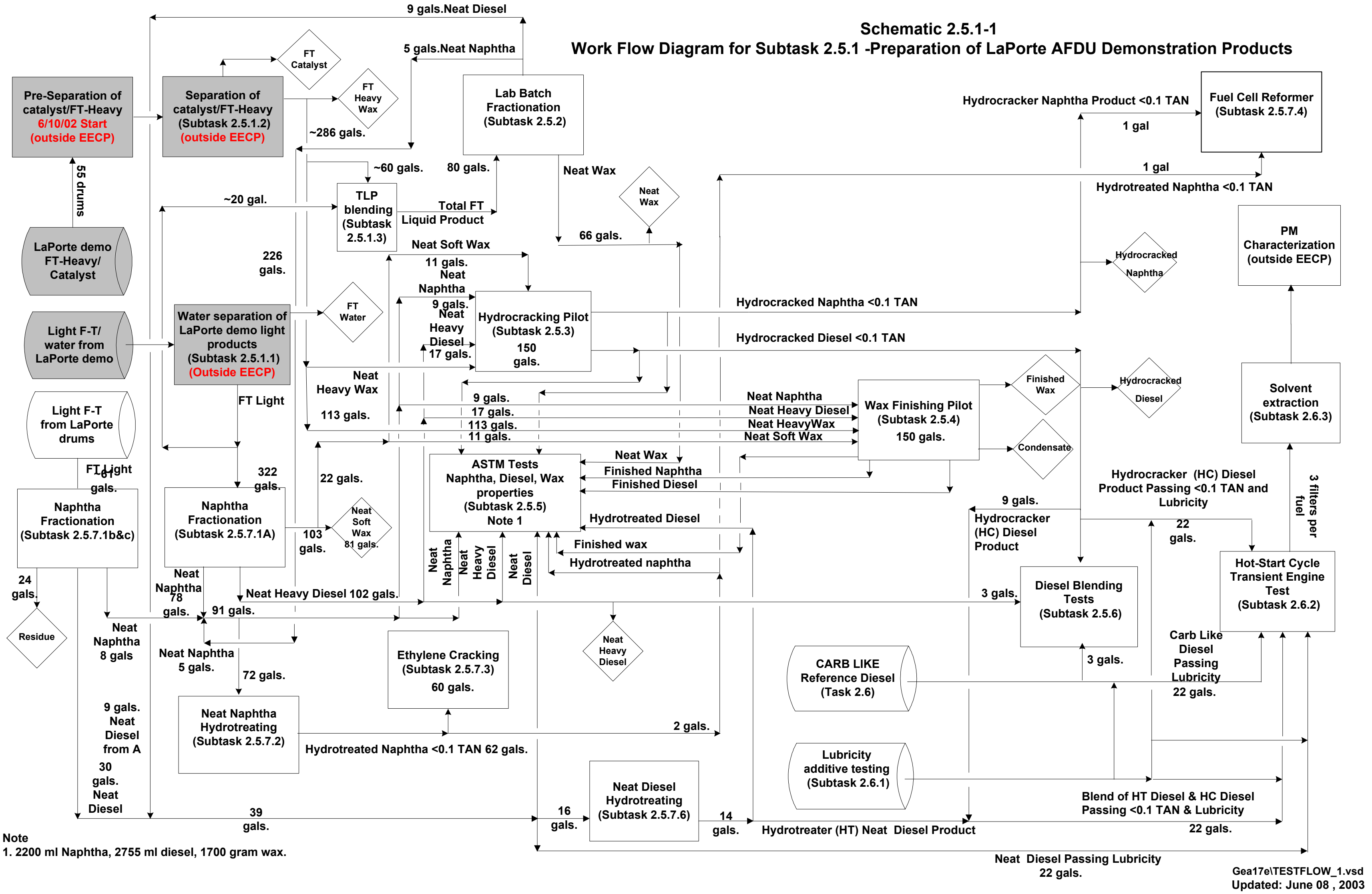
Results and Discussion

Subtask 2.5.1.1 Water Separation from F-T Light Product

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

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

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



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

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

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Updated: June 08 , 2003

Subtask 2.5.1.2 Catalyst Separation from F-T Heavy Product

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

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

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

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

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

Fischer-Tropsch Product Upgrading (Task 2.5)

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

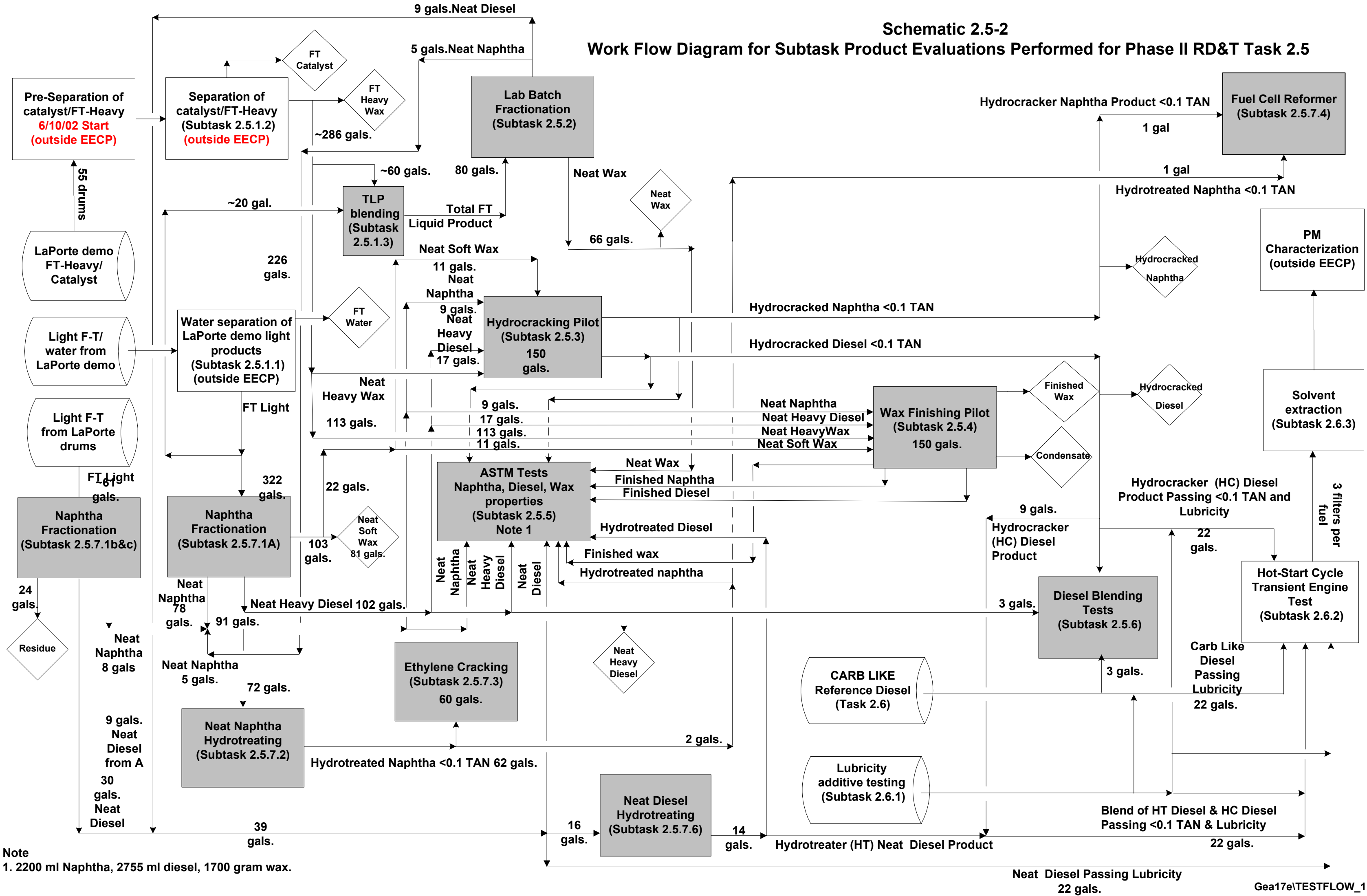
While some product upgrading licensor technologies have not been applied to the F-T product liquids, previous information indicates that these licensor technologies are adaptable. Therefore, the technical risks associated with F-T product upgrading based on available knowledge of feed properties is considered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

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

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

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

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



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

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Updated: June 08 , 2003

Subtask 2.5.2 Lab Batch Fractionation

Experimental

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

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

Results and Discussion

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

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

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

Table 2.5.2-2 - Subtask 2.5.2			
Neat F-T Naphtha Product Properties From Subtask 2.5.2 Lab Batch Fractionation (Blend Component with Subtask 2.5.7.1.b and c Neat F-T Naphtha)			
ILT ID No.		**2066772**	
Gravity, °API		**57.1**	
Specific Gravity		**0.7503**	
Nitrogen	**ppmw**	**2.5**	
Sulfur	**ppmw**	**<6**	
		Temperature, (K)	**(°F)**
Simulated Distillation, V%			
	1%	**334**	**141**
	5%	**360**	**188**
	10%	**369**	**204**
	30%	**422**	**300**
	50%	**432**	**319**
	70%	**447**	**345**
	90%	**466**	**379**
	95%	**468**	**383**
	99%	**470**	**387**

Table 2.5.2-3 - Subtask 2.5.2

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

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

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

Table 2.5.2-4 - Subtask 2.5.2

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

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

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

Subtask 2.5.3 Hydrocracking Pilot

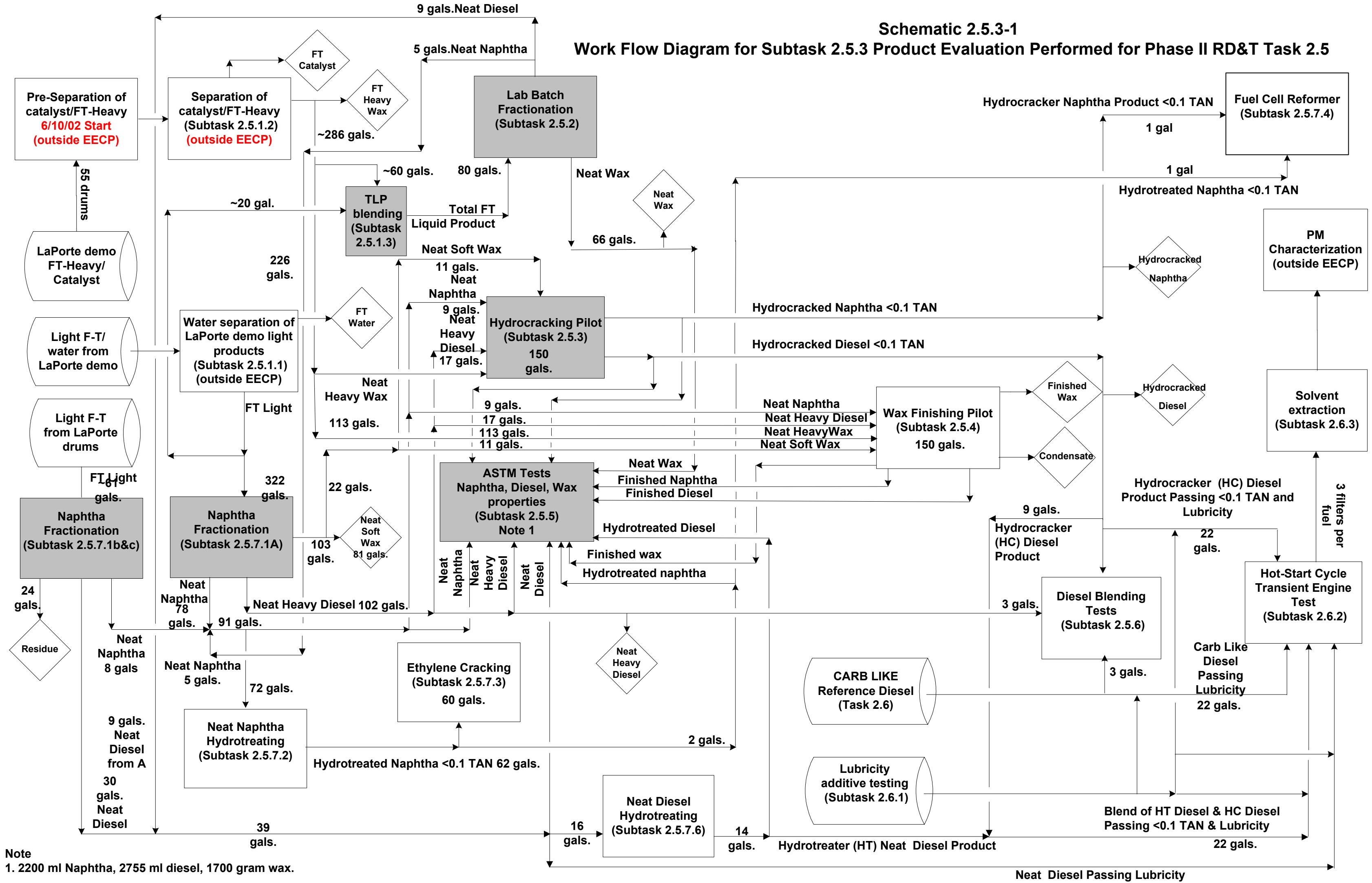
Experimental

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

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

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

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



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

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Updated: June 08 , 2003

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

Equipment

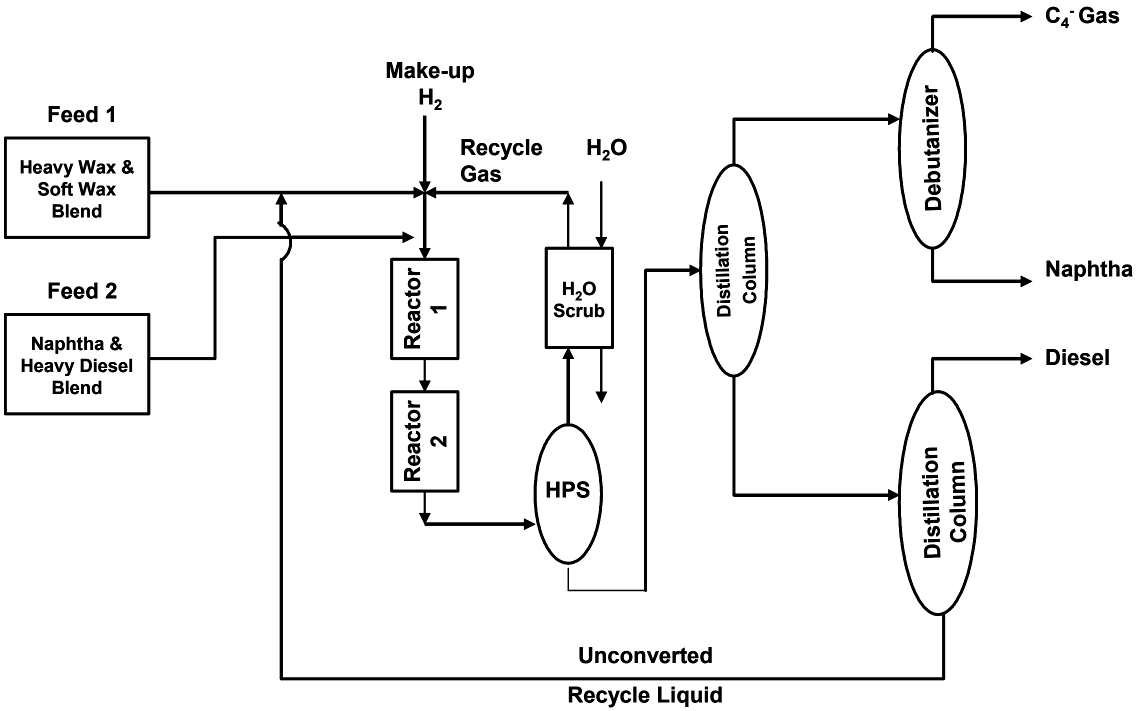
Chevrontexaco Technology Marketing (TEMA) performed Pilot Plant Run 81-143 for the hydrocracking test of the Fischer-Tropsch product. **Figure 2.5.3-1** shows the block flow diagram of the pilot plant setup for the hydrocracking test. This is the standard configuration for a hydrocracking pilot plant.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

Feed Composition

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

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

Figure 2.5.3-1
Hydrocracking Pilot Plant Block Flow Diagram



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

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

Results and Discussion

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

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

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

Table 2.5.3-1 Hydrocracker Feed Blends

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

Table 2.5.3-2

Feed Properties for Hydrocracking Pilot Plant

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

Table 2.5.3-3

Yields Relative to Feed and Product Properties

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

Diesel Production and Blended Product Qualities

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

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

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

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

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

Table 2.5.3-4 Hydrocracked Diesel Blends for Testing

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

Table 2.5.3-5

Hydrocracked Product Properties

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

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

Subtask 2.5.4 Wax Finishing Pilot

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

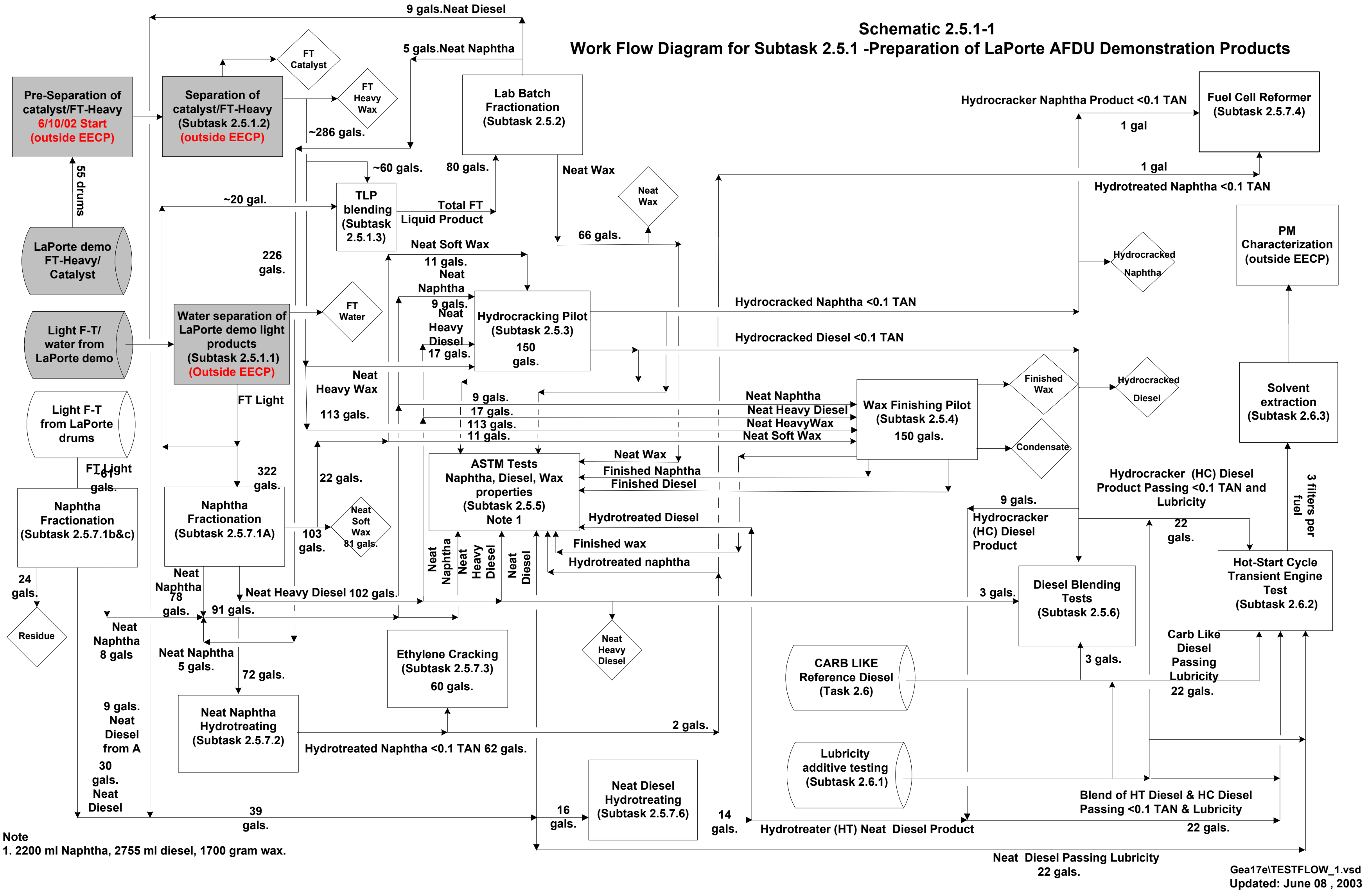
The LaPorte AFDU F-T heavy product wax contains mostly normal paraffins with minor amounts of olefins, oxygenates, and acids. The value of the wax, with appropriate upgrading to maximize finished high-melting point, food-grade wax product, is expected to benefit the economics of the EECP. The expected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

Specialty Low- and Medium-Melting Point Waxes

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

Specialty High Melting Point Waxes

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



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

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

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Updated: June 08 , 2003

Table 2.5.4-1

Desired Low- and Medium-Melting Point Wax Product Properties

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

Table 2.5.4-2

Desired High-Melting Point Wax Product Properties

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

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

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

Experimental

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

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

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

Equipment

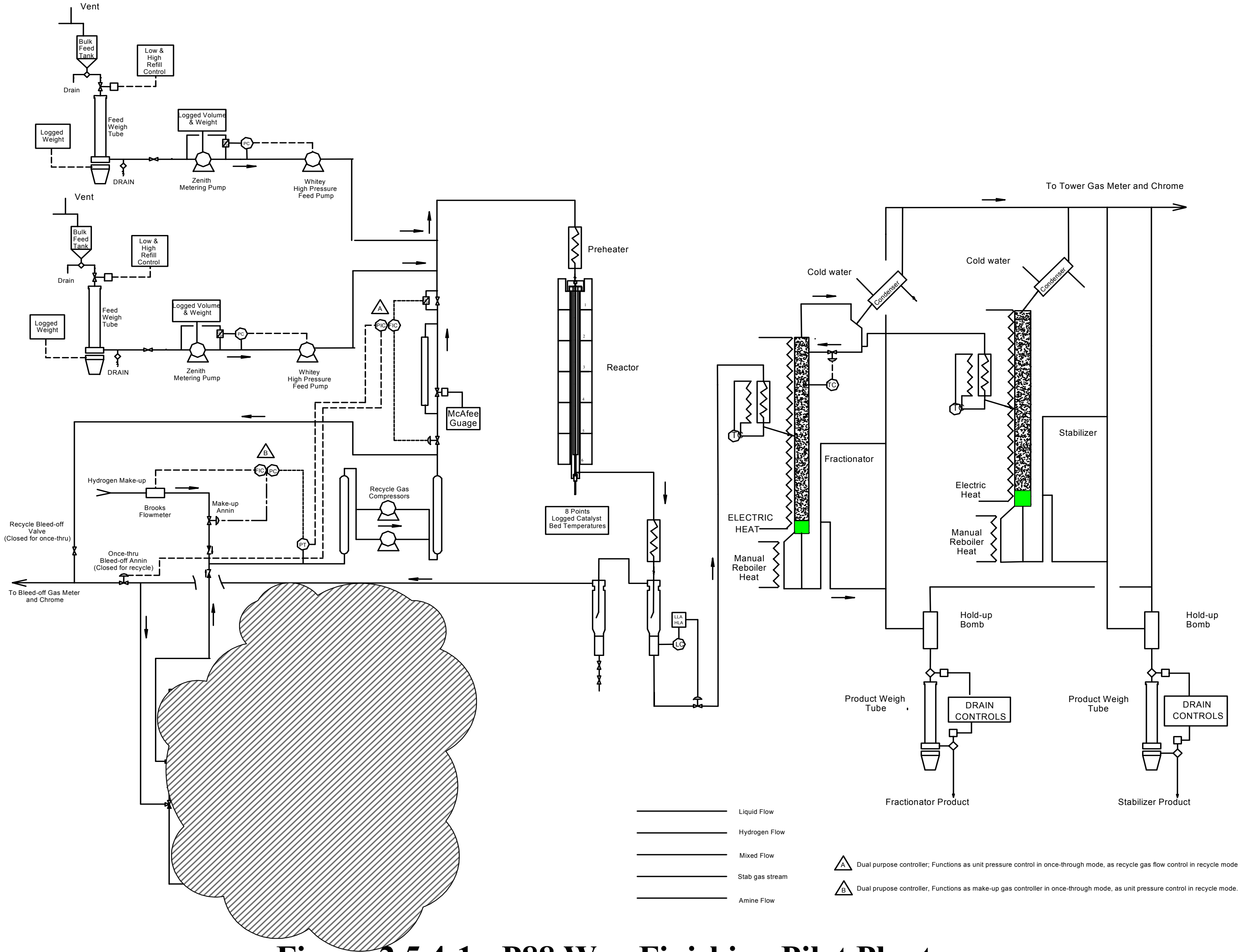
Figure 2.5.4-1 presents a simplified process flow diagram of the P88 wax finishing pilot plant. The naphtha/diesel feed (2) and the wax feed (1) are separately charged into bulk feed tanks, then routed to a feed weigh tube. The weight is logged. The feeds are pumped into the preheater using a metering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

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

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

Table 2.5.4-3 - Feedstock Inspection Testing

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



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

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

Figure 2.5.4-1 - P88 Wax Finishing Pilot Plant

Results and Discussion

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

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

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

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

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

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

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

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

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

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

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

Major results of the wax finishing pilot plant tests include:

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

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

   The catalyst is very susceptible to temperature runaway.

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

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

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

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

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

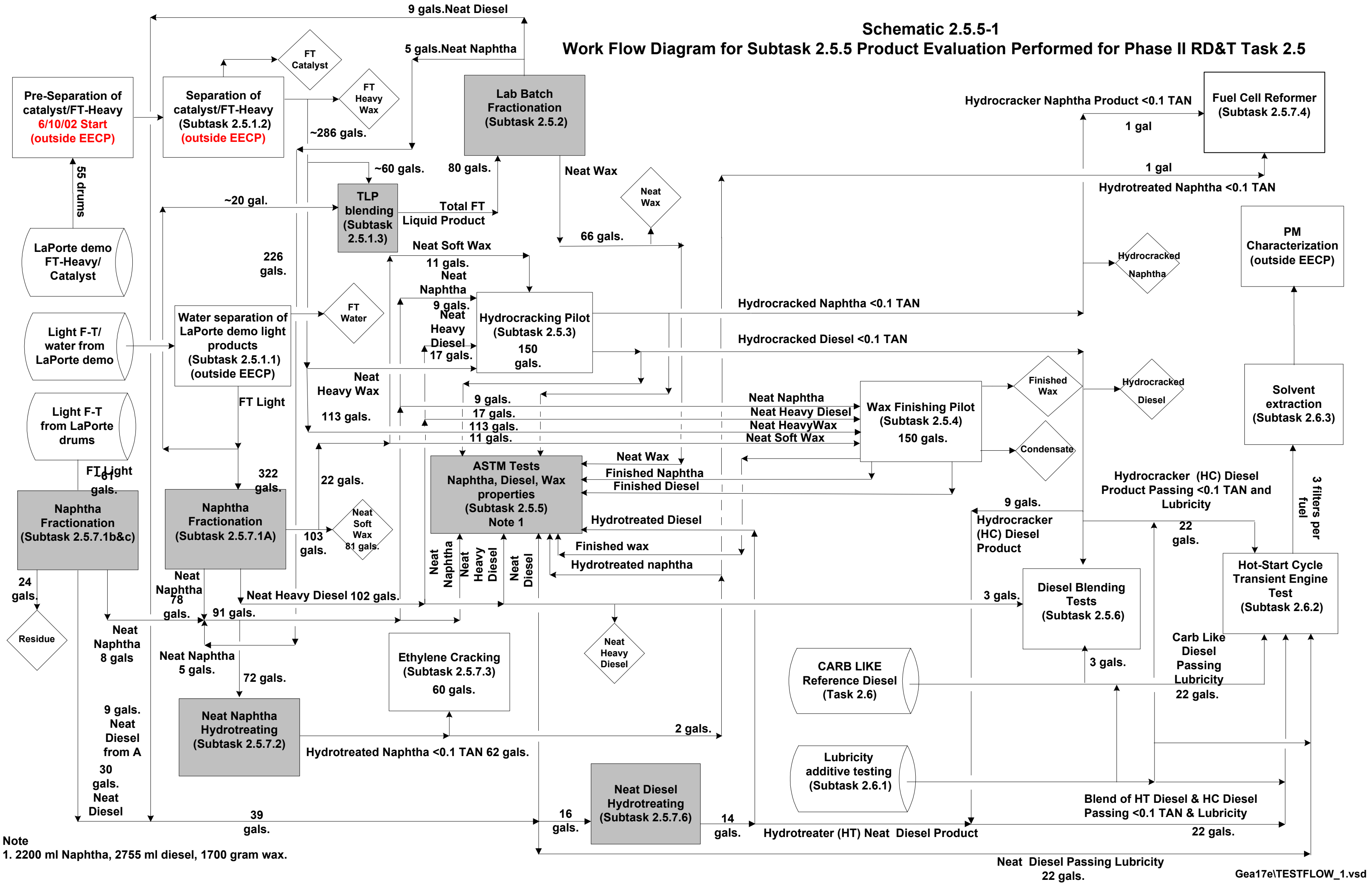
Inspection testing was conducted as a continuing quality assurance check that fuel and specialty wax product specifications were being met for Task 2.5 product evaluations. The flow of work for Subtask 2.5.5 is illustrated in **Schematic 2.5.5-1**. Subtask 2.5.5 entitled “ASTM Naphtha, Diesel, Wax Properties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

Oxygen Concentration Determination

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

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

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



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

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Updated: June 08 , 2003

Table 2.5.5-1
Naphtha Characterization Testing Schedule for Subtask 2.5.5

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

Table 2.5.5-2
Diesel Characterization Testing Schedule for Subtask 2.5.5

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

Table 2.5.5-3
Wax Characterization Testing Schedule for Subtask 2.5.5

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

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

Subtask 2.5.6 Diesel Blending Tests

Experimental

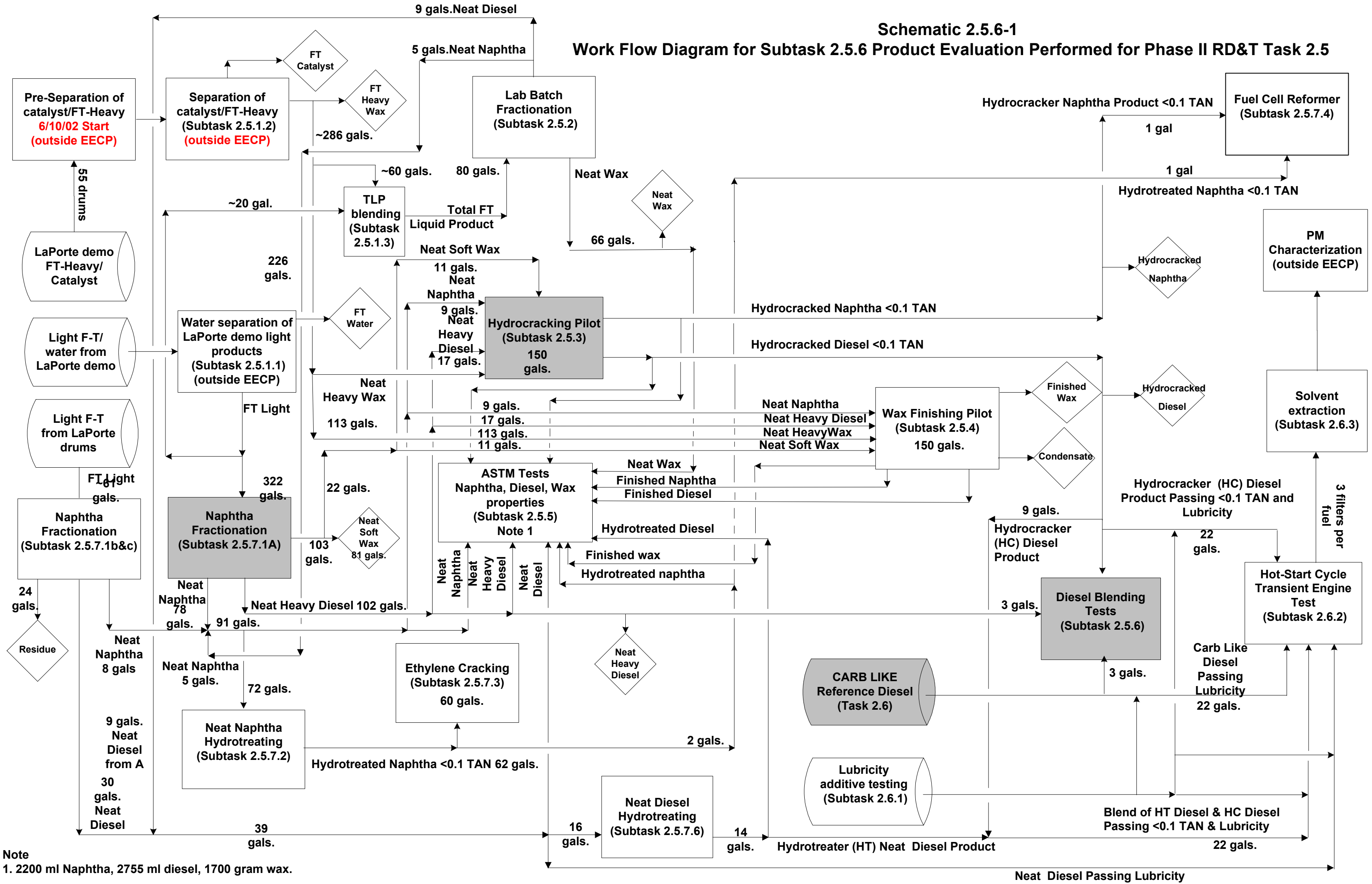
A summary is presented of the important results which mitigated potential risks to the EECP as result of the work conducted in the Subtask 2.5.6 entitled “Diesel Blending Tests” are found in the Subtask 2.5.6 Test Report which is included as Appendix E to this Topical Report. The flow of work for Subtask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

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

Neat F-T Diesel Direct Blending to Transportation Fuel

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

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



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

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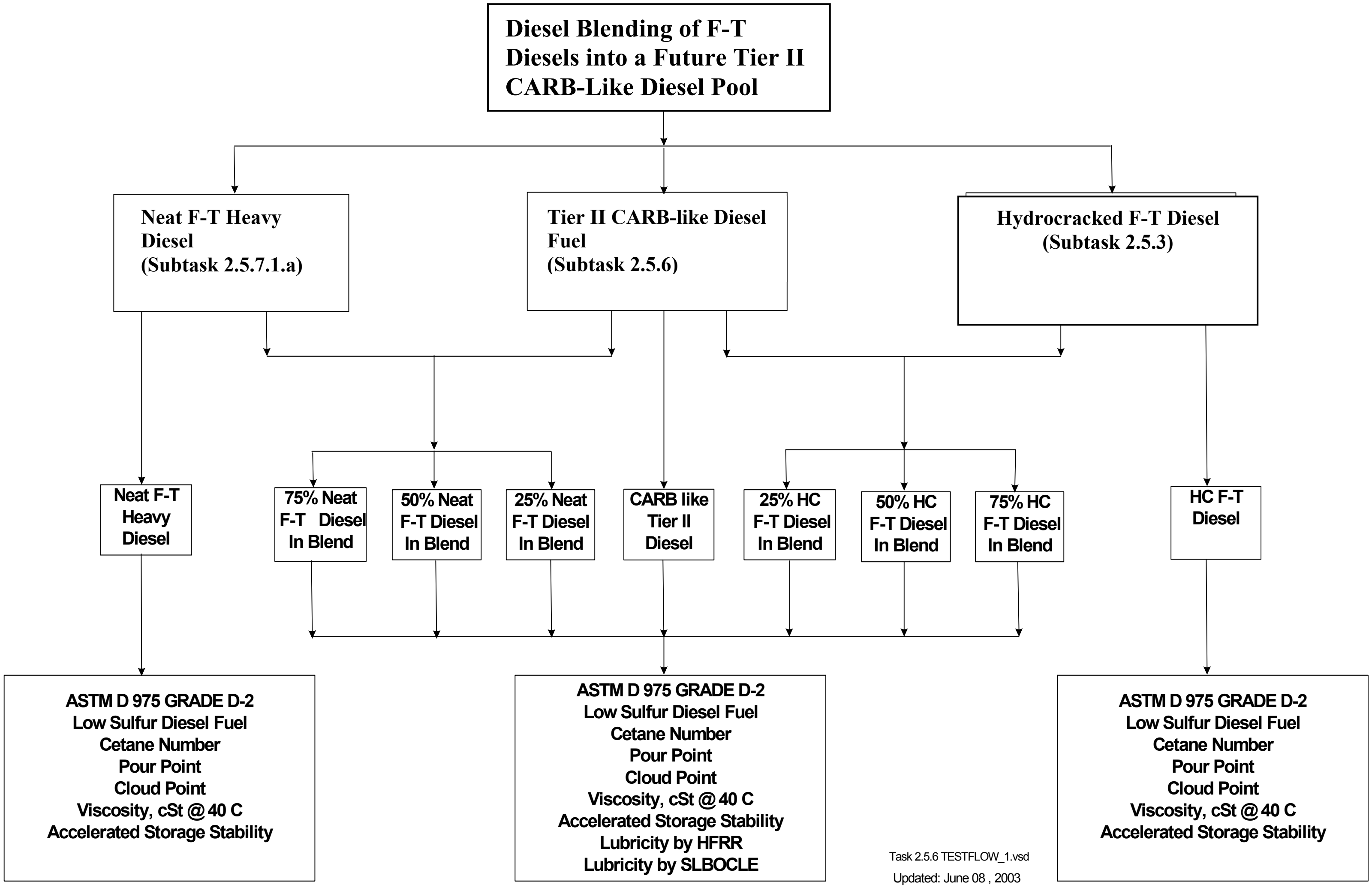
Schematic 2.5.6-2
Flow of Work for Subtask 2.5.6 Diesel Blending Testing



Hydrocracker F-T Diesel Direct Blending to Transportation Fuel

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

Results and Discussions

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

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

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

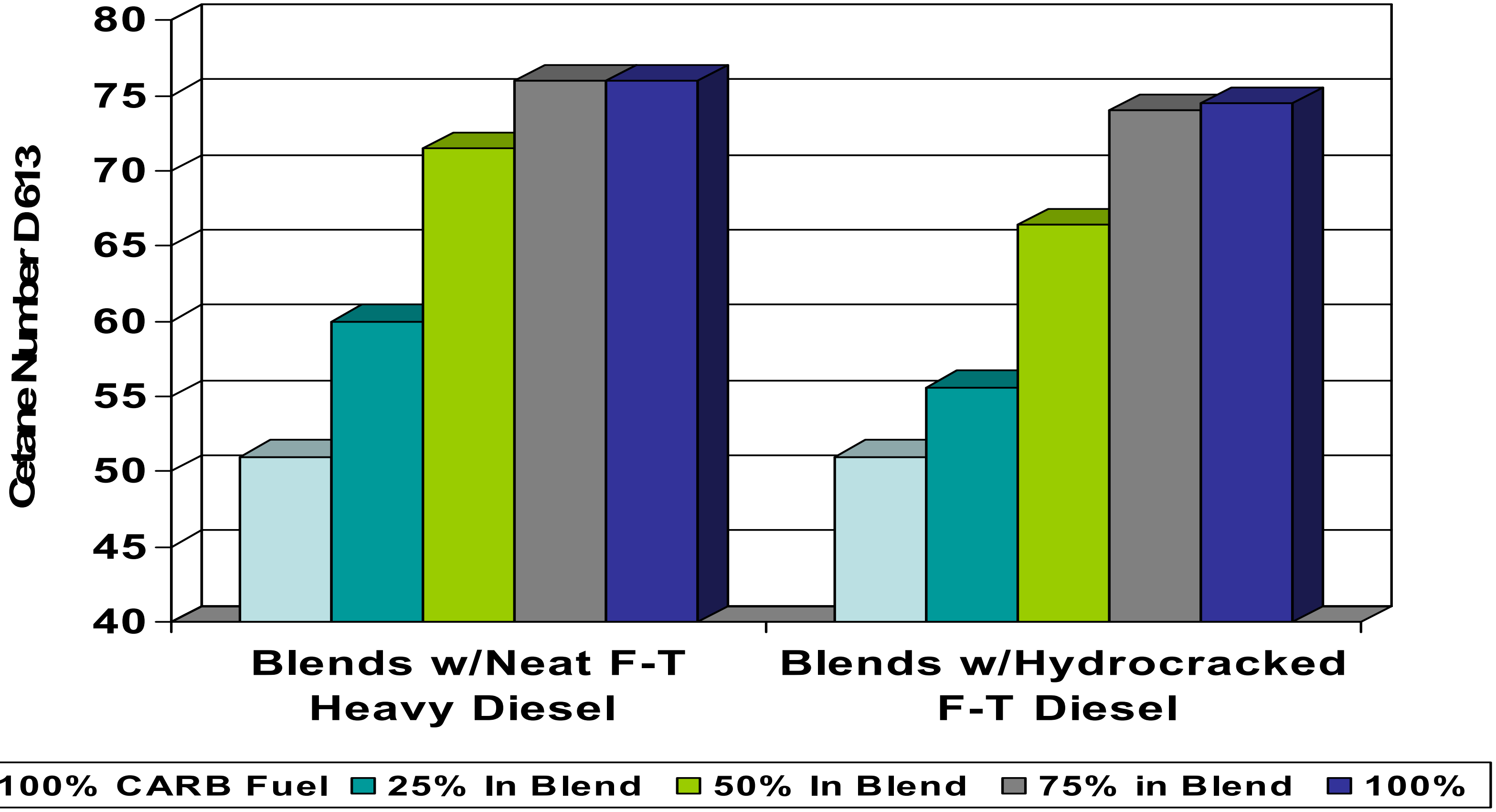
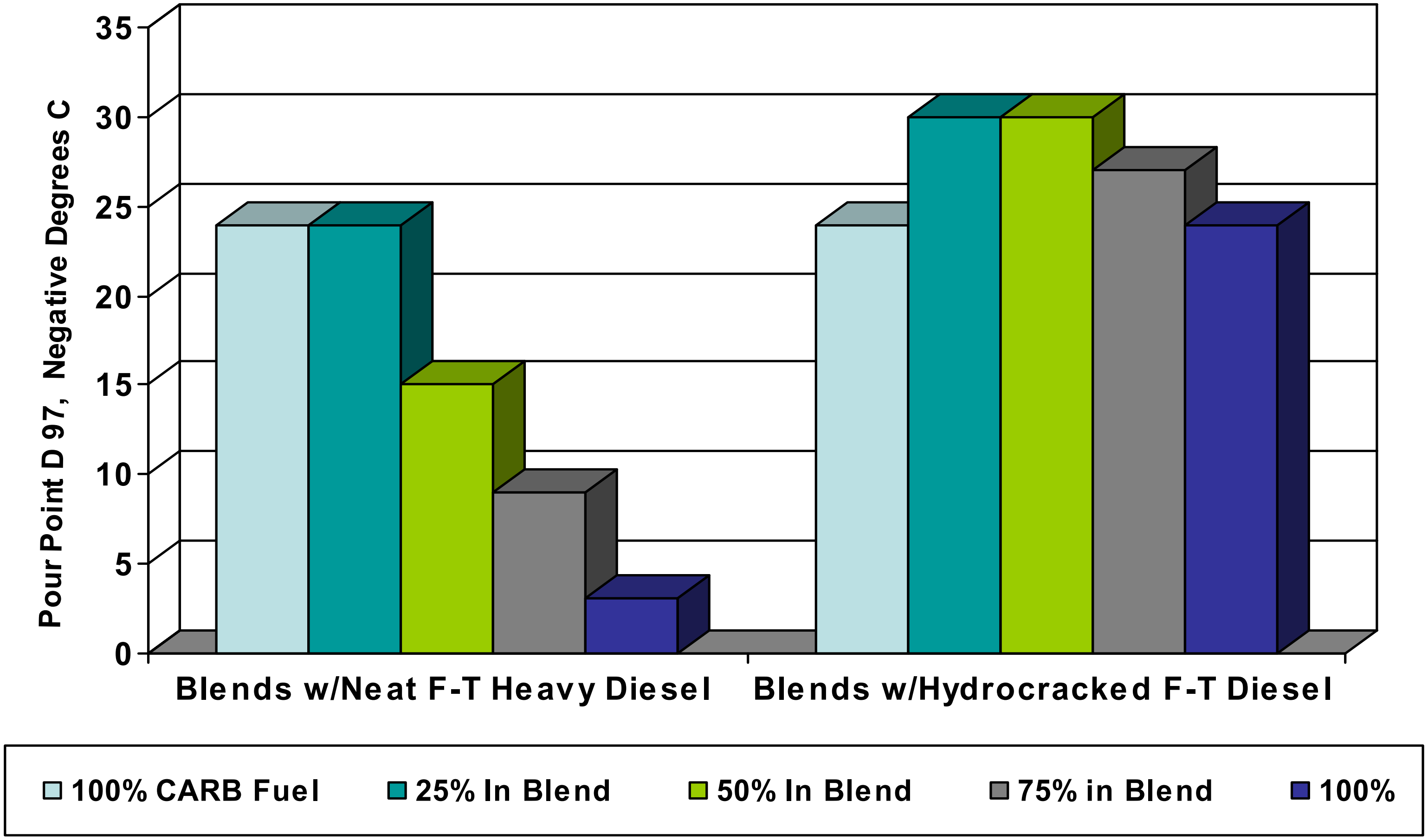


Figure 2.5.6-2 – Pour Point Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



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

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

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

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

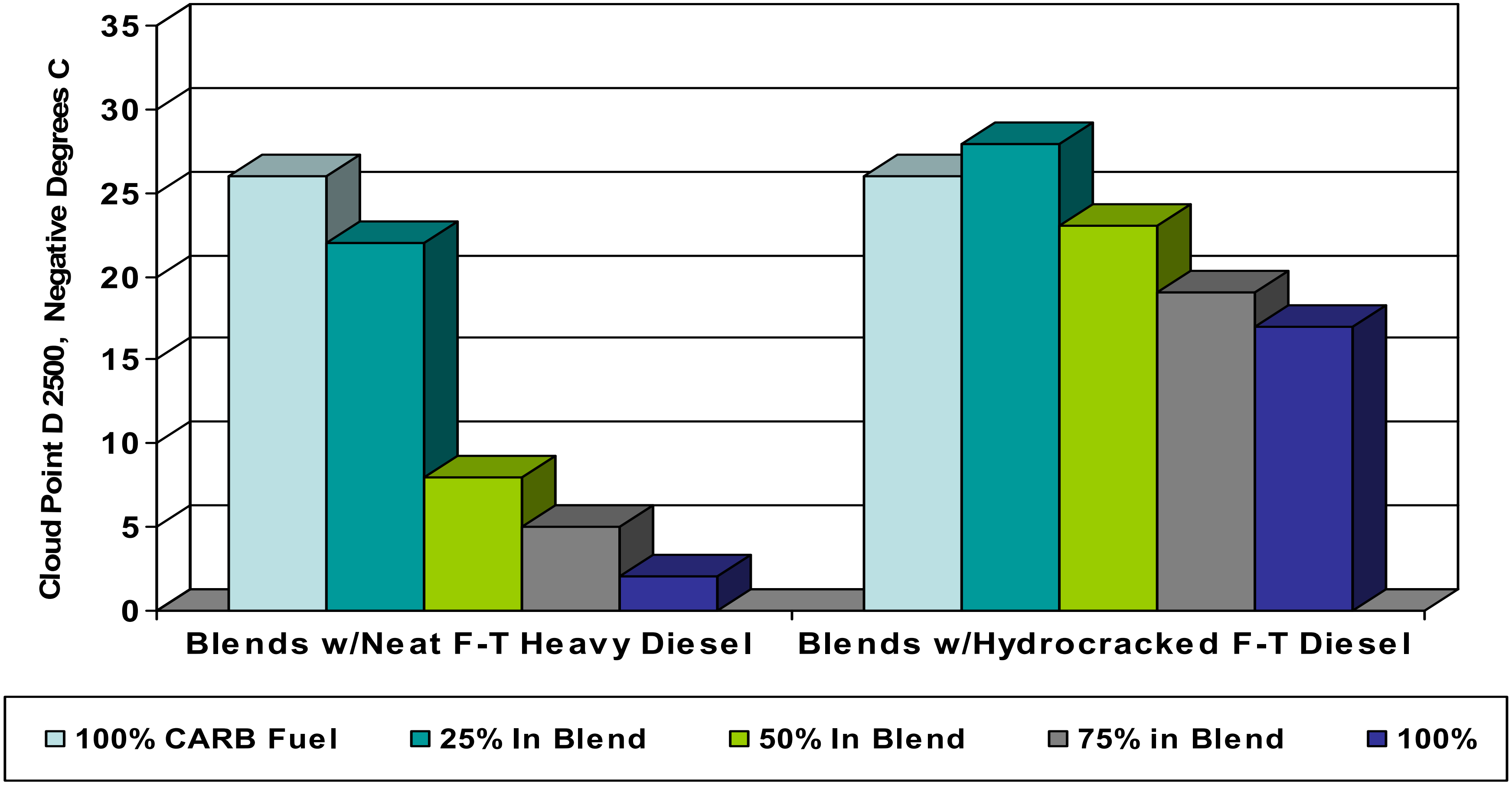
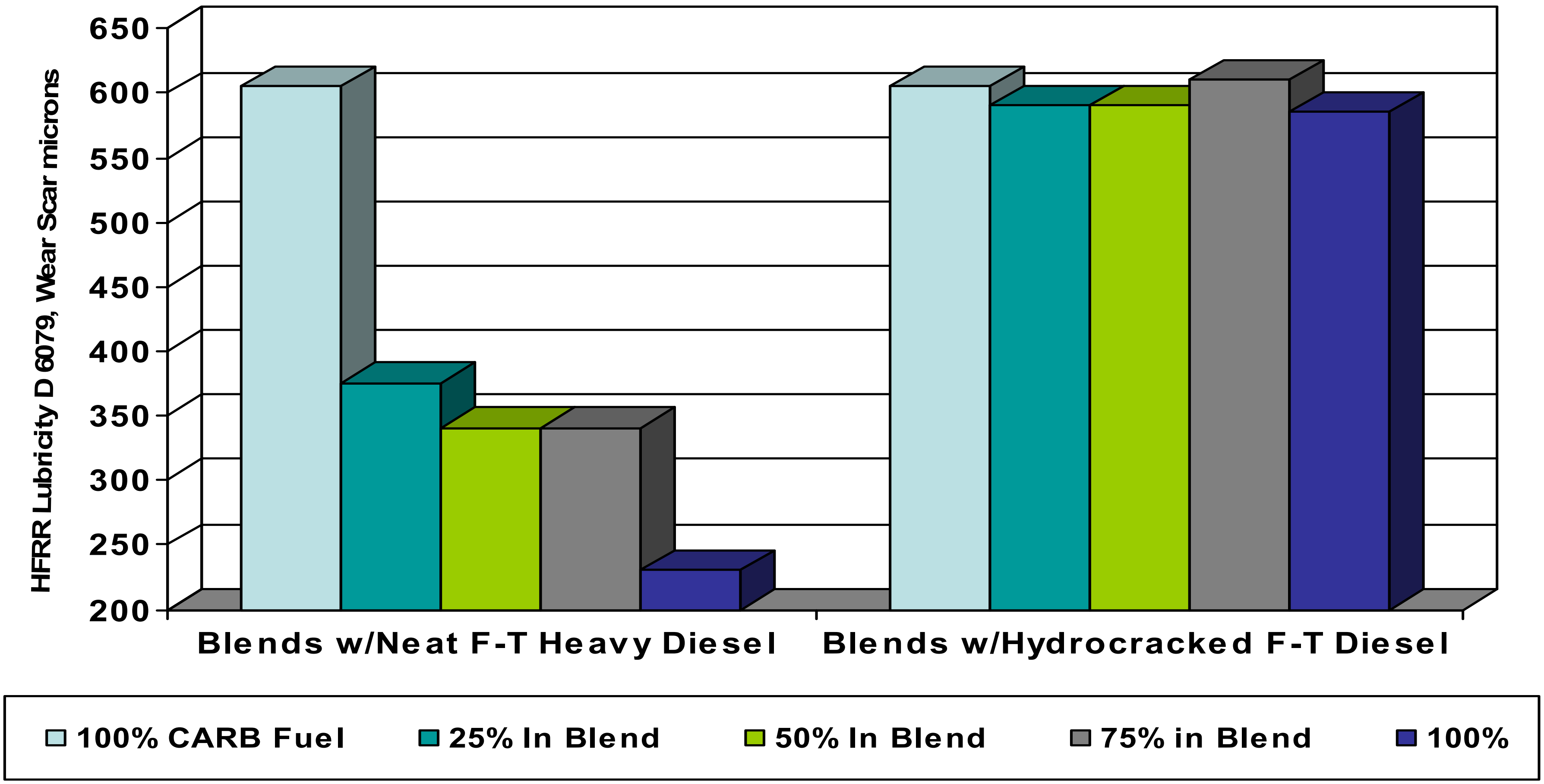


Figure 2.5.6-4 – HFRR Lubricity Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool



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

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

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

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

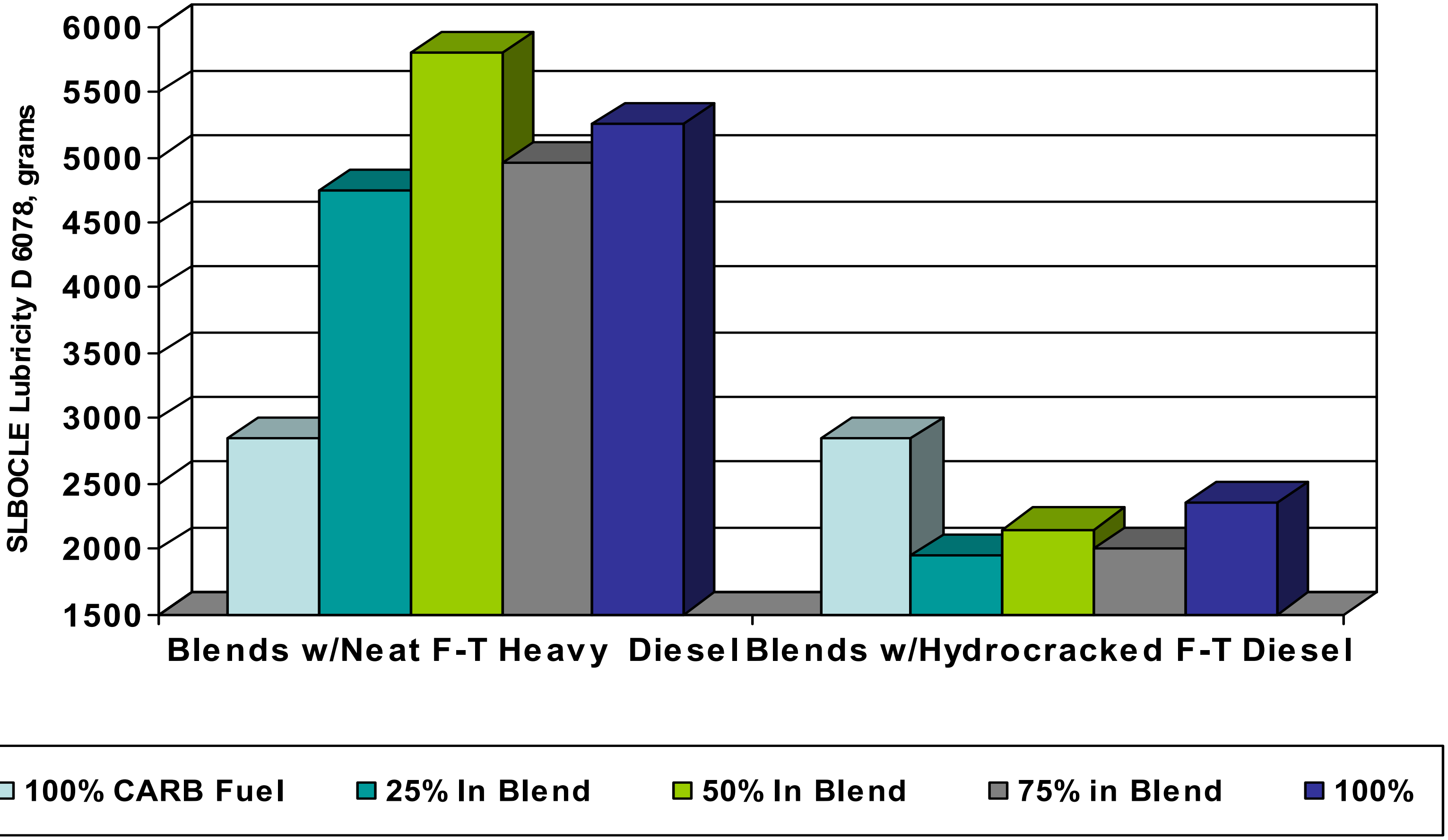
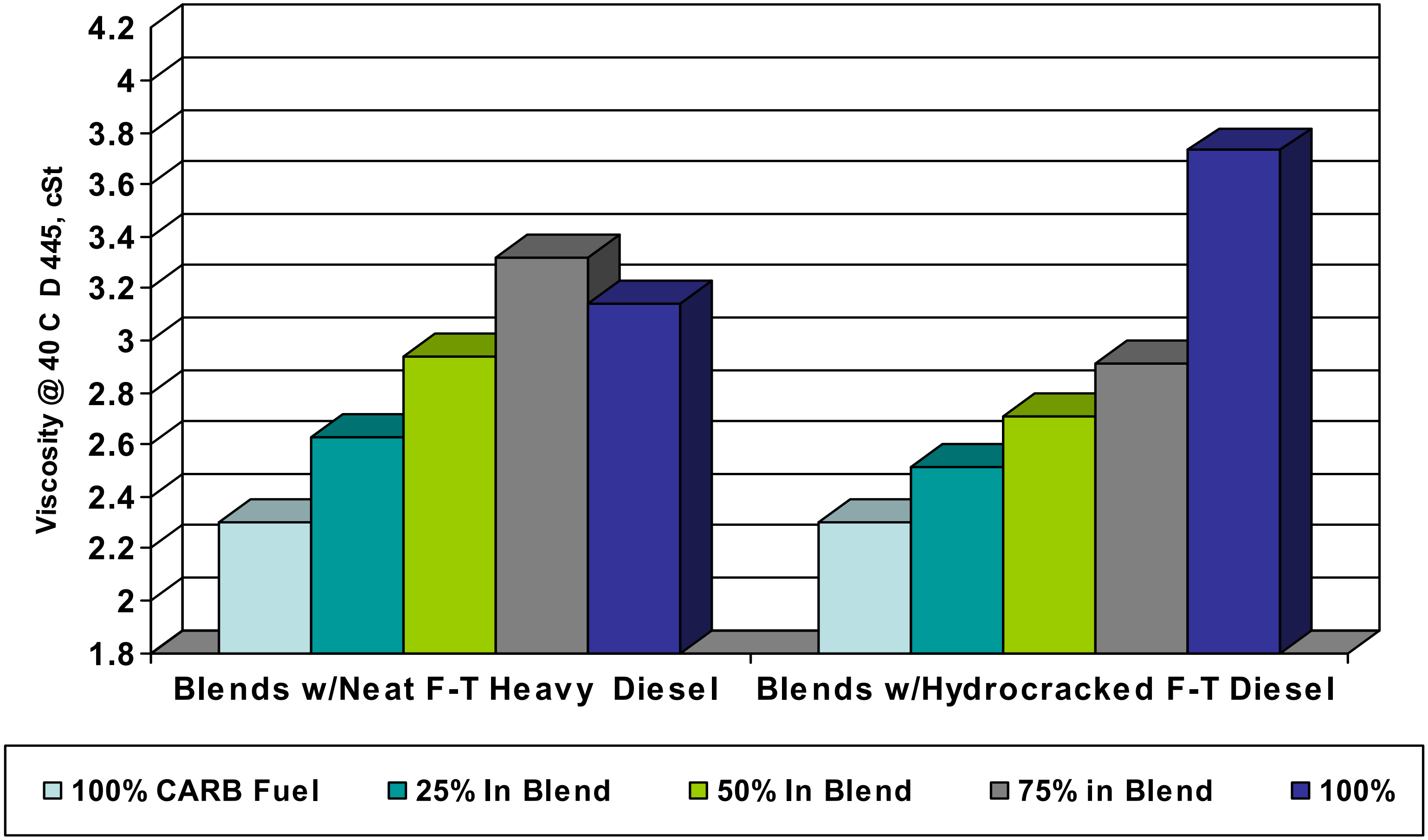


Figure 2.5.6-6 – Viscosity @ 313K (40°C) Response to Direct Blending F-T Diesels into a Future Tier II CARB-Like Diesel Pool

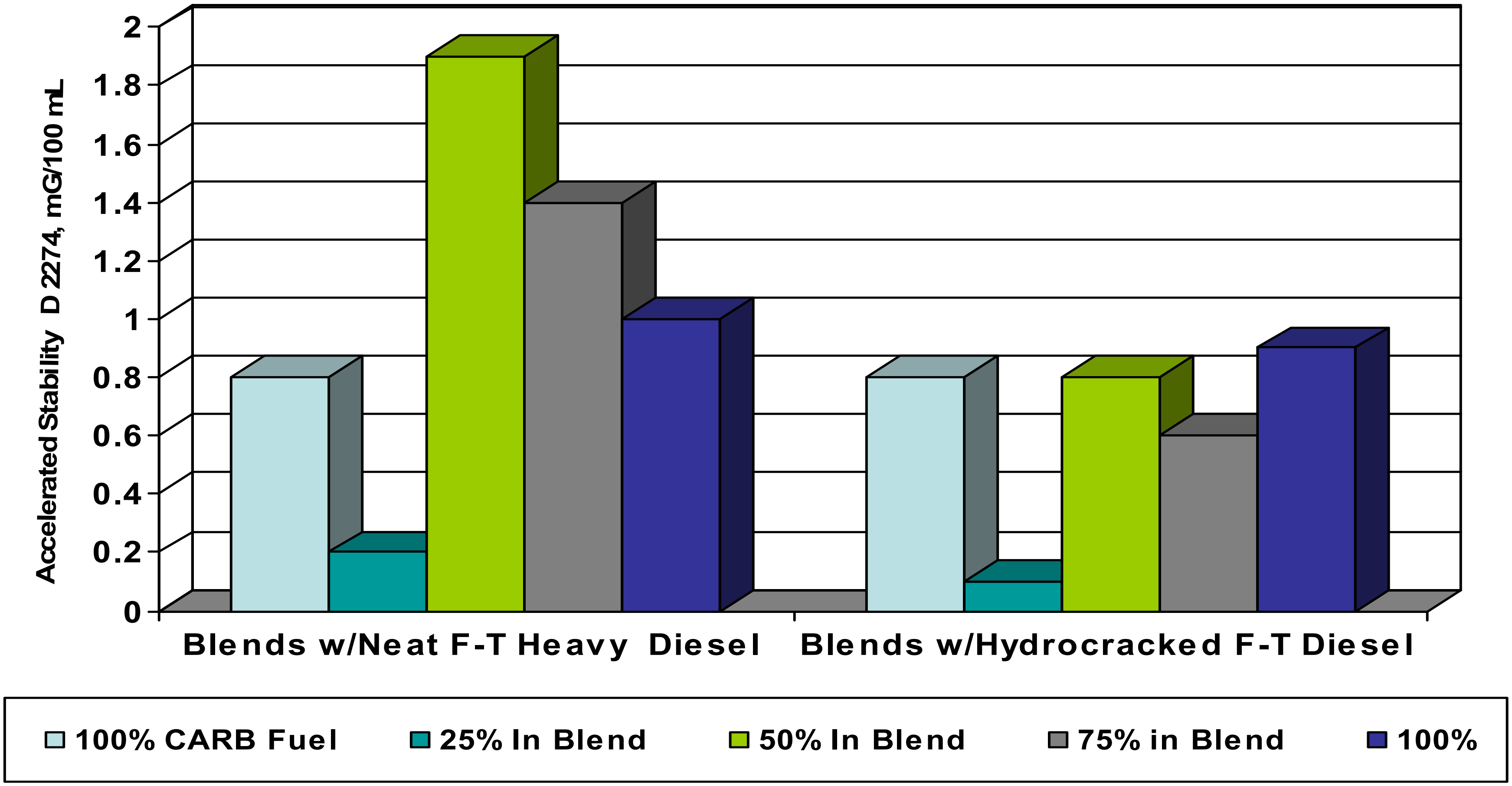


All of the test fuel blends composed of the neat F-T diesel, the HC F-T diesel, and the Tier II CARB-like diesel reference fuel had passing ASTM D-975 centistokes values for kinematic viscosity at 313K (104°F).

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

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

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



Subtask 2.5.7.1.a, b, and c Naphtha Fractionation

Experimental

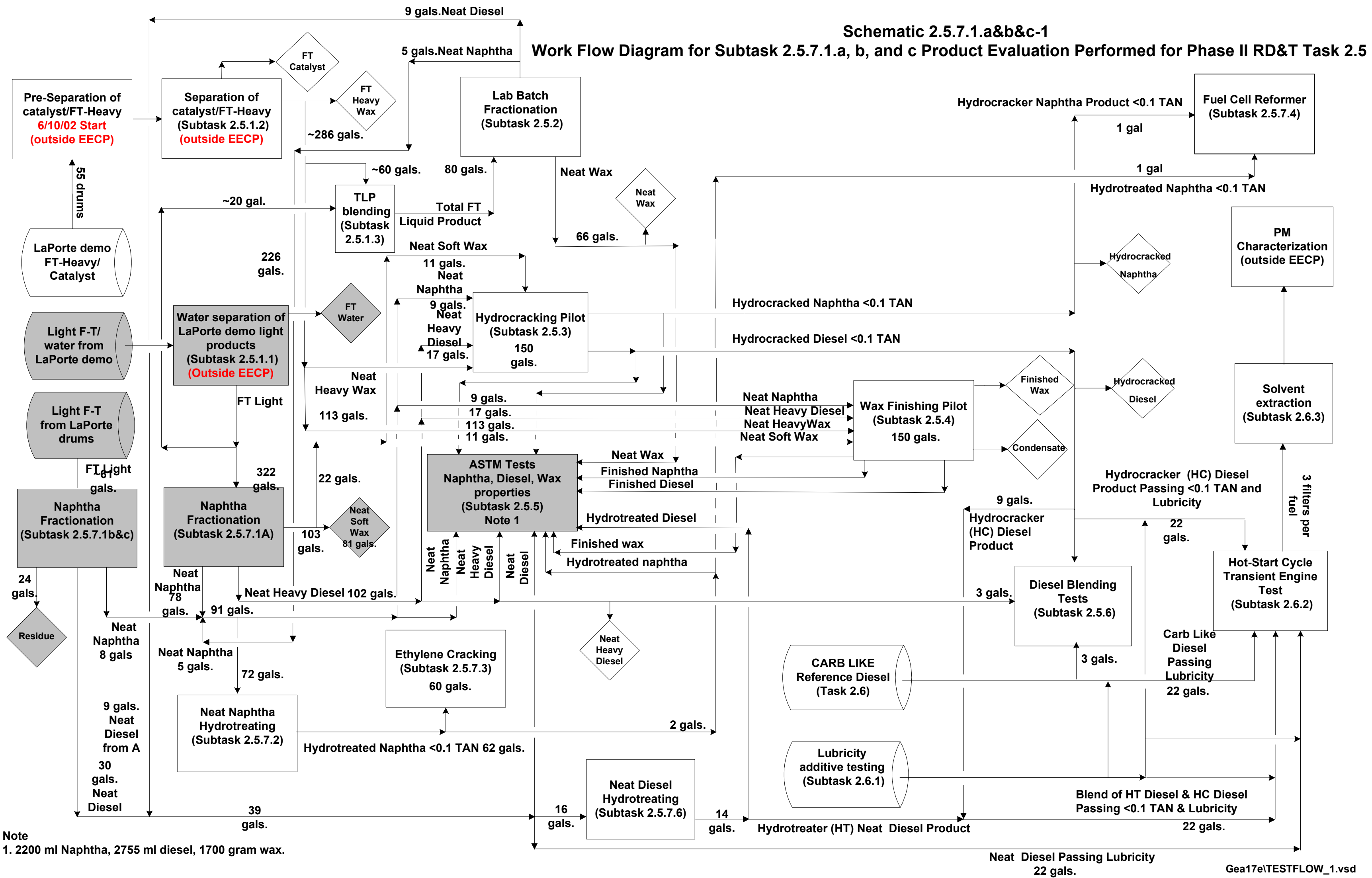
The risks to be mitigated by distillations conducted under Subtask 2.5.7.1.a, b, and c distillations were the maximum recoveries of an IBP-466K (380°F) neat F-T naphtha, a 466K (380°F) to 644K (700°F) neat F-T diesel, and a 644K (700°F) plus neat F-T soft wax product. These fractions meet fuel and specialty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

Results and Discussion

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

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

Schematic 2.5.7.1.a&b&c-1
Work Flow Diagram for Subtask 2.5.7.1.a, b, and c Product Evaluation Performed for Phase II RD&T Task 2.5



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Table 2.5.7.1-9			
Inspection Tests on Neat F-T Diesel Products Task 2.5.2 and Subtask 2.5.7.1a, b, and c Distillation Products Blending for End-use Product for Task Sub 2.5.7.6 Neat F-T Diesel Hydrotreating			
Subtask	**2.5.2**	**2.5.7.1.b**	**2.5.7.1.c**
Product Identification	**Diesel 466K-644K (380°F-700°F)**	**Diesel 466K-644K (380°F-700°F)**	**Diesel 466K-644K (380°F-700°F)**
Analyses			
Gravity, API	**43.5**	**43.7**	**43.7**
Specific Gravity	**0.8086**	**0.8076**	**0. 8076**
Sulfur, ppmw	**<6**	**1.3**	**<1**
Nitrogen, ppmw	**11**	**2**	**2**

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

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

Major results of the naphtha fractionation tests include:

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

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

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

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

Subtask 2.5.7.2 Neat Naphtha Hydrotreating

Experimental

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

Feed Composition

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

Equipment

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

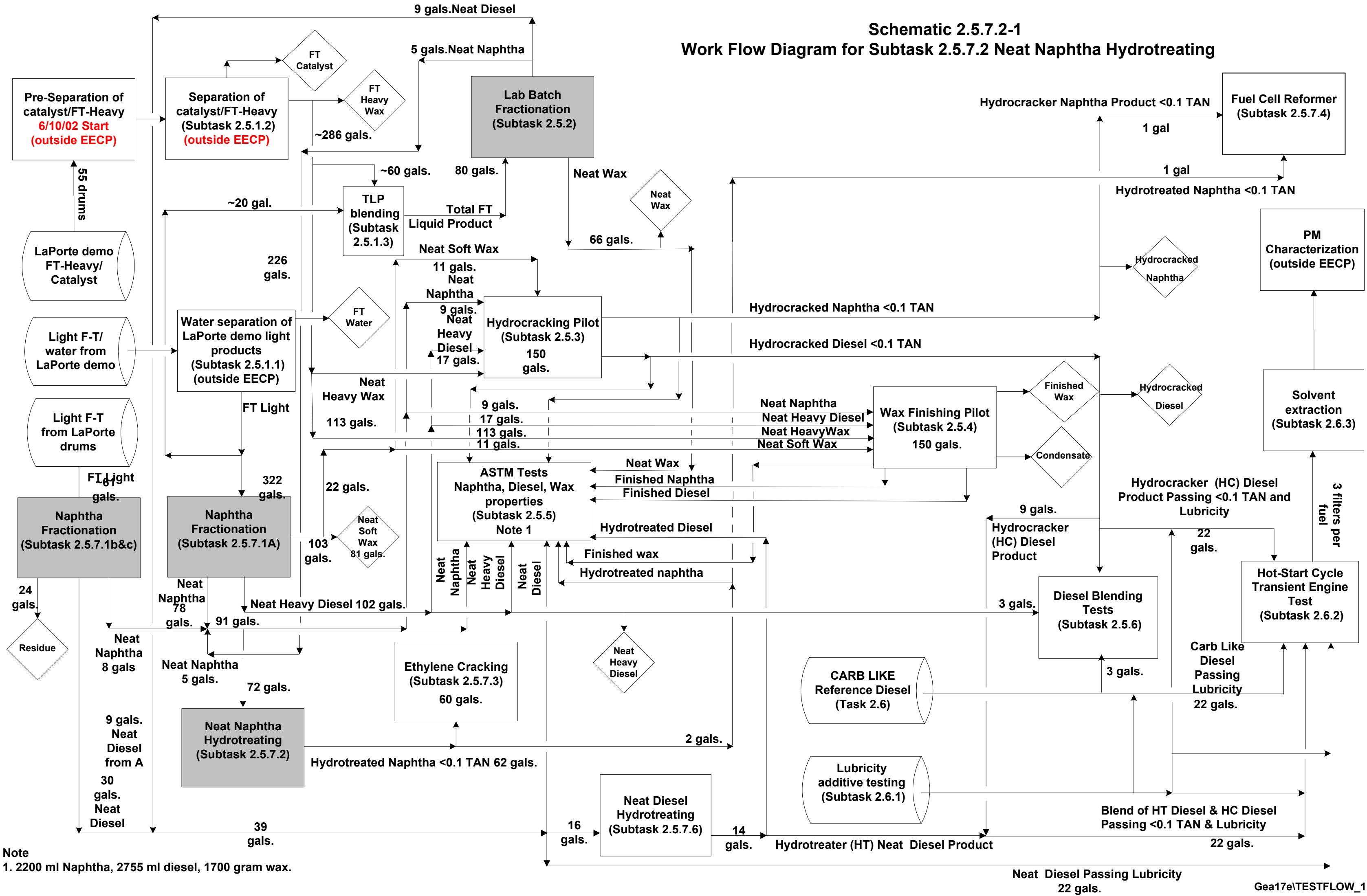
Results and Discussion

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

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

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

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



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

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Table 2.5.7.2-1

Naphtha Feed Properties for Hydrotreating Pilot Plant

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

Figure 2.5.7.2-1
Naphtha Hydrotreating Pilot Plant Block Flow Diagram

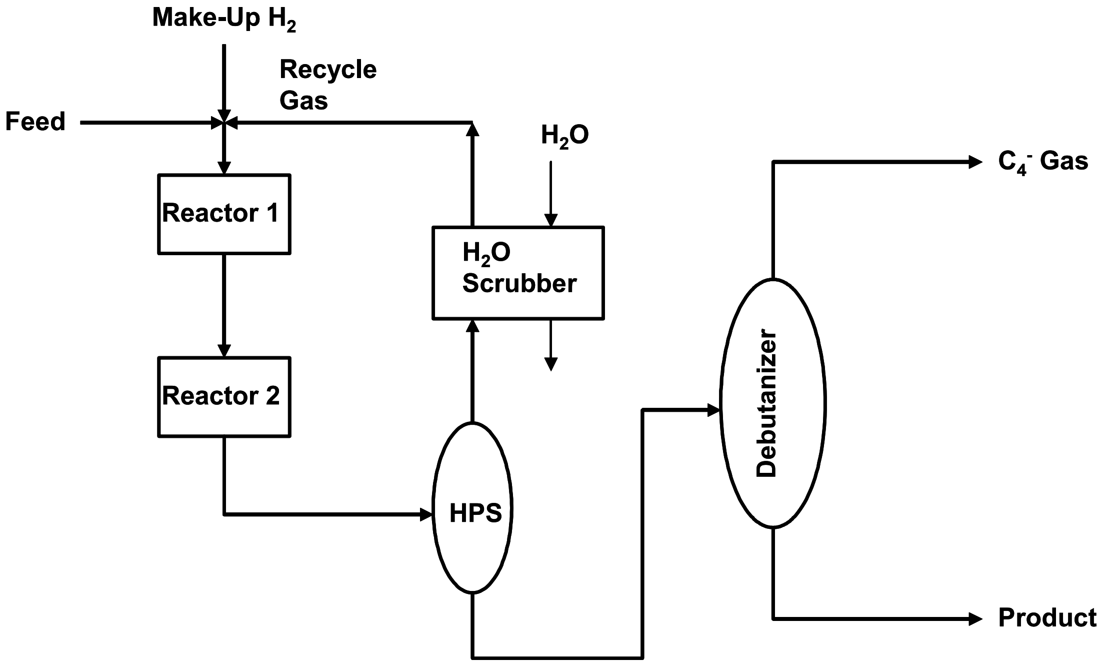


Table 2.5.7.2-2

Yields (Calculated by D2887) for Hydrotreating Naphtha

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

Table 2.5.7.2-3

Hydrotreated Naphtha Properties

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

Subtask 2.5.7.3 Ethylene Cracking

Experimental

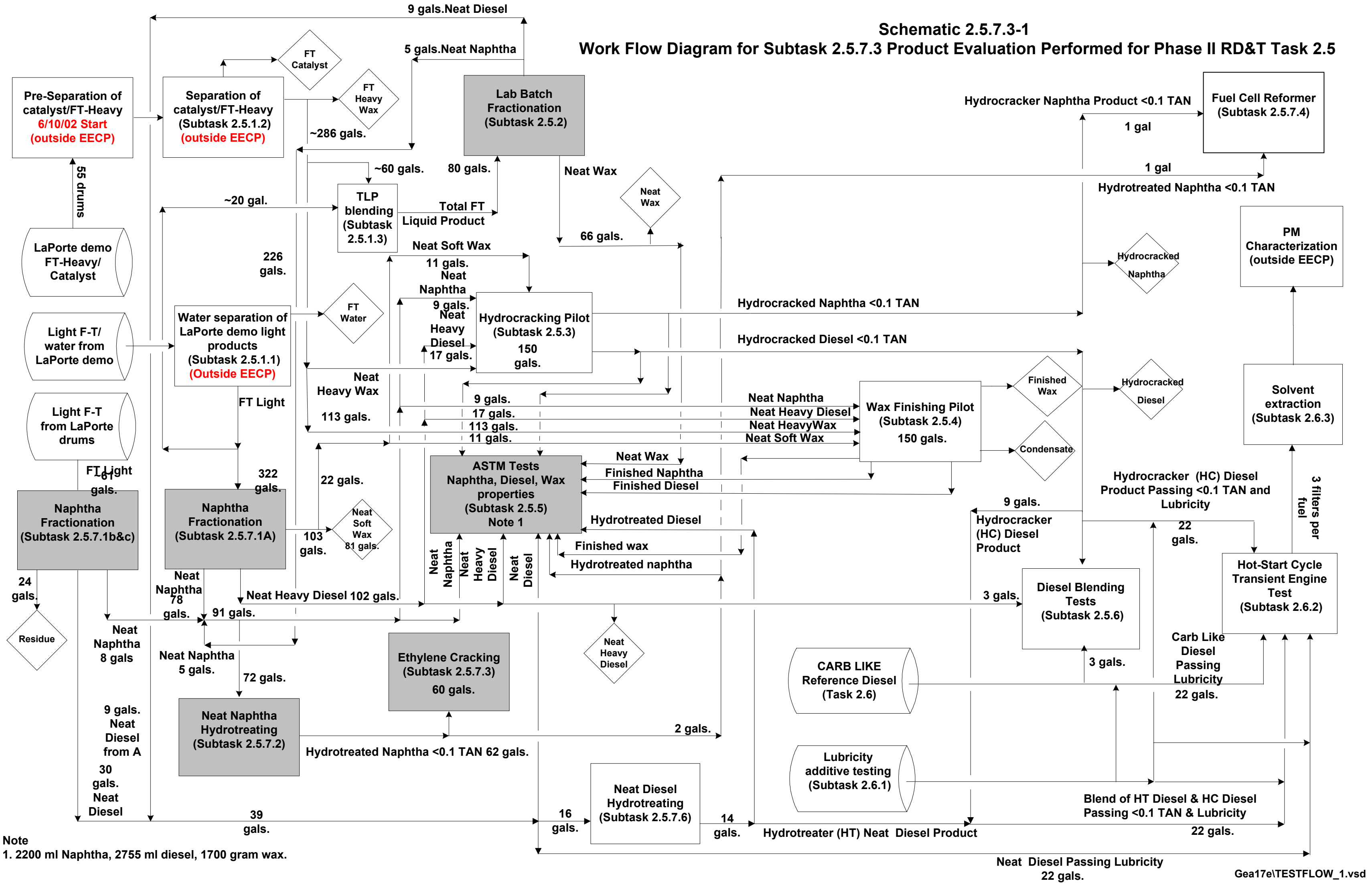
The potential technical and economic risks to the EECP from Task 2.5 can be mitigated by demonstrating that the F-T naphtha end-use product derived from the upgrading of the total F-T liquid product can meet or exceed current specifications for the manufacture of ethylene and propylene chemicals. A summary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

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

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

Schematic 2.5.7.3-1

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



Note

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

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

Feedstock Component

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

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

Reaction Mechanism

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

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

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

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

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

Kinetics

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

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

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

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

Cracking Severity

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

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

Residence Time

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

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

Equation Number 1: Residence time = VcMP/GRT

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

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

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

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

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

Effect of Operating Variables on Yields

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

Feedstock Hydrogen Content

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

$$\begin{aligned}
\text{D 3343 Equation: \%Hydrogen} = \quad & + (0.06317*\text{Gravity}) \\
& - (0.041089*\text{Aromatics}) \\
& + (0.000072135*\text{Aromatics}*\text{D86 Distillation Average}) \\
& + (0.00005684*\text{Gravity}*\text{D86 Distillation Average}) \\
& - (0.000496*\text{Gravity}*\text{Aromatics}) \\
& +10.56
\end{aligned}$$

Where:

Gravity = gravity, API
Aromatics = volume percent aromatics
D86 Distillation Average = average of 10, 50, and 90 percent distillation data, ^{o}F

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

Decoking

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

Results and Discussion

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

Feedstock Composition Results

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

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

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

Figure 2.5.7.3-1

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

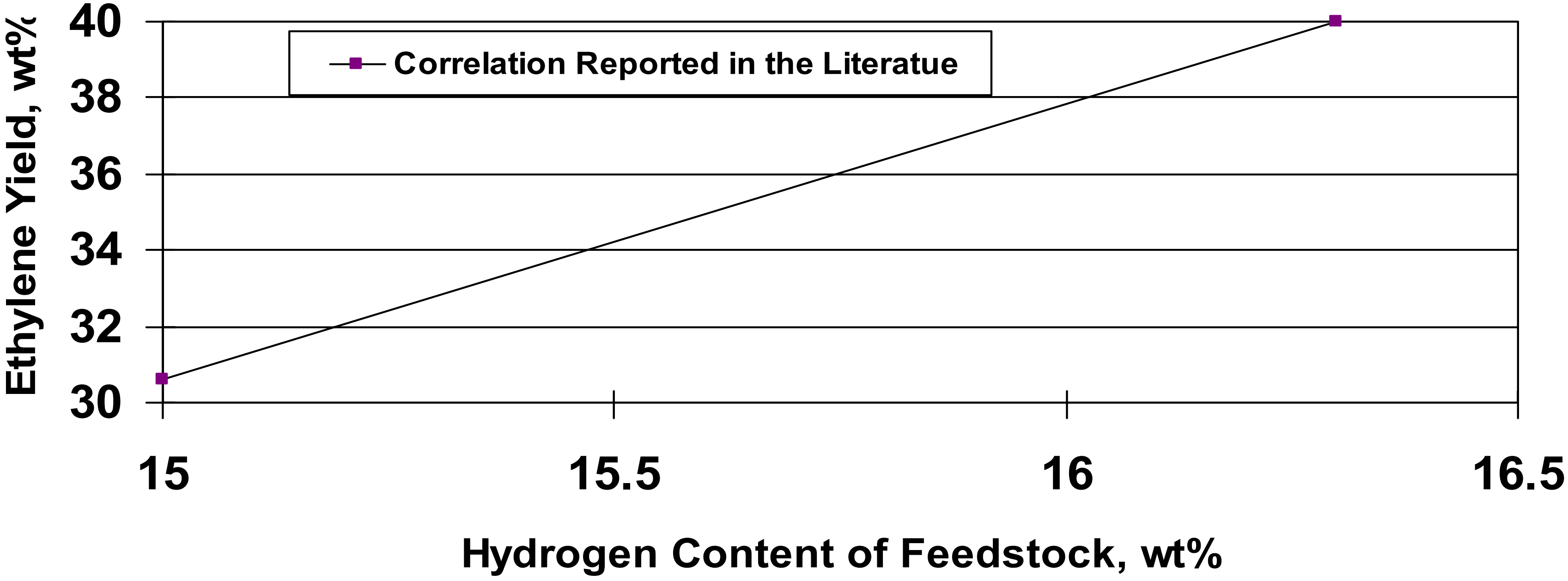


Table 2.5.7.3-1

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

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

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

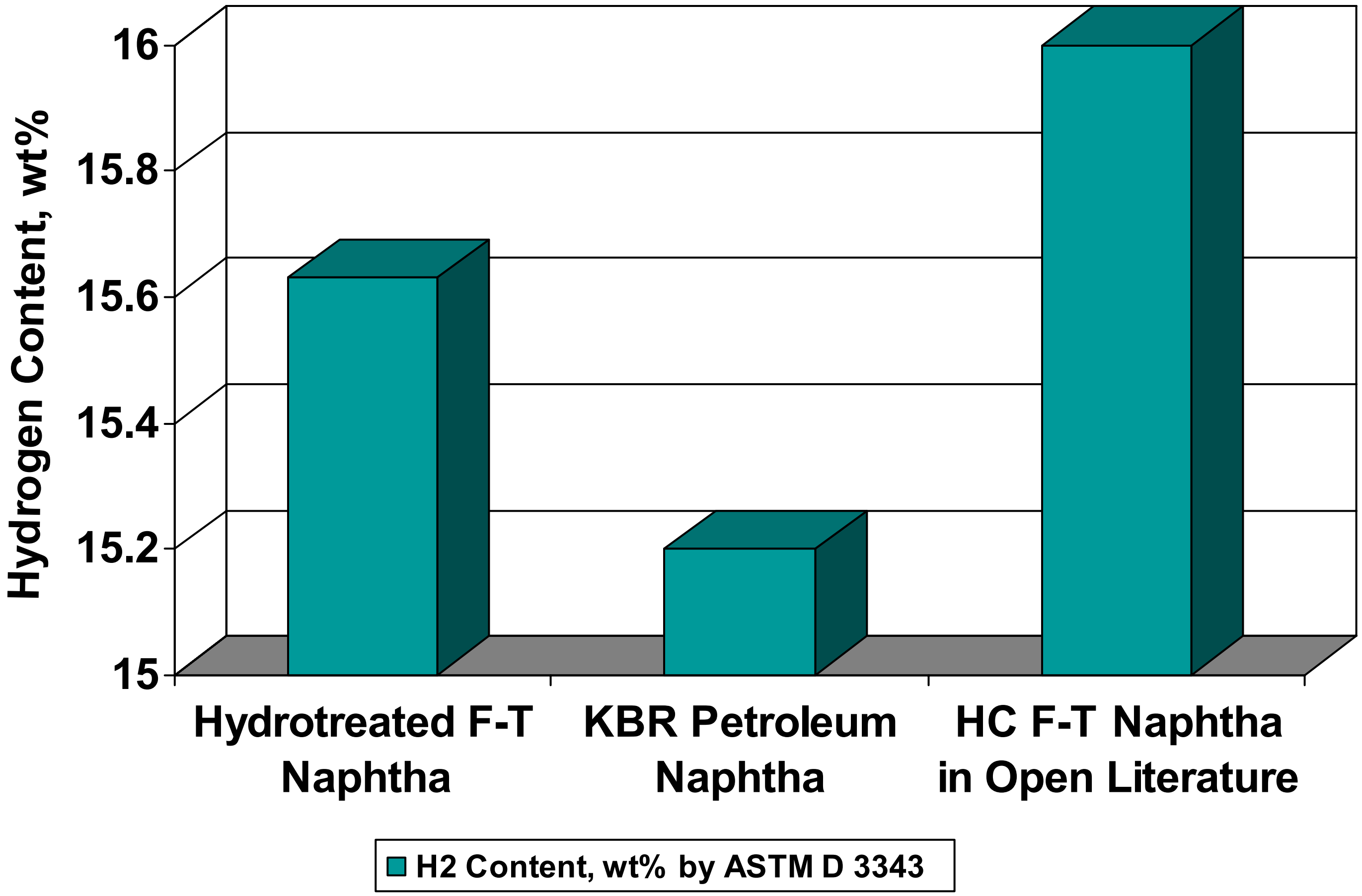
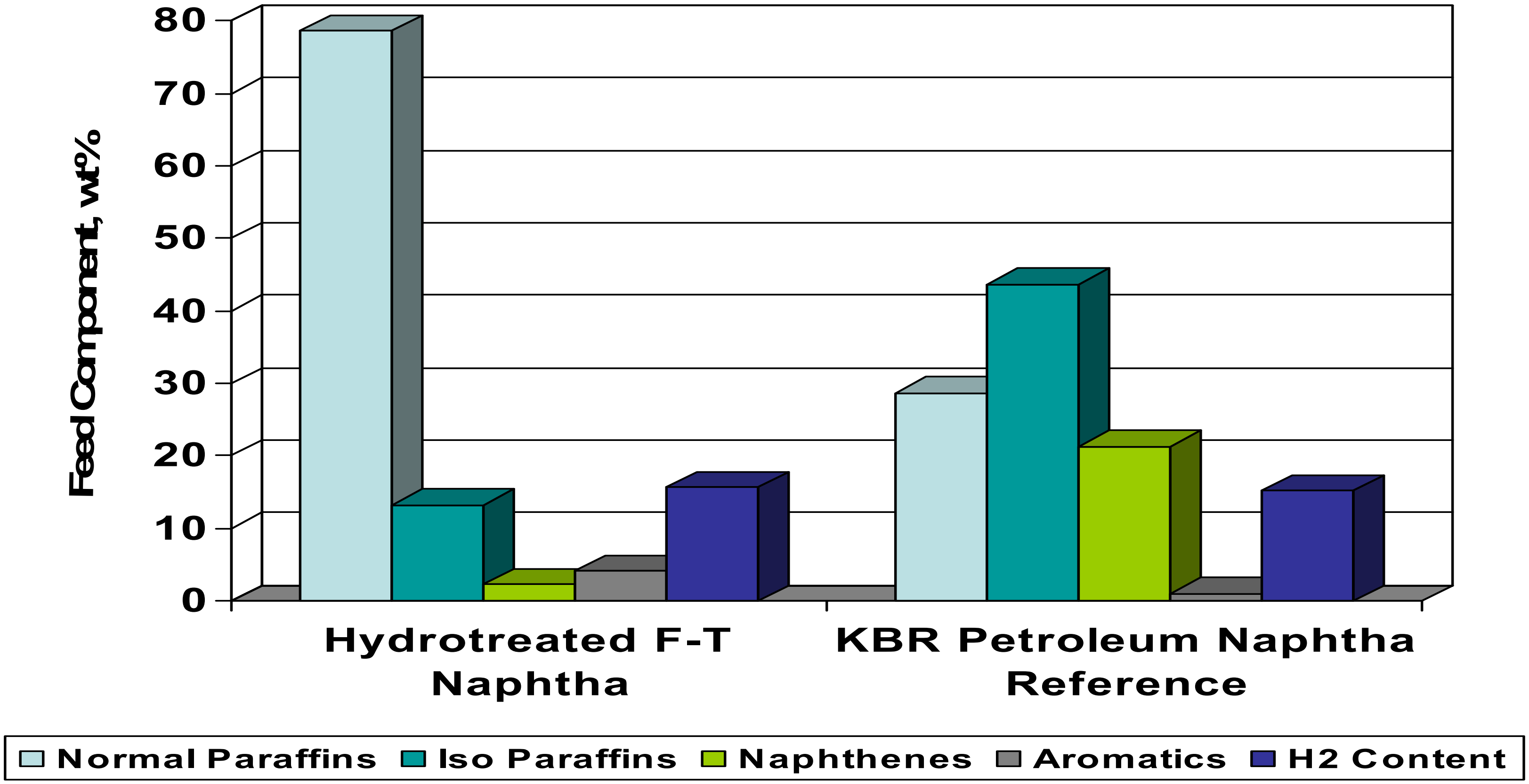


Figure 2.5.7.3-3 – Feed Inspection Tests on Hydrotreated F-T Naphtha versus KBR Petroleum Naphtha Reference



Commercial Ethylene and Propylene Yield Predictions

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

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

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

Figure 2.5.7.3-4

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

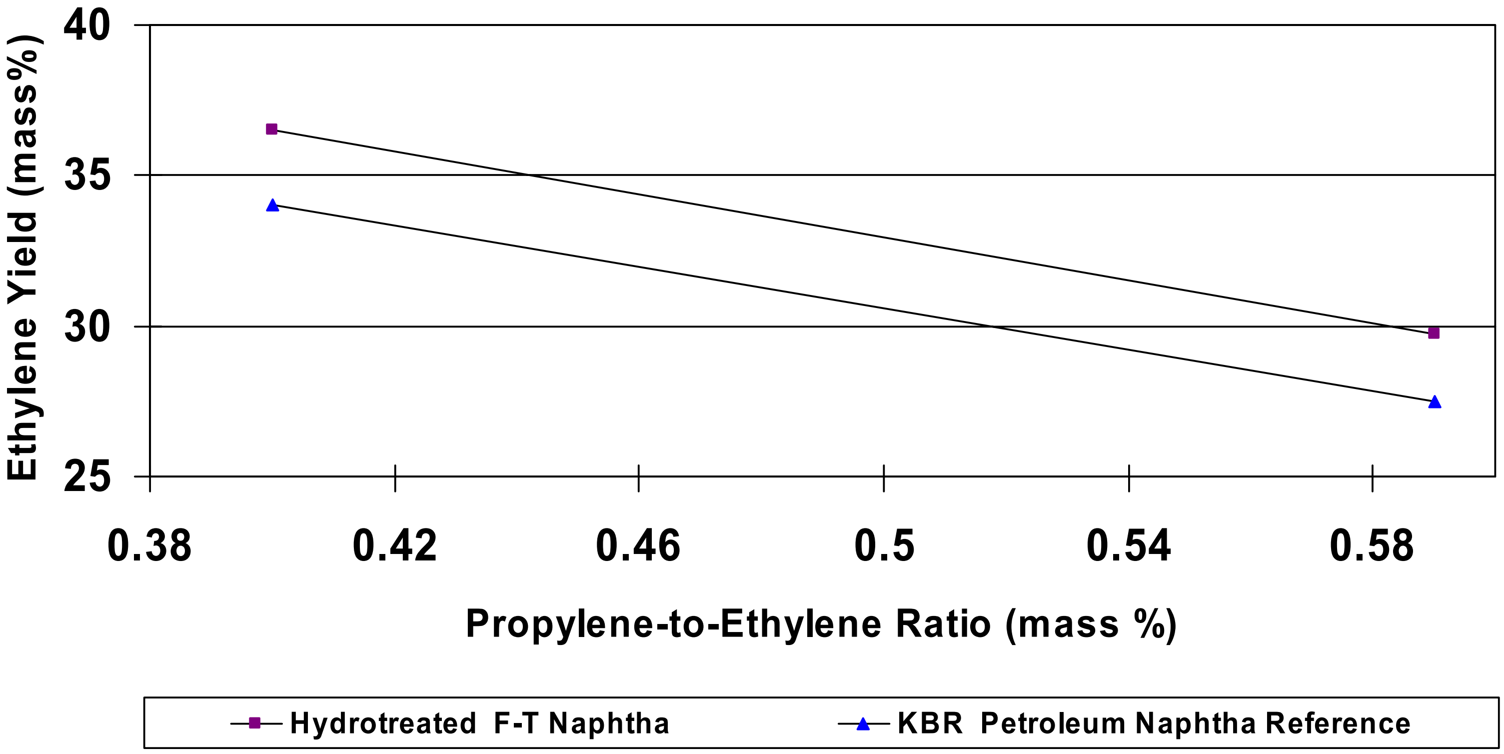
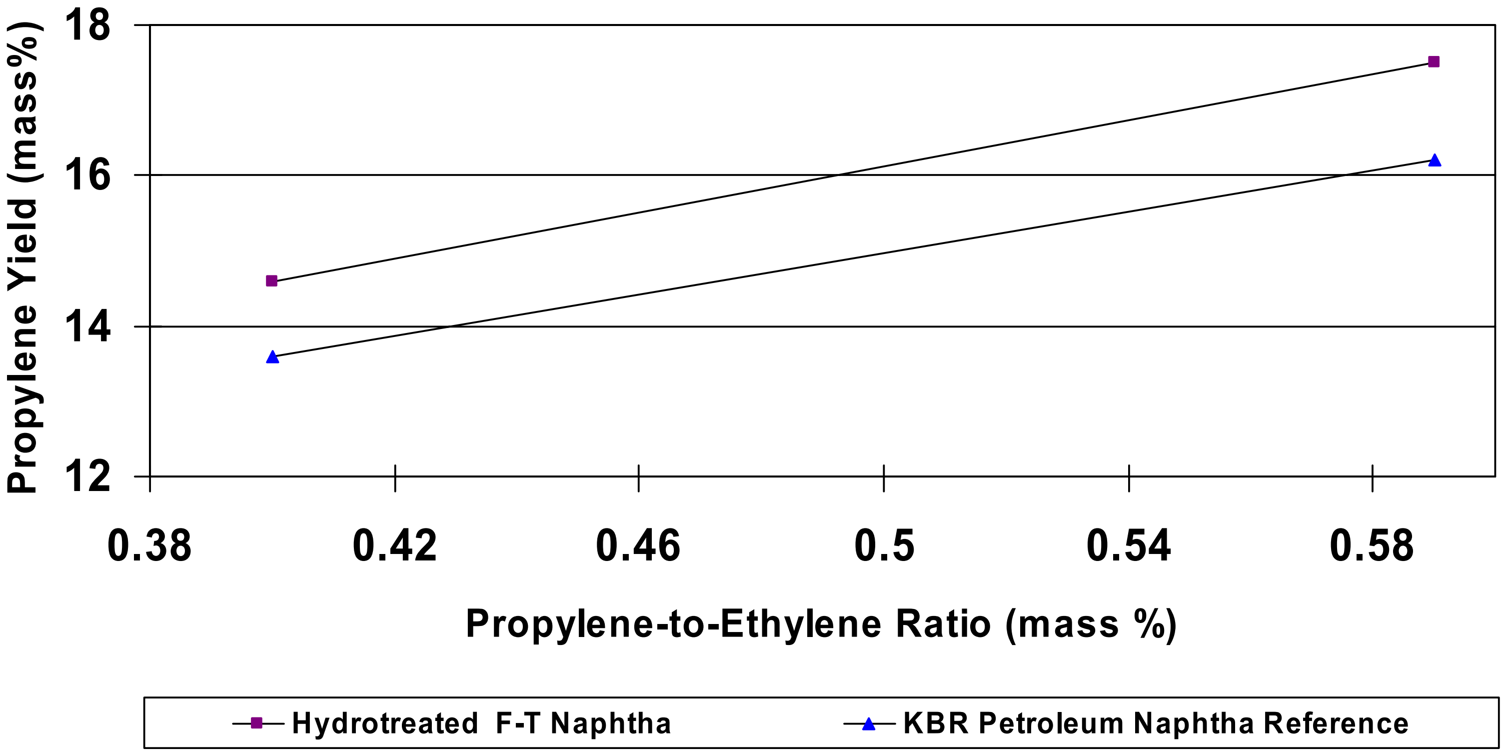


Figure 2.5.7.3- 5

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



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

Subtask 2.5.7.4 Fuel Cell Reformer

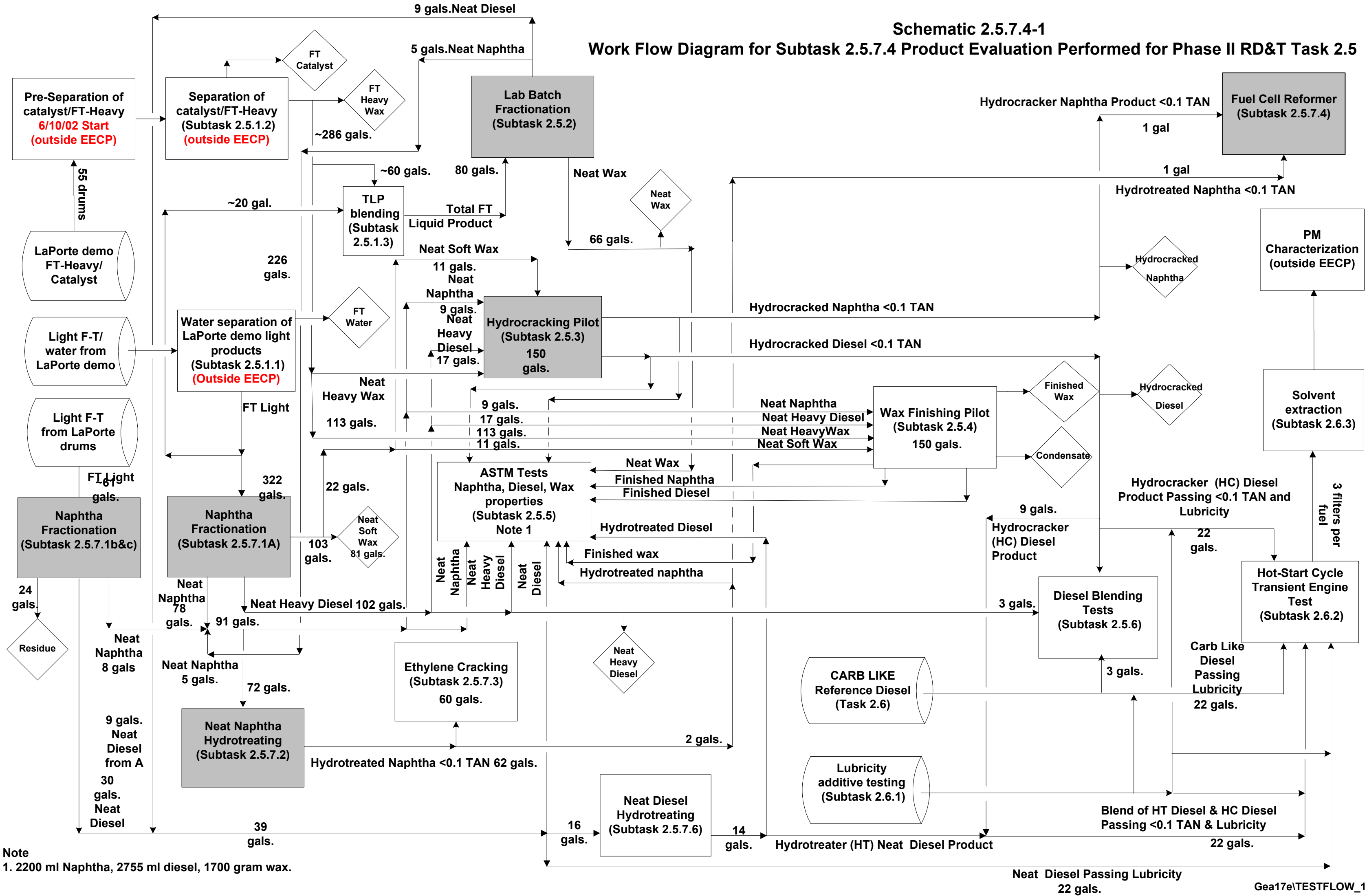
There are several technical and economic risks that need to be mitigated to determine the final product market disposition of the neat F-T naphtha product, hydrotreater F-T naphtha product, and hydrocracker F-T naphtha products. A summary is presented of the important results which mitigated potential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

Replacement for Subtask 2.5.7.5 Catalytic Reforming Pilot

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

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

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



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

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

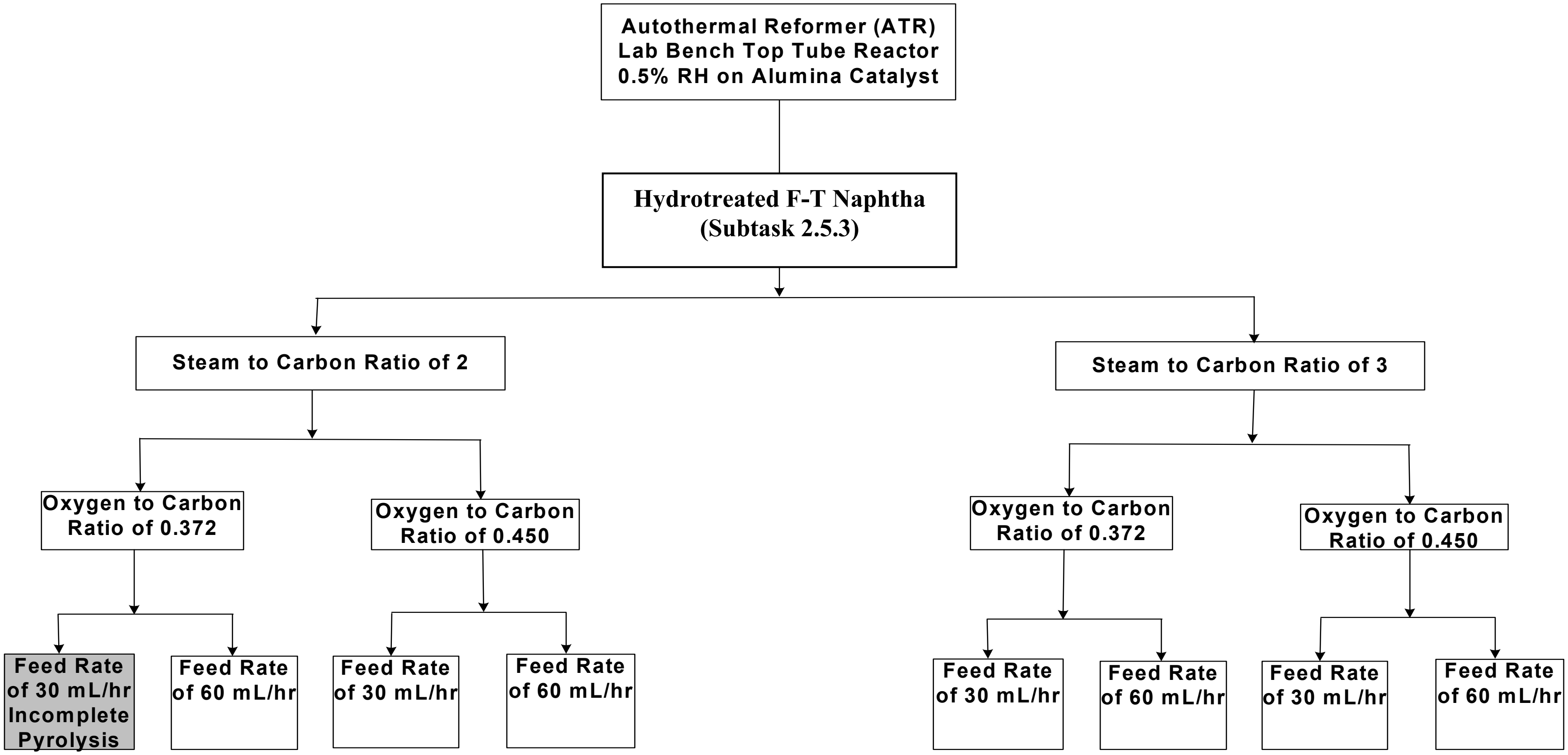
To mitigate the technical and economic risks associated with the final product market disposition of F-T naphtha product an alternative product end-use market was identified for F-T naphtha products**.** A new Subtask 2.5.7.4 entitled "Fuel Cell Reformer" was added to the Phase II to evaluate individually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

Experimental

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

Schematic 2.5.7.4-2

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



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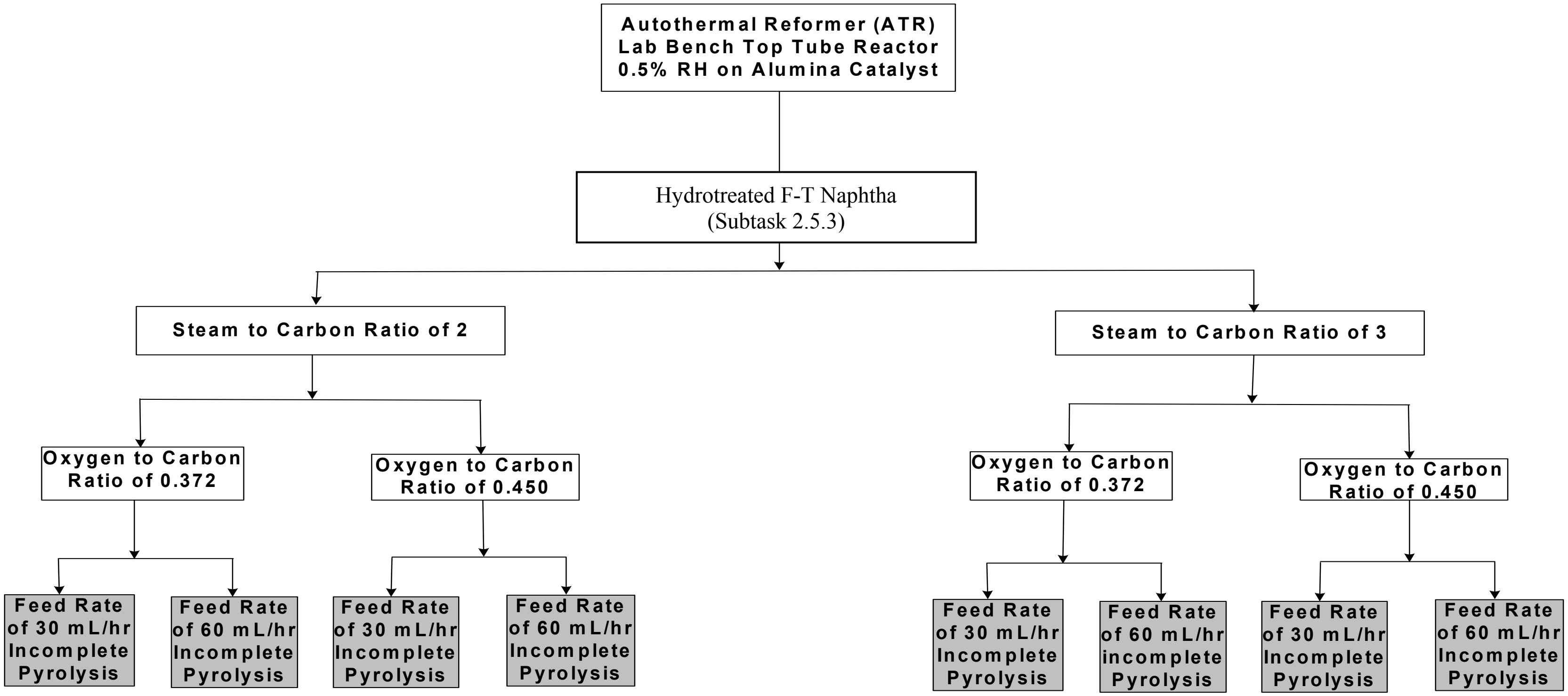
Schematic 2.5.7.4-3
Flow of Work for Subtask 2.5.7.4 Fuel Cell Reformer Evaluation of HC F-T Naphtha Feed



Task 2.6.2&Task 2.6.3 Fuel/
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Results and Discussion

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

FeedStock Composition Results

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

ATR Reformer Carbon Balances Results

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

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

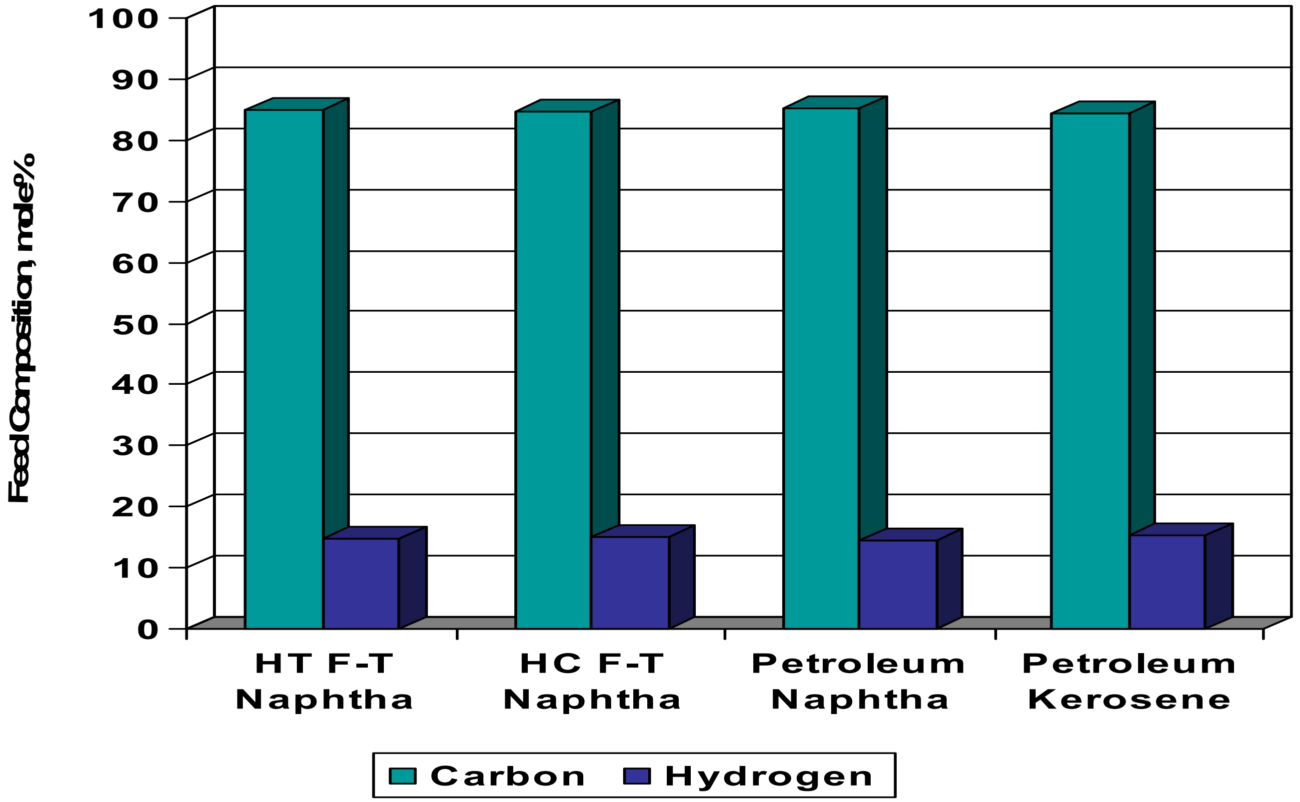
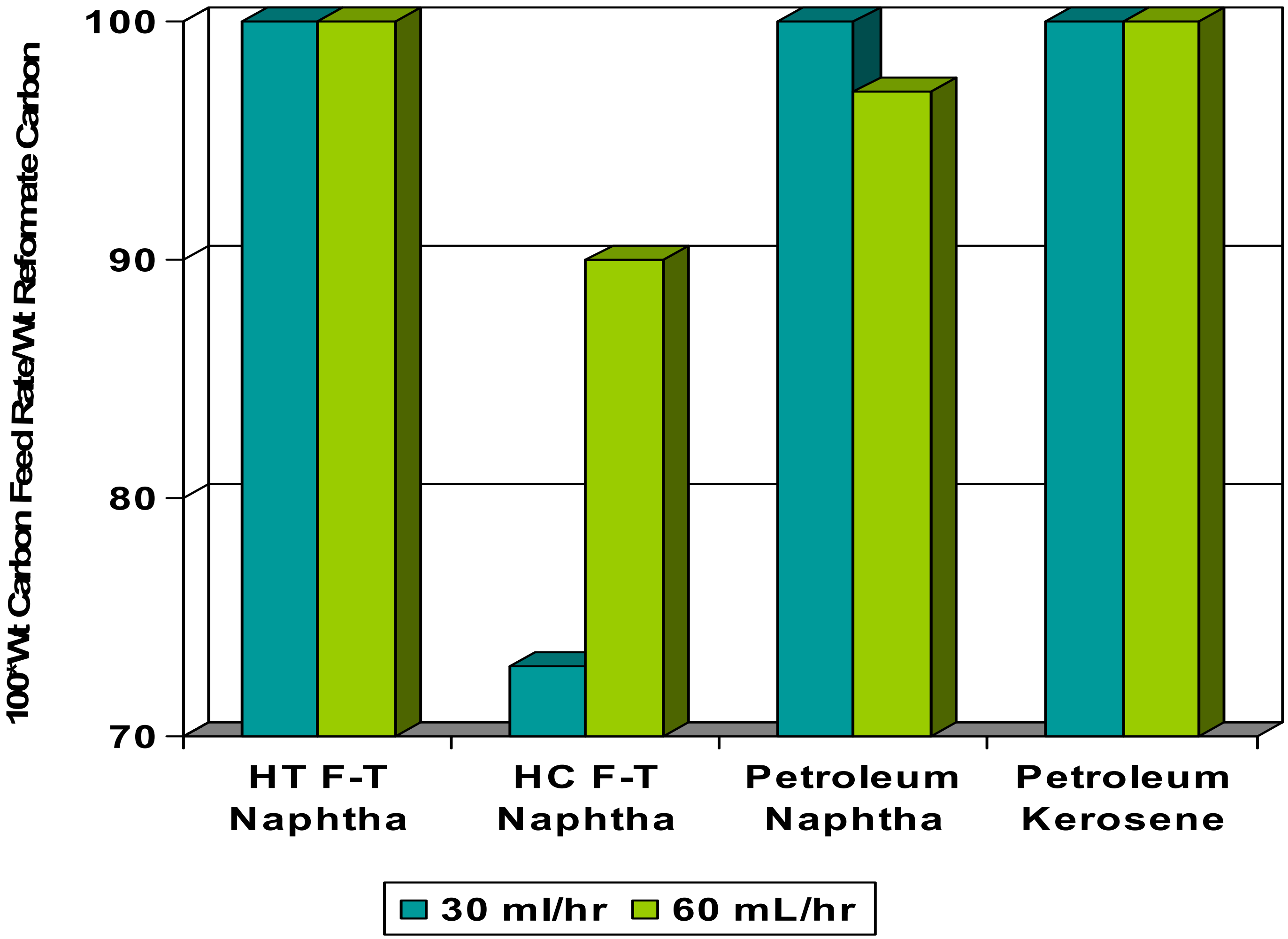


Figure 2.5.7.4-2 – Carbon Balances for F-T Naphthas and Petroleum Feeds

Indication of Complete Pyrolysis of Feed Ahead of ATR Catalyst Bed

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



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

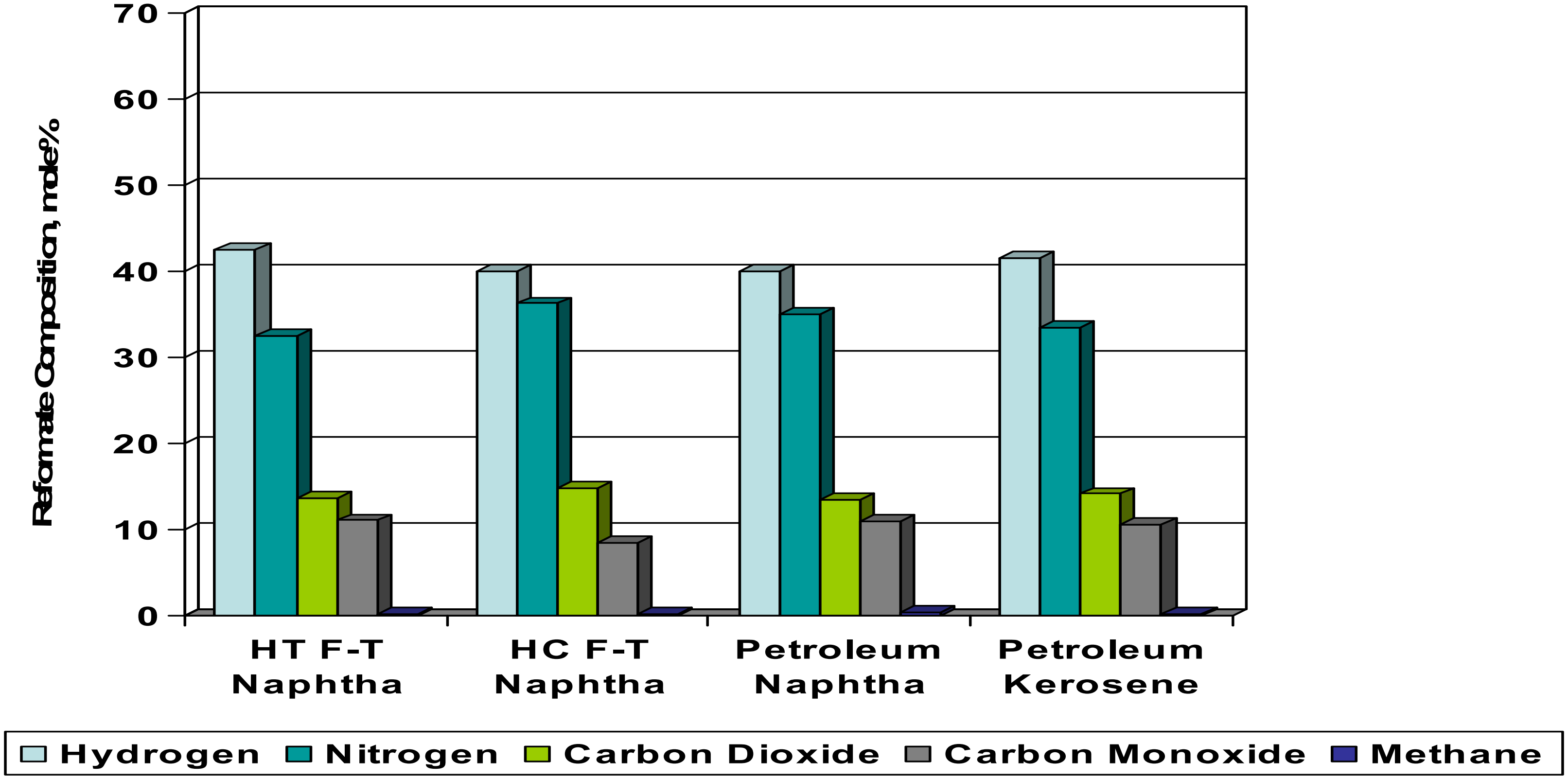
ATR Reformer Hydrogen Fuel Generation Results

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

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

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

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



Subtask 2.5.7.5 Catalytic Reforming Pilot

Experimental

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

Results and Discussion

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

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

Subtask 2.5.7.6 Neat Diesel Hydrotreating

Experimental

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

Feed Composition

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

Equipment

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

Results and Discussion

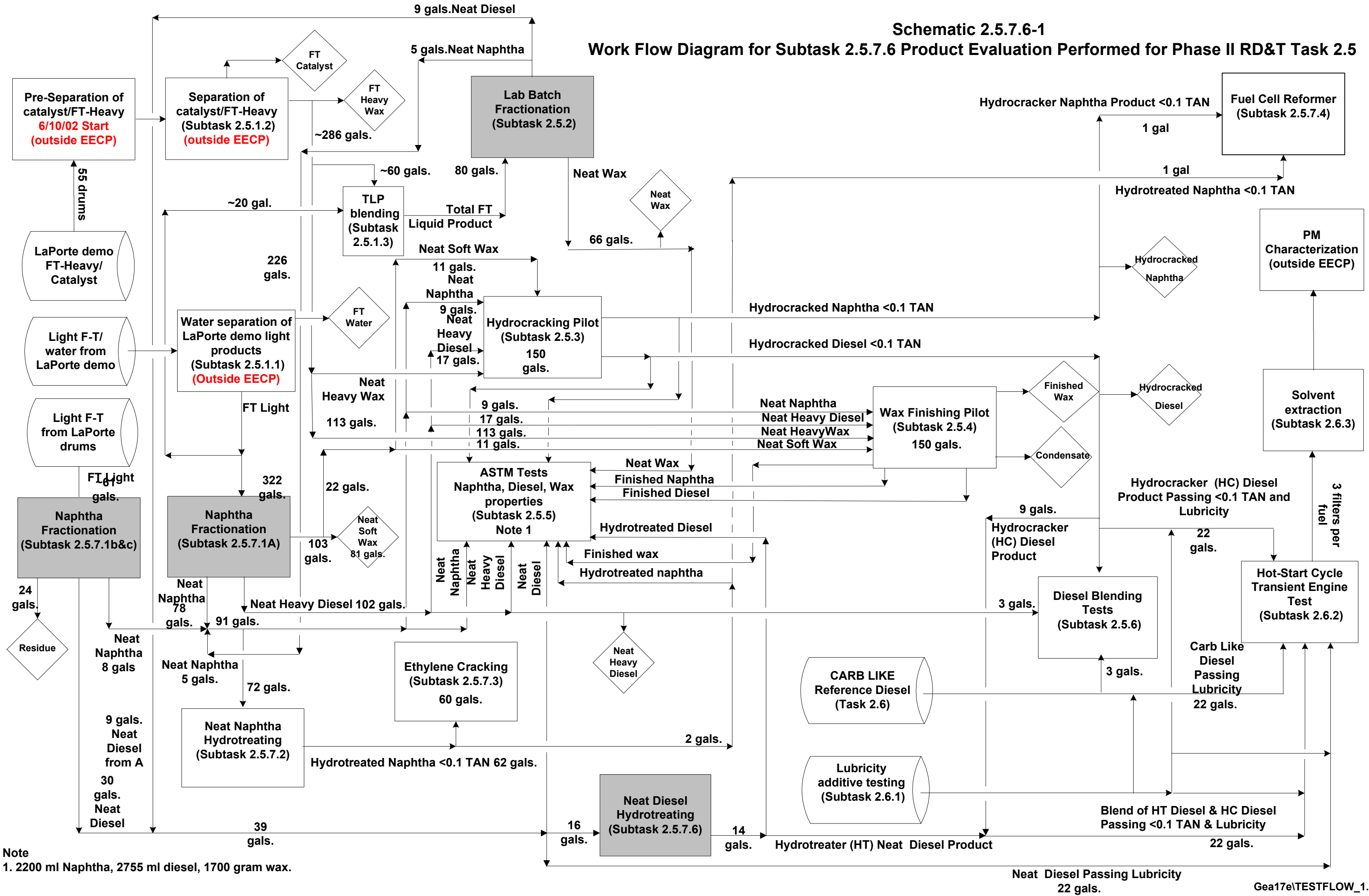
The objective of the Subtask 2.5.7.6 product evaluation entitled "Neat Diesel Hydrotreating" was the successful removal of coke precursors in the form of reactive olefins, acids, and oxygenates present in the neat F-T diesel feed. A TAN specification of less than 0.1 milligrams of KOH titrated per gram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

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

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

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

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



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

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Updated: June 08 , 2003

Table 2.5.7.6-1

Diesel Feed Properties for Hydrotreating Pilot Plant

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

Figure 2.5.7.6-1
Diesel Hydrotreating Pilot Plant Block Flow Diagram

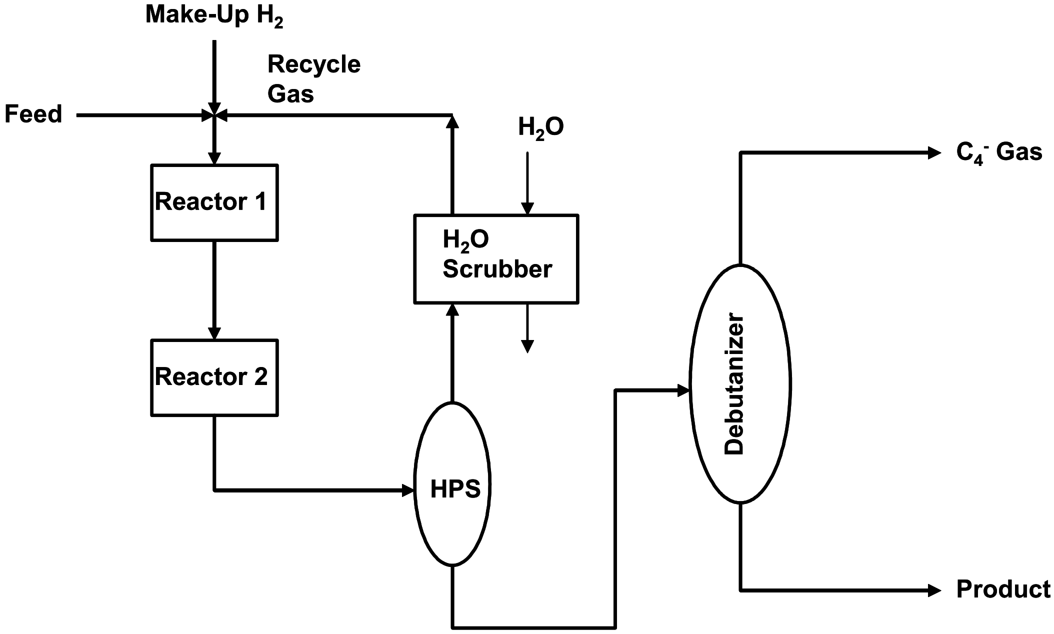

Table 2.5.7.6-2

Yields for Hydrotreating Diesel

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

Table 2.5.7.6-3 Diesel Hydrotreating Product Blend & Distillation

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

Table 2.5.7.6-4 Diesel Hydrotreating Product Properties

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

Subtask 2.5.8 Wax Fractionation

Experimental

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

Results and Discussion

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

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

Conclusions

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

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

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

Bibliography

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

List of Acronyms and Abbreviations

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

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