EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.3: Fischer-Tropsch Catalyst/Wax Separation

Reporting Period:	January 2001 to May 2003
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Disclaimer

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 (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, Inc. GE is providing combustion turbine technology, Praxair is providing air separation technology, and KBR is providing engineering.

Each of the EECP subsystems were assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified catalyst/wax separation as a potential technical and economic risk. To mitigate risks to the proposed EECP, Phase II RD&T included tests of an alternative (to Rentech's Dynamic Settler) primary catalyst/wax separation device and secondary catalyst/wax separation systems. The team evaluated multiple technologies for both primary and secondary catalyst/wax separation.

Based on successful testing at Rentech (outside of DOE funding) and difficulties in finalizing a contract to demonstrate alternative primary catalyst/wax separation technology (using magnetic separation technology), ChevronTexaco has selected the Rentech Dynamic Settler for primary catalyst/wax separation. Testing has shown the Dynamic Settler is capable of producing filtrate exceeding the proposed EECP primary catalyst/wax separation goal of less than 0.1 wt%.

The LCI Scepter® Microfiltration system appeared to be best suited for producing a filtrate that met the EECP secondary catalyst/wax separation standards of 10 parts per million (weight) [ppmw]. The other technologies, magnetic separation and electrostatic separation, were promising and able to reduce the solids concentrations in the filtrate. Additional RD&T will be needed for magnetic separation and electrostatic separation technologies to obtain 10 ppmw filtrate required for the proposed EECP. The Phase II testing reduces the technical and economic risks and provides the information necessary to proceed with the development of an engineering design for the EECP Fischer-Tropsch catalyst/wax separation system.

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

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Executive Summary

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

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). Catalyst/wax separation was identified as one of the most important technical risks of the Fischer-Tropsch (F-T) Synthesis Unit. There are two main purposes for the catalyst/wax separation system. The first purpose is to maintain the catalyst inventory in the reactor. If the separation system does not work properly, then the reactor will lose catalyst in the product filtrate. The second purpose is to clean up the solids from the heavy F-T liquid product before sending it to the F-T product upgrading unit. Catalyst/wax separation represents a high economic risk to the EECP. To ensure product value, the solids in the heavy F-T liquid product must be reduced to at least 10 parts-per-million (weight) [ppmw]. Currently, the design for the catalyst/wax separation system is split it into two stages: the primary separation stage and the secondary separation stage. The primary separation must be able to fulfill the first purpose of maintaining the catalyst inventory within the reactor. Its objective is to perform the bulk separation by removing a filtrate stream with less than 0.1 weight percent (wt%) solids from a slurry containing 20+ wt% solids and returning all the catalyst back to the reactor. The second stage catalyst/wax separation system will remove the remaining catalyst solids from the filtrate before sending to the F-T product upgrading. The objective is to reduce the solids content from 0.1 wt% to ~10 ppmw. To mitigate risks to the proposed EECP, Phase II RD&T included tests of alternate technologies (to Rentech's Dynamic Settler) for primary and secondary catalyst/wax separation. The team evaluated multiple technologies for both primary and secondary catalyst/wax separation.

Based on successful testing at Rentech (outside of DOE funding) and difficulties in finalizing a contract to demonstrate alternate primary catalyst/wax separation technology (using magnetic separation technology), Texaco Energy Systems LLC (TES) has selected the Rentech Dynamic Settler for primary catalyst/wax separation. Testing has shown the Dynamic Settler is capable of producing filtrate exceeding the proposed EECP primary catalyst/wax separation goal of less than 0.1 wt%.

The LCI Scepter® Microfiltration system appeared to be best suited for producing a filtrate that met the EECP secondary catalyst/wax separation standards of 10 ppmw. The other technologies, magnetic separation and electrostatic separation, were promising and able to reduce the solids

concentrations in the filtrate. Additional RD&T will be needed for magnetic separation and electrostatic separation technologies to obtain 10 ppmw filtrate required for EECP.

The results from the EECP Phase II testing for primary and secondary catalyst/wax separation reduce the technical and economic risks of the proposed EECP. The Rentech Dynamic Settler and the LCI Scepter® Microfiltration system will allow the EECP to produce wax containing less than 10 ppmw of solids.

Background

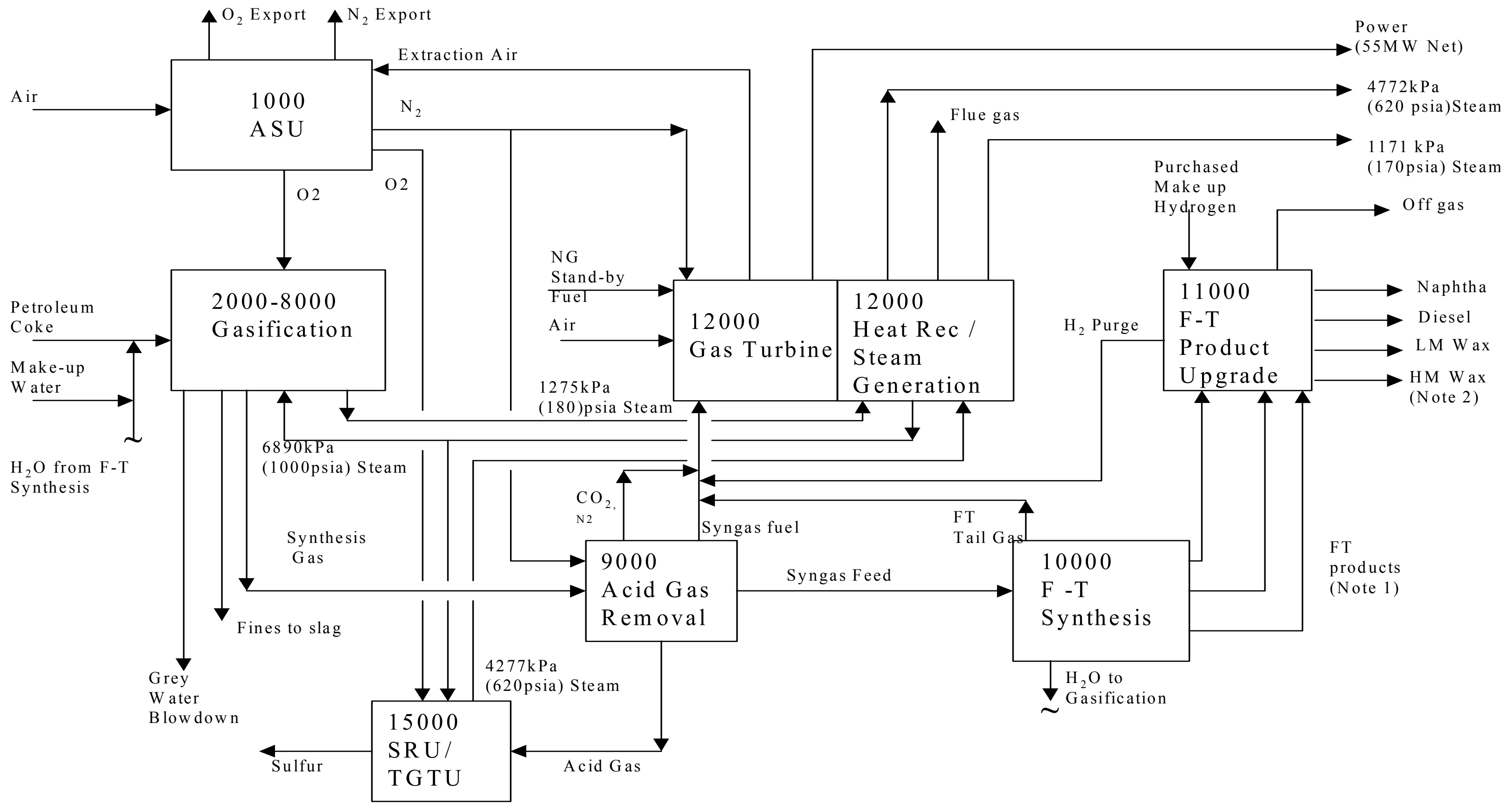
The overall objective of this project is the three phase development of an EECP which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology.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

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

EECP Concept

Petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit (see schematic 1). 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 (H_2O), and carbon dioxide (CO_2) with small amounts of hydrogen sulfide (H_2S), methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. One portion of the stream is treated in the AGR to remove CO_2 and H_2S and 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 GE frame 6FA gas turbine. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release 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 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 reduce nitrogen oxide emissions.

Overall, approximately 75% of the sweetened syngas is sent to the gas turbine as fuel. The remaining 25% is first passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur and then forwarded to the F-T Synthesis Unit. In the F-T reactor, CO and H_2



Kellogg Brown & Root, Inc.
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Technical Services, Inc.

NOTES:

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

DOE EARLY ENTRANCE COPRODUCTION PLANT
PORT ARTHUR REFINERY

OVERALL BLOCK FLOW DIAGRAM

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

Schematic 1 – EECP Concept

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

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

The power block consists of a GE PG6101 (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 the start-up and backup fuel, and a mixture of syngas from the gasifier, offgas 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 nitrogen oxide (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 inert blanketing. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor, hence oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums as they enter the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS gas, oxygen, and air to a burner. In the thermal reactor, the 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 in which 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 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. H2S is removed from the quenched tail gas in an absorber by lean methyldiethanolamine (MDEA) solvent from the AGR Unit, and the tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

Catalyst/Wax Separation

Synthesis gas (H_2 and CO) is fed to the F-T Synthesis Slurry Reactor where it reacts in the presence of catalyst to form a mixture of hydrocarbons and water (Refer to Schematic 2). The light hydrocarbons, water, and unconverted synthesis gas leave the reactor as a vapor. The heavy hydrocarbon (wax) stays in the reactor as a liquid. A portion of the wax is removed to prevent build up in the reactor.

F-T slurry reactors require the separation of product wax from catalyst in order to maintain the catalyst concentration in the reactor and to obtain a product suitable for further processing. Catalyst slurry concentration in the reactor is typically 20 wt%. For some applications the product wax must be filtered to 10 ppmw. It is generally recognized that there is no single separation technology presently available that can reduce the catalyst concentration by this four orders of magnitude.

Catalyst/wax separation removes the liquid products of the F-T reaction from the solid catalyst particles. The purpose is to remove clean liquid products from the F-T reactor while maintaining the catalyst inventory within the reactor. The separation may occur inside or outside of the F-T reactor. In the proposed EECP design, the catalyst/wax separation is accomplished in two stages. The first stage removes the liquid products as filtrate while maintaining reactor catalyst inventory. The second stage removes the remaining catalyst solids from the liquid products being sent to the F-T Product Upgrading Section. The catalyst solids removed from the second stage are processed for disposal (see Task 2.10 Topical Report).

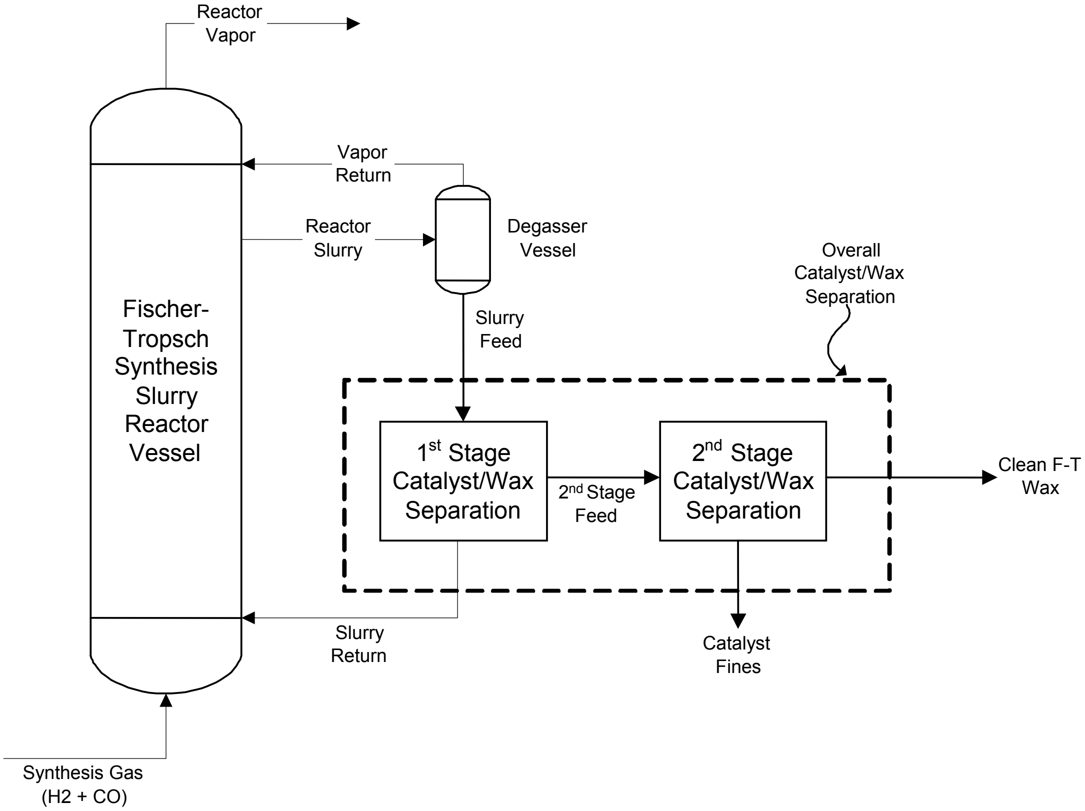
Catalyst/wax separation is one of the most critical technical risks of the F-T Synthesis Unit. Catalyst/wax separation represents a high economic risk to the EECP. To ensure product value, the solids in the heavy F-T liquid product must be reduced to at least 10 ppmw.

Primary Separation Stage

The primary separation must be able to maintain the catalyst inventory within the reactor. Its objective is to perform the bulk separation by removing a filtrate stream with less than 0.1 wt % solids from a 20+ wt% slurry and returning all the catalyst back to the reactor. Since a medium level risk to the EECP exists in this area, two methods were explored in parallel. The first method, the Rentech Dynamic Settler was built and tested for the LaPorte Alternate Fuels Development Unit (AFDU) demonstration (outside of DOE funding). A second method of alternative primary separation based on magnetic separation was proposed for testing during Phase II of the EECP Project.

Secondary Separation Stage

The second stage catalyst/wax separation system removes the remaining catalyst solids from the filtrate before sending to the F-T Product Upgrading. The objective is to reduce the solids content from 0.5 wt% to ~10 ppmw. A number of possible methods were identified for accomplishing this task. They included various filtration methods, settling, magnetic separation, electrostatic separation, etc.



Schematic 2 – Catalyst/Wax Separation Process Flow Diagram

EECP Alternate Primary Catalyst/Wax Separation (Task 2.3.1)

In the RD&T Plan, primary catalyst/wax separation was identified as having a potential medium risk to the EECP. TES proposed to test an alternative technology to mitigate the risk of Rentech's catalyst/wax separation system (Dynamic Settler). The team started discussions with a company to provide a magnetic separation device for demonstration in the EECP Project. However, TES was unable to negotiate an agreement with the company to pursue the demonstration their separation technology.

In November 2000, TES and Rentech conducted the F-T demonstration at the LaPorte AFDU (outside of DOE funding). The LaPorte AFDU bubble column reactor (BCR) is 0.56 meters (22 inches) in diameter and 12.2 meters (40 feet) tall. This demonstration included a skid-mounted Dynamic Settler system for catalyst/wax separation of the approximately 4,536 kilograms (10,000 pounds) of F-T wax produced in LaPorte. The demonstration Dynamic Settler was larger than the systems used on Rentech's BCR in Denver, Colorado. Between January 2001 and January 2003, Rentech conducted additional tests using the Dynamic Settler (outside of DOE funding). The results indicate that the Dynamic Settler should be able to meet the EECP design requirements of less than 0.1 wt % solids in the filtrate. Based on these Dynamic Settler test results, Alternate Primary Catalyst/Wax Separation was removed from the EECP Phase II RD&T. However it should be noted that additional scale-up data are needed to commercialize Rentech Dynamic Settler. Below is a discussion of the Rentech Dynamic Settler.

Rentech Dynamic Settler

As shown on Figure 1, the Rentech Dynamic Settler (U.S. Patent 6,068,760) has a sealed vertical chamber into which a vertical feed conduit (5) extends downwardly into the settler chamber for a substantial length so as to form an annular region (6) between the inner walls of the chamber and the feed conduit. At the lower portion of the settler chamber there is a slurry removal outlet for removal of the slurry to be returned back to the F-T reactor. As the slurry flows into the annular region at the bottom of the settler the heavier catalyst particles are carried down and are removed as the slurry at the bottom of the settler to be recycled back to the reactor (7). The wax rises up in the annular section (8) and this clarified wax is removed by a wax outlet pipe at the top. The outlet pipe can optionally have a filter or some other secondary catalyst/wax separation system (10) to further purify the wax for downstream wax upgrading section.

The concept has the following advantages relative to other primary separation devices:

- Does not rely on small-pore filter elements that will irreversibly plug due to carbon and catalyst fines present in the slurry.
- Operates continuously.
- Does not require backwashing nor the complicated valving and controls required to affect backwashing.
- Equipment cost should be low.
- Operating costs should be low.

The main disadvantages are:

- Advantage 1 above can be taken as a disadvantage since catalyst fines will be lost. However, that is likely preferable to plugging filter elements.
- The concept has not been demonstrated at full scale so the filtrate flow capacity is not known.
- Process upsets may result in increased catalyst loss from the system due to time required to reach steady state operations within the settler.

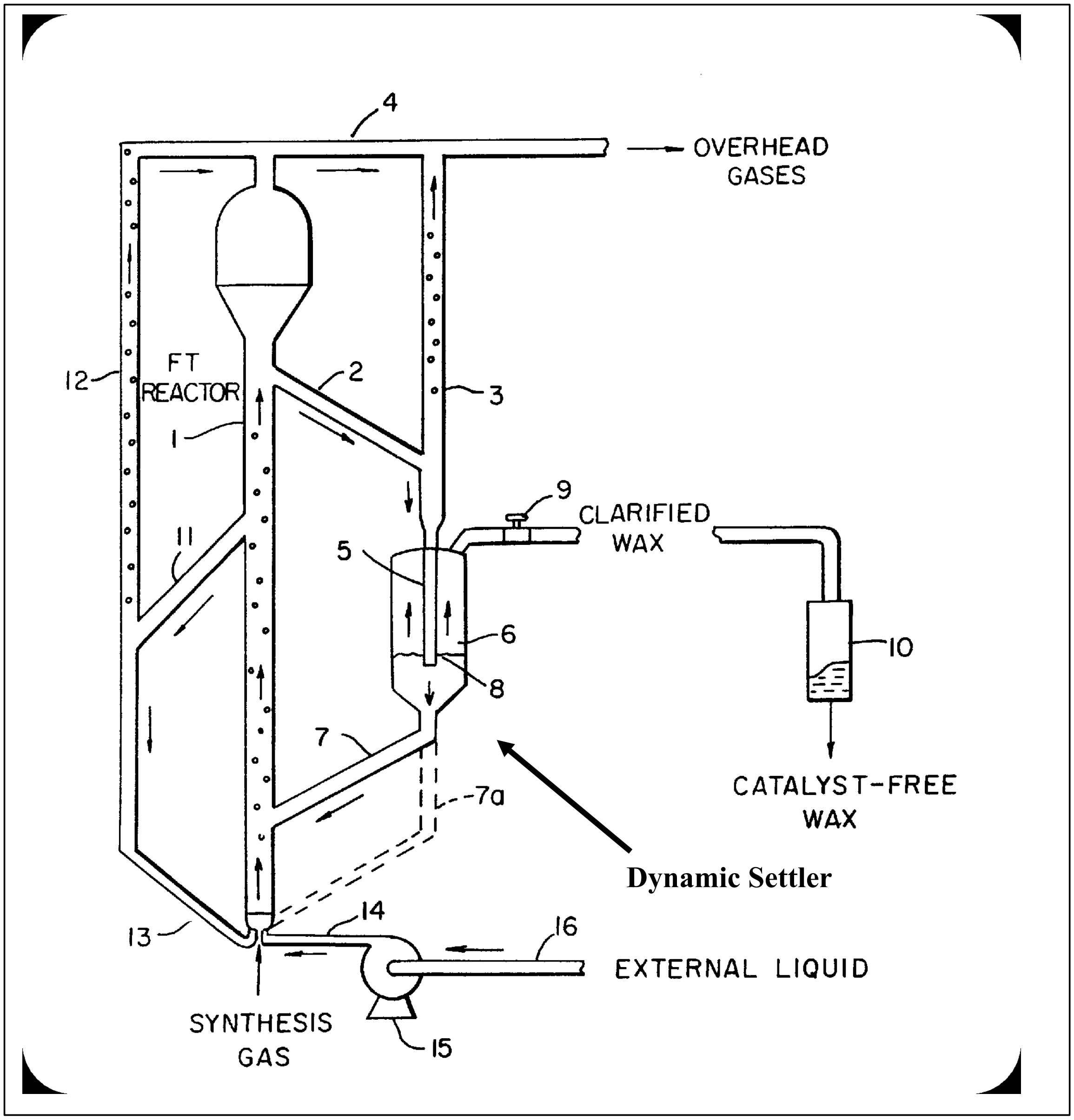


Figure 1. Rentech Dynamic Settler Attached To a Slurry Bubble Column Reactor

Test Results

The Rentech Dynamic Settler has been used extensively on Rentech's BCR in Denver, Colorado. Additionally, Rentech has also tested a larger Dynamic Settler (2.5 times the diameter of the Dynamic Settler on the BCR) on Rentech's catalyst/wax separation hot-loop. The hot-loop is capable of circulating high temperature catalyst/wax slurries at various flow rates (up to 19 liters per minute/5 gallons per minute). In BCR operation, the Dynamic Settler has consistently produced filtrate at the proposed EECP primary separation goal of 0.1 wt% solids (from 15+ wt% slurry). In the larger Dynamic Settler tests, slurry from the LaPorte AFDU was cleaned from ~10 wt% to ~0.35 wt%. The unstable process operations of the LaPorte test did not allow the Dynamic Settler to reach steady-state operations. The Dynamic Settler was used in Task 2.1.3: F-T Confirmation Run.

Based on the results of testing (outside of DOE funding), the Rentech Dynamic Settler device was selected as the primary catalyst/wax separation system for the proposed EECP. The Dynamic Settler operates continuously and does not require backflushing.

EECP Secondary Catalyst/Wax Separation (Task 2.3.2)

Rentech and TES screened and tested multiple technologies to meet the EECP secondary catalyst/wax separation system objective of removing the remaining catalyst solids from the filtrate before sending the filtrate to the F-T Product Upgrading. The filtrate solids content from the primary catalyst/wax separation system will be less than 0.1 wt %, however for secondary catalyst/wax separation feed with 0.5 to 1 wt% slurry was assumed as a design feed. The higher feed solids concentration tested the ability of the secondary catalyst/wax separation system to handle process upsets. The secondary catalyst/wax separation system must remove the solids to the 10 ppmw level.

Several separation technologies were reviewed for F-T catalyst/wax separation. They included magnetic separation, barrier filtration, electrostatic separation, crossflow filtration, and a spinning basket design. The technologies ranged from established technologies and new, developmental technologies. This project represented the first F-T application for many of the technologies. The review process consisted of TES and Rentech reviewing applicable technology based on current and prior applications, company size and reputation, and the ability to test and operate at the required high temperatures. Outside of the EECP Project, TES and Rentech conducted small-scale screening tests at Rentech's Catalyst/Wax Separation Hot and Cold Loop in Denver, Colorado. These tests help to identify the most likely candidate technologies.

Secondary catalyst/wax separation of the F-T liquids is not as trivial as it might appear. The F-T liquids must stay at high temperature to maintain low viscosity and not form wax crystals. Since the primary catalyst/wax separation system removes the larger, easier to remove particles, the secondary catalyst/wax separation system must remove the smallest particles. Attrition in iron-based F-T catalysts slurry operations is well documented (Datye et al., 1996 and Kohler et al., 1994). The F-T particles in the feed to the secondary catalyst/wax separation system can be several orders of magnitude smaller than the starting F-T catalyst. The smaller particle size makes the task of producing a 10 ppmw filtrate very difficult.

After reviewing the requirements for secondary catalyst/wax separation, the available technologies, and previous testing results (outside of DOE funding) TES and Rentech chose three technologies for Phase II testing. The selected technologies included magnetic separation, electrostatic separation, and a crossflow filtration system.

The general test plan for all three technologies was similar. Initial testing was done using an catalyst/oil slurry. If the technology was successful when tested the catalyst/oil slurry, a test with catalyst/paraffin wax slurry was conducted. Finally, it that test were successful, the final test would use the actual F-T catalyst/wax slurry. For all the tests, the success of technology was measured against the required goal of getting the slurry cleaned to 10 ppmw solids.

The catalyst/oil slurry was selected for initial tests since it allowed for a quick screening test at low temperatures (the oil viscosity is approximately the same as the wax viscosity at temperature). This allowed the screening to be done at ambient conditions. Since the amount of F-T catalyst/wax required for most tests exceeded the material TES had available, the catalyst/paraffin wax slurry was used for the next series of tests. The catalyst/paraffin wax test was done at higher temperatures and gave second level of screening which has more realistic parameters than the catalyst/oil test. If any of the technologies passed the above two tests, the final tests were done with F-T catalyst/wax slurry.

Magnetic Separation

The active form of iron F-T catalyst contains iron carbide, which is ferromagnetic. For that reason magnetic separation is one of several technologies that was considered for the secondary catalyst/wax separation step. Testing with a leased, commercially available magnetic separation device was conducted at Rentech's Denver, Colorado facility. Selection of the device used in Phase II testing was based on bench-scale testing at the vendor's site and previous testing with Rentech F-T material.

Tests were conducted with catalyst/oil slurry, wax/paraffin catalyst slurry, and F-T catalyst/wax slurry all starting at 3000 to 4000 ppmw solids concentration. Results with the catalyst/oil slurry were very promising and produced essentially clear oil, estimated to be below the desired 10 ppmw solids concentration. Testing with paraffin and F-T catalyst/wax slurry produced wax with about 120 ppmw solids concentration. Since it was not immediately obvious how to achieve further separation with the magnetic unit, it was decided to stop any further testing until competing secondary separation technologies could be evaluated.

Test Description

To accomplish the EECP objective, four separate tests were conducted as shown in Table 1:

Test #	Media	Location	Date
1	Oil/catalyst	Vendor Site	March, 2001
2	Oil/catalyst	Rentech	May, 2001
3	LaPorte fines	Rentech	June, 2001
4	catalyst/paraffin wax	Vendor Site	February, 2002

Table 1. Overview of Magnetic Separation Testing

In Table 1, "media" refers to the catalyst/wax (or surrogate) used in the test. Catalyst/oil in tests #1 and #2 is a slurry made of mineral oil and activated F-T catalyst fines. This slurry is a liquid at room temperature and was chosen for the first tests because it greatly simplifies the testing requirements, especially in terms of heating. The mineral oil is Penreco Peneteck Technical Mineral Oil.

The slurry used in Test #3 is made from F-T wax and catalyst fines from the LaPorte AFDU demonstration (conducted outside of DOE funding) after a settling operation.

The media used in Test #4 is composed of F-T catalyst fines removed from the Rentech BCR that is mixed with commercial paraffin wax to yield a large quantity of slurry having a solids content of approximately 4000 ppmw. This paraffin wax has a narrow range of molecular weights centered on C28 as compared to pure F-T wax which has a very wide range of molecular weights up to C100. The catalyst in Test #4 was not specially treated to produce a finer particle size distribution but was taken directly from the Rentech F-T BCR. This slurry was used in several tests of alternate secondary catalyst/wax separation technologies in addition to the magnetic testing described in this section. As compared to a true F-T catalyst/wax slurry that will be sent to a secondary catalyst/wax separation unit in commercial practice, this feed is expected to be easier to separate due to the lighter wax and the larger catalyst particles. Thus, any catalyst/wax separation results obtained when this slurry is used are not conservative.

Results and Discussion

Test #1 was done in batch mode at the vendor facilities. The slurry was manually poured through the wire mesh with the magnetic field engaged. There was no attempt to optimize the process, only to screen the technology. Magnetic field strength was 4500 gauss. TES and Rentech personnel observed this test which yielded clear oil. Figure 2 shows the starting slurry on the right and the clean oil produced by the magnetic separation device on the left. Based on these positive results, the magnetic separation device designed to operate at higher operating temperature was leased by TES and shipped to Rentech for more extensive testing in the Rentech catalyst/wax separation test loop.

Figure 2. Magnetic Separation Product from Test #1.

Test #2 was done at Rentech's hot test loop, see Figures 3 and 4 for details. This test loop allowed continuous operation and testing with catalyst/oil or catalyst/wax slurries at expected commercial operating temperatures.

Figure 3. Test Loop at Rentech

As discussed previously, Test #2 used a F-T catalyst/mineral oil fines slurry. This oil has a nominal viscosity of 0.003 Pa-sec (3 cp) at 313 K (104 ^{o}F). The F-T catalyst was from the Rentech BCR and was passed through a gear pump to produce fines. The purpose of this was to confirm the results from the bench-scale test done at the vendor's shop but done in a continuous flowing loop.

Figure 4 shows a sample of the composite clean oil produced during the test.

Figure 4. Magnetic Separation Product from Test #2

Based on the success of Test #2, testing began with F-T catalyst/wax slurry in test #3. This slurry originated from the run conducted at the LaPorte AFDU and was separated by gravity settling to give a supernatant containing approximately 3600 ppmw solids concentration and a small-particle distribution simulating the F-T catalyst/wax slurry that will be produced by a primary separator in a commercial application. Testing was conducted at a slurry temperature of 443 K (338 ^{o}F).

Numerous tests were made adjusting the physical characteristics of the magnetic separation device. However, no tests yielded more than about a 2/5 removal of catalyst, i.e. the cleanest filtrate had a solids concentration of about 2000 ppmw.

The reason for the difference between the excellent performance with the catalyst/mineral oil slurry versus the relatively poor performance in Test #3 with the F-T catalyst/wax slurry is not clear. The catalyst used for Test #2 was activated in the Rentech BCR while that for Test #3 was activated in the LaPorte AFDU reactor. Also, two different catalyst vendors supplied these two catalysts. It is possible that the difference in the catalyst or the activation procedure could have produced differing carbide/oxide ratios in the catalyst which might have impacted magnetic separation. Physical properties of the mineral oil and paraffin wax are not significantly different. The mineral oil was selected partly on the basis of matching oil viscosity at ambient temperature with that of F-T wax at higher temperature. Another possibility is that the slurry from the LaPorte AFDU had a larger fraction of fine particles and the magnetic force on those particles would be very significantly reduced (Oberteuffer, 1974).

At this point it appeared that the only other variable left to test was the magnetic field strength. In Test #4, the vendor used a field strength of 7600 to 14,000 gauss with their magnetic separation unit. Table 2 shows the four runs made at the vendor's site, again in the batch mode. The unit was heated electrically and the slurry was batch heated before it was poured into the unit. The slurry was composed of F-T catalyst removed from the Rentech BCR and mixed with commercial paraffin wax to yield a slurry concentration that was approximately 4000 ppmw solids.

Run #	Electromagnetic Current/Magnetic Field Strength (Amps / Gauss)	Filtrate (ppmw)
# 1	70/14,000	310
# 2	40/7,600	250
# 3	40/7,600	130
# 4	70/14,000	120

Table 2. Results of Magnetic Separation Test 4 at Vendor Site.

As each run progressed, the product appeared to become cleaner. As shown in Table 2, the best results were 120 ppmw solids content for Run #4. Figure 6 shows a sample of the wax.

Figure 5. Magnetic Separation Product from Test #4.

The results of Test #4 were encouraging because they produced the cleanest wax that had been seen with the magnetic separation device, about 120 ppmw solids. Since Test #3 used a slurry of F-T wax while Test #4 used a slurry with mostly paraffin wax, it is unknown whether the difference between these two waxes or the higher magnetic field strength gave the improved performance in Test #4.

In discussing the need for additional testing with the magnetic separation device, team members considered results to date and also considered planned testing of competing secondary filtration technologies. Although significant progress was made with the magnetic separation unit, an important consideration is that the vendor does not offer a unit operating at higher magnetic field strengths than the 14,000 gauss used for Test #4. It seemed that higher magnetic field strength might be necessary to achieve the desired 10 ppmw solids concentration in the wax. For these reasons, a decision was made to defer additional testing with the magnetic separation unit until such a time those other methods of secondary separation have been evaluated. In the event that none of those are successful, the team could perform additional testing on the magnetic separation unit.

The magnetic separation unit successfully separated F-T catalyst/mineral oil slurry from 4000 ppmw to 10 ppmw. The unit was less successful in separating F-T catalyst from paraffin wax or F-T wax producing no less than 120 ppmw solids in the cleaned material. While further optimization could reduce this solids concentration further, it was decided to delay further testing with the unit until other separation technologies have been evaluated.

Electrostatic Separation

The patented GULFTRONIC® Separator System (U.S. Patent 3928158, Japan 1,053,054, and other patent pending) was used and is designed for efficient removal of large to sub-micron particulate material from liquids with low electrical conductivity, using a force called dielectrophoresis. Conventional mechanical filters experience rapid buildup of pressure drop due to plugging of filtering elements when the catalyst particles are very fine. The F-T iron catalyst particles are very fine causing shorter cycles with the mechanical filters. The GULFTRONIC® Separator technology is presently used to remove catalyst particles from Fluid Catalytic Cracking Unit slurry oil to less than 1 ppmw.

Test Description

For the GULFTRONIC® Separator System six objectives were identified:

- Clean F-T catalyst/wax slurry with 5000 to 10000-ppmw to 10-ppmw solids.
- Confirm the Gulftronic® Separator will remove catalyst particles.
- Define module size for a commercial unit.
- Determine Module Solids holding capacity.
- Evaluate operating temperature and voltage.
- Provide data for comparison with competing secondary separation technologies.

To accomplish the Six-test objective four separate tests were conducted as shown below in Table 3.

Test #	Feed Tested	Purpose	Sample Designation
1	F-T Catalyst/Oil	Evaluate electrical conductivity of F-T catalyst	GA 380
2	LaPorte AFDU F-T Catalyst/Wax	Evaluate activated F-T catalyst and F-T wax slurry from the LaPorte AFDU	GA 388
3	F-T Catalyst/Paraffin Wax	Evaluate mixture of activated F-T catalyst and paraffin wax slurry	GA 392
4	F-T Catalyst/Wax	Evaluate mixture of activated F-T catalyst and F-T wax slurry from Rentech Primary Separation Device	GA 393

Table 3. Gulftronic® Separator Test Overview

Test #1: Slurry made of mineral oil and activated F-T catalyst fines. This slurry was selected because it is liquid and simplifies testing requirements, especially in terms of heating. The mineral oil is Penreco Peneteck Technical Mineral Oil.

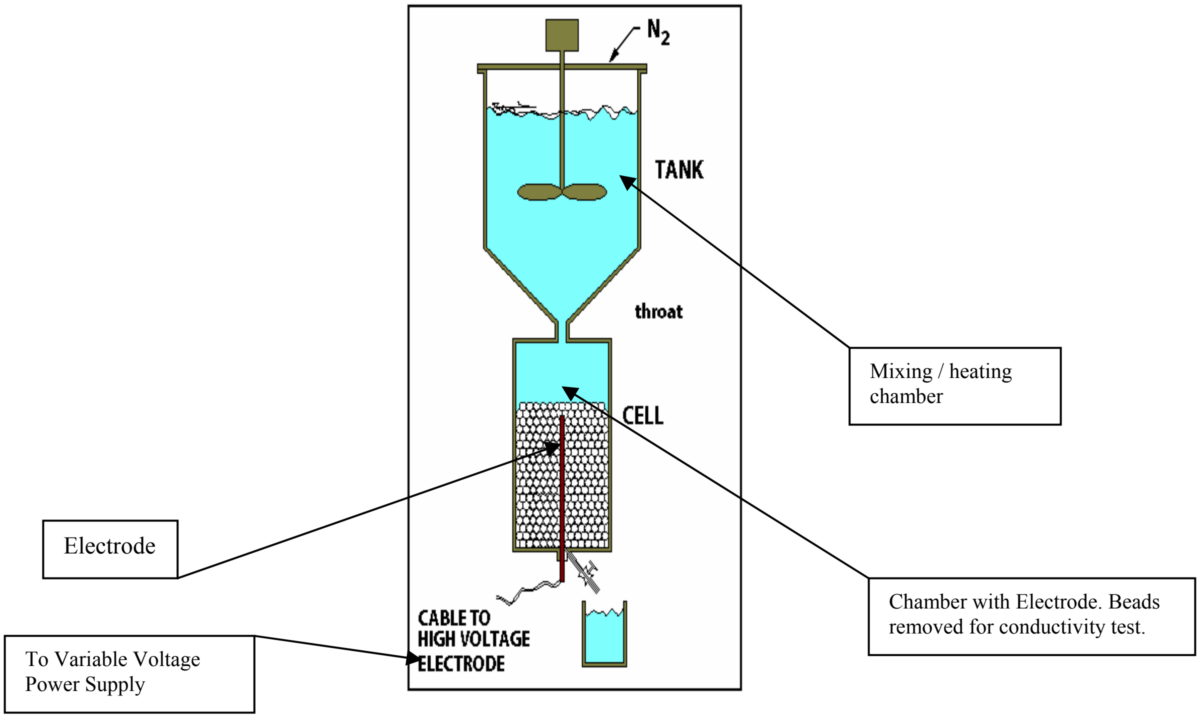
Test #2: LaPorte F-T catalyst/wax slurry made from F-T wax and activated catalyst from the LaPorte AFDU demonstration. The slurry collected at LaPorte AFDU had 5 to 10 wt% catalyst in the slurry. The LaPorte AFDU slurry was heated and allowed to settle. The supernatant or lean slurry from the settling operation was used for this test.

Test #3: The F-T catalyst/paraffin wax is F-T catalyst removed from the Rentech BCR and mixed with commercial paraffin wax to yield a large quantity of approximately 8000-ppmw slurry concentrations. This paraffin wax has a narrow range of molecular weights centered on C28 as compared to pure F-T wax which has a very wide range of molecular weights. The catalyst was taken directly from the Rentech BCR and not specially treated to produce a finer particle size distribution. Compared to true F-T catalyst/wax slurry sent to a secondary catalyst/wax separation unit in commercial practice, this feed was expected to be easier to separate due to the lighter wax and larger catalyst particles. This slurry was used in several tests of alternative secondary catalyst/wax separation technologies, in addition to the GULFTRONICS® tests. Any results from this slurry should not be considered conservative.

Test #4: The F-T catalyst/wax in Test #4 is the actual F-T catalyst/wax slurry. The slurry was prepared in the Rentech BCR and processed through the Rentech first stage catalyst/wax separation – Dynamic Settler. This slurry represented the slurry with catalyst size and Fischer-Tropsch wax expected as feed to the second stage of commercial catalyst/wax separation system.

Tests #1 to 4 were carried out in the test apparatus shown in Figure 6. The actual test unit is shown in Figure 7.

Figure 6. Gulftronic® Laboratory Test Unit



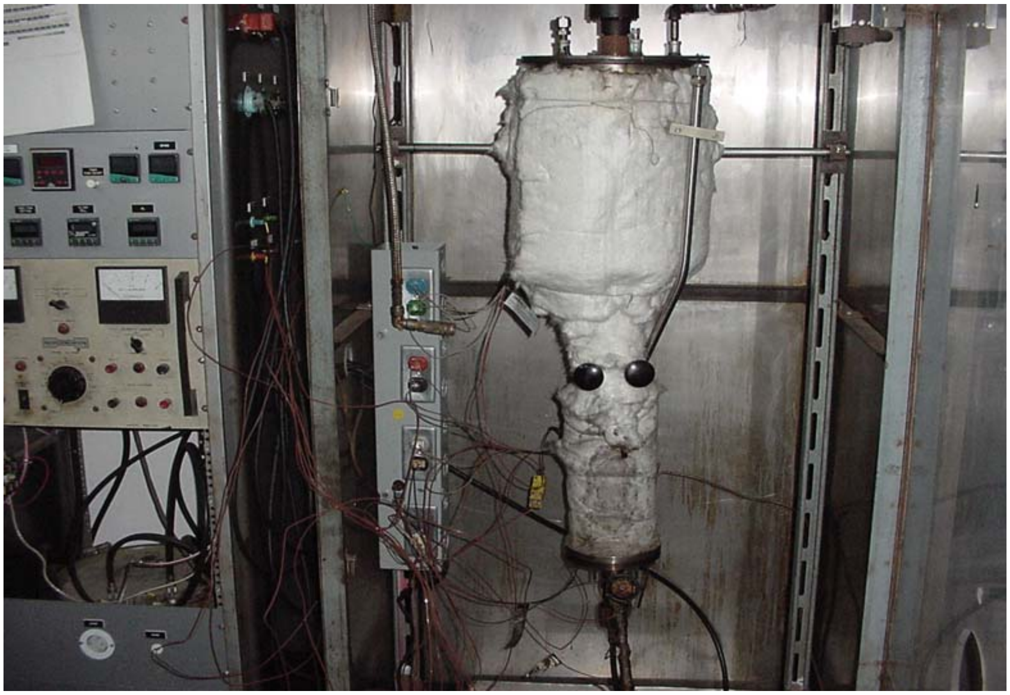


Figure 7. GULFTRONICS® Laboratory Test Unit Picture

Results and Discussion

1. Product Sample GA380 Electrical conductivity Test:

Description:

Gulftronic has developed a standard electrical conductivity test for Resid Fluid Catalytic Cracking (RFCC) or Fluid Catalytic Cracking (FCC) slurry oils. Separation of particles from slurry oil depends on the electrical conductivity of the oils. Oils with electrical conductivity below 0.3 milliamps are consider excellent for separation of catalyst from slurry oil.

The electrical conductivity test was performed without Gulftronic Glass Beads. The sample was heated and placed in a chamber with a 4-inch electrode (Figure 4 pg 14); power was slowly applied to the electrode to a maximum of 30 KVDC at a temperature of 294^{o} F.

Test Results:

Sample GA380 has low conductivity of 0.07 Milliamps confirming as an excellent feed for separation of catalyst from slurry.

2. Feed and Filtrate Ash Analysis:

Ash analysis on feed and filtrate was done by TES and Rentech and results for each of the feeds and filtrates are shown below:

Test	Feed Tested	Feed ppmw iron	Filtrate ppmw iron
1	GA 380	Conductivity	Conductivity
2	GA 388	8300	800
3	GA 392	8000	< 2
4	GA 393	6100	5000

Table 4. Gulftronic® Separator Test Results

Test Sample 1 GA 380: Slurry made of mineral oil and activated F-T catalyst fines. This slurry was selected because it is liquid and simplifies the testing requirements especially in terms of heating. The mineral oil is Penreco Peneteck Technical Mineral Oil. No ash analysis was done on this sample.

Test Sample 2 GA 388: La Porte AFDU F-T catalyst/wax feed and filtrate ash analysis showed a removal of 90 % of slurry feed iron.

Test Sample 3 GA 392: The F-T catalyst/paraffin wax feed and filtrate ash analysis showed removal of 99.98 % of slurry feed iron, this met the minimum 10 ppmw filtrate needs. It should be noted that catalyst particles size in feed slurry is not small as expected from a commercial first stage catalyst/wax separation system and wax properties are not similar to F-T wax expected from an iron catalyst based F-T synthesis reactor. The paraffin wax is mostly normal paraffin, while the F-T wax contains olefins and oxygenates in addition to normal paraffin.

Test sample 4 GA 393: The BCR F-T catalyst/wax feed and filtrate ash analysis showed only a 20 wt% feed iron removal efficiency. The poor removal could be attributed to interference to dielectrophoresis from the F-T wax.

The GULFTRONIC® unit successfully separated F-T catalyst/paraffin wax to less than 10 ppmw. The unit was less successful in separating the Rentech BCR Dynamic Settler F-T catalyst/wax producing no less than 5000 ppmw solids in the cleaned material. While further optimization could reduce this solids concentration further, additional RD&T would be required. It was decided to delay further testing with the unit until other separation technologies have been evaluated.

Crossflow Filtration

LCI's Scepter® Microfiltration modules use a smooth titanium dioxide filter surface with controlled openings sintered to the inside diameter of porous stainless steel tubes to retain fine solids and pass liquids. The tubes are arranged in modules similar to heat exchanger designs. These modules are equipped with pumps, pipes, valves and controls to form a reliable system.

LCI was contracted in evaluating removal efficiency and production rates for micro-filters processing two products, designated BCR catalyst/wax and LaPorte catalyst/wax slurries. The BCR wax was prepared in Rentech BCR and processed through first stage catalyst/wax separation system. The LaPorte catalyst/wax slurry was produced as supernatant from LaPorte AFDU catalyst/wax slurry by heating and settling the larger catalyst particles. Because BCR wax was available in small quantities while LaPorte wax was available in larger quantities, it was decided to test LaPorte wax and use the results as an analog of the BCR wax to predict the filtration behavior of BCR wax. BCR wax data obtained in this test were compared to those obtained by Rentech in parallel experiments (outside DOE funding) and to LaPorte wax data to evaluate LaPorte wax as analog for BCR wax in future tests.

Tests were conducted with LaPorte F-T catalyst/wax slurry and BCR F-T wax/catalyst slurry both starting at 5000 ppmw solids concentration. It was determined that the catalyst/oil slurry test was not needed since LCI's testing facility was setup to handle the temperatures required for the catalyst/wax tests. Tests with both the BCR F-T wax/catalyst and LaPorte catalyst/wax slurries produced F-T wax with less than 10 ppmw solids concentration. Based on the positive test results, TES concluded that parametric testing of the LCI Scepter® Microfiltration modules be continued under Task 3.0: Additional Research, Development, and Testing.

Test Description

LCI conducted tests with the BCR wax and the LaPorte wax. The catalyst/wax slurries were prepared as described above. The BCR wax/catalyst is F-T catalyst removed form the Rentech pilot reactor mixed with wax produced from the Rentech BCR. Testing was conducted at LCI's testing facility using the SCEPTER® model 2.5F-750A1-P1HP (see Figure 8) in Charlotte, North Carolina.

Using the BCR wax these tests were designed to:

- Compare baseline data before and after testing.
- Investigate the effects temperature or velocity or pressure on flux.
- Investigate the effects of other test parameters on flux.
- Gather data from a concentration scan.
- Compare the flux before and after the tests and after cleaning of the test module with hexane.

Using the LaPorte wax these tests were designed to:

- Compare performance with LaPorte wax with performance with the BCR wax under similar operating conditions.
- Investigate the effects of velocity or temperature on flux.
- Gather data from a concentration scan.
- Determine if the LaPorte wax and catalyst is appropriate for the parametric testing (Task 3.0).
- Compare the flux before and after the tests and after cleaning of the test module with hexane.
- Following the tests with LaPorte wax, retest with the BCR wax to determine if there are any hysterisis effects and, again clean and test with hexane.

Figure 8 shows the filtration tubes of a typical single-pass Scepter® Microfiltration test module for illustration. An all-welded module containing several filter tubes in parallel was used in the tests.

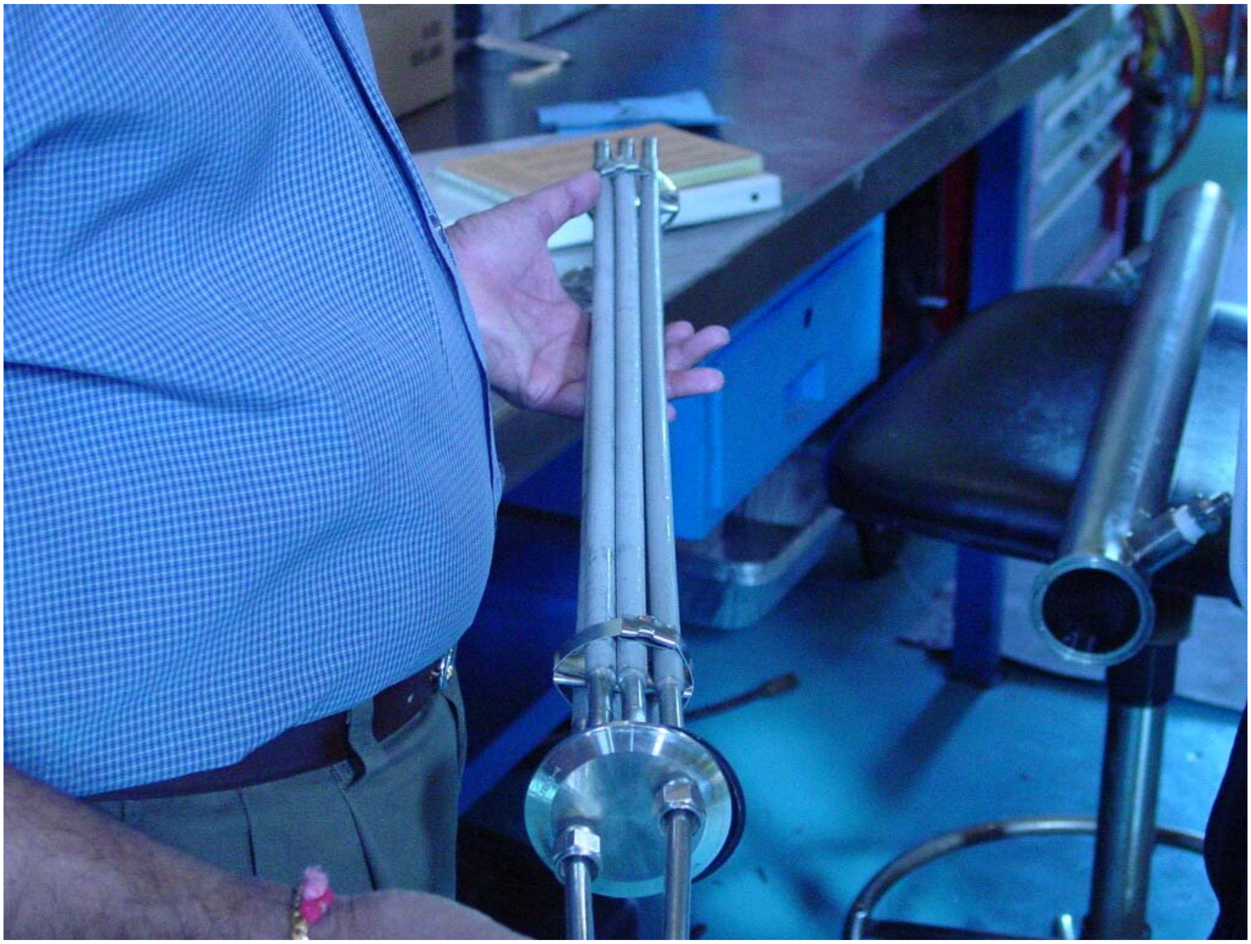


Figure 8. LCI's Scepter® Microfiltration Elements Removed From Shell

Figure 9. TES - BCR and LaPorte Waxes
Flux vs. Temperature
Arrhenius Presentation

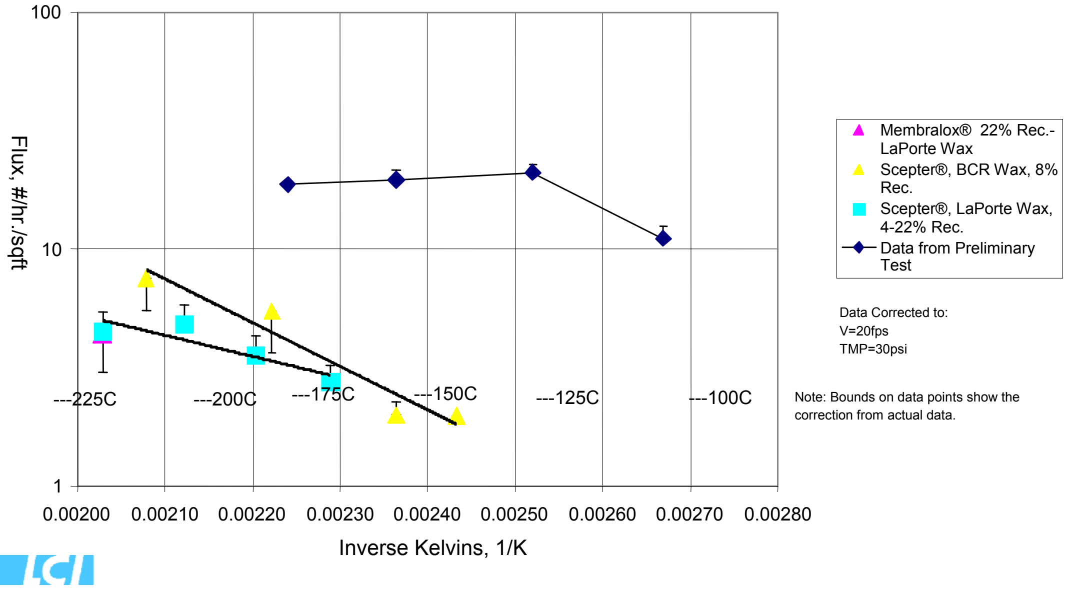


Figure 9 shows the temperature response to flux, in pounds per hour per square feet (#/hr/sqft) for the Scepter® micro-filter processing both BCR and LaPorte waxes. Data taken from the preliminary tests are also presented with along with a single datum from a Membralox® ceramic tube tested during the LaPorte test.

Figure 10. TES - BCR and Laporte Waxes

Flux vs. Pressure

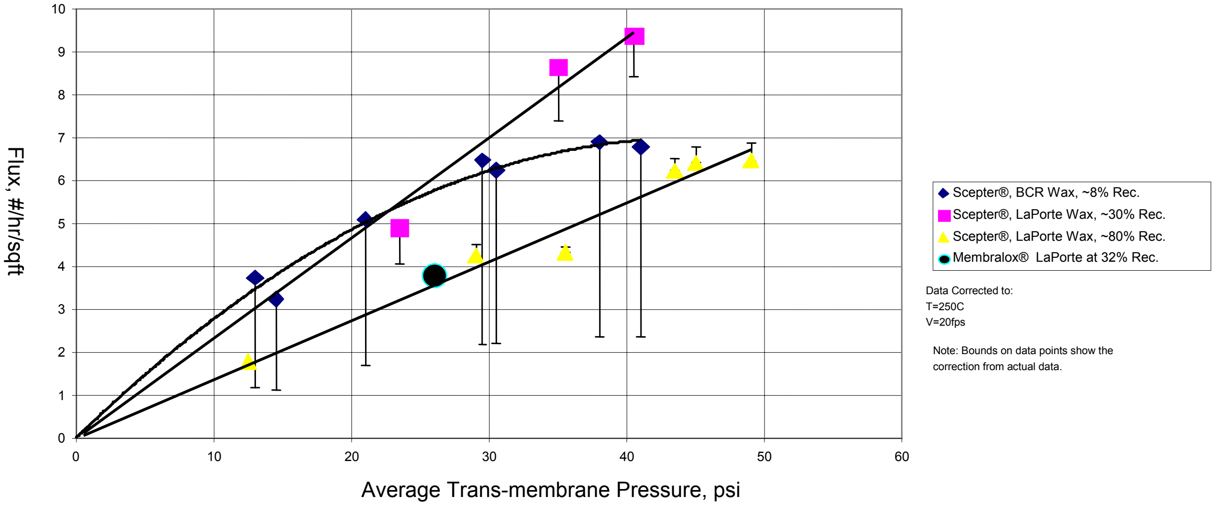
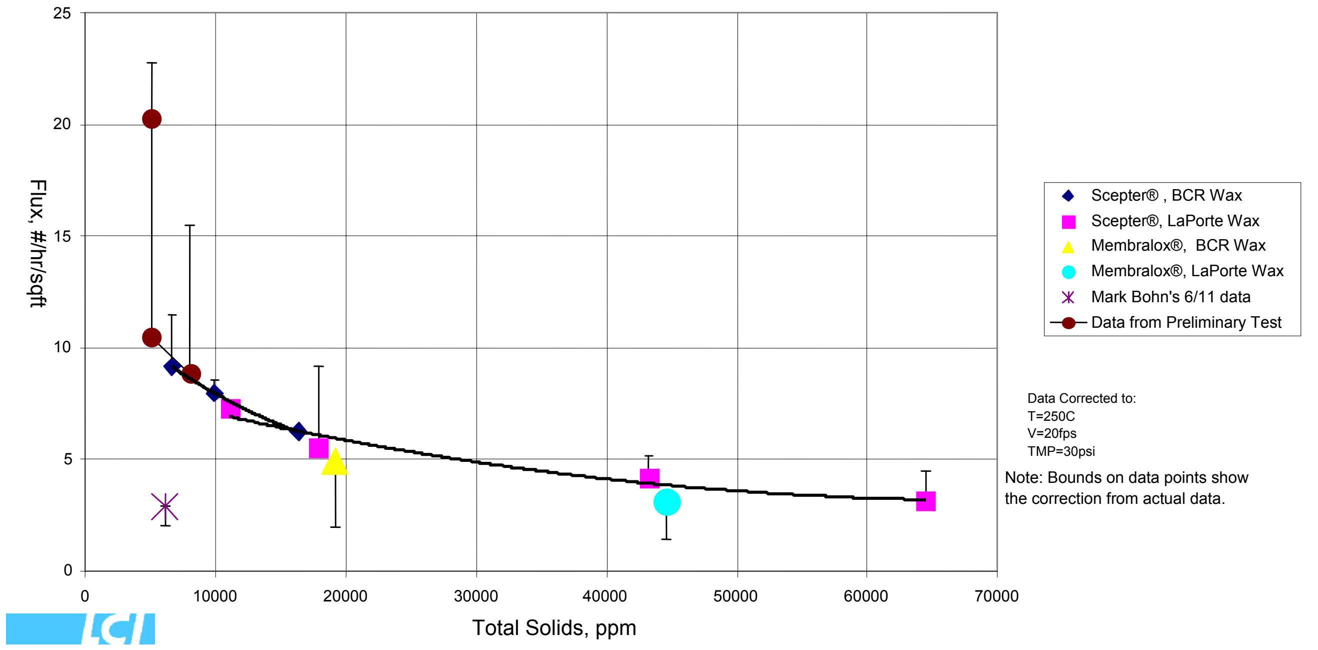


Figure 10 shows pressure responses of flux to for both BCR and LaPorte waxes. While fluxes are similar at similar conditions the BCR wax data suggest a non-linear pressure profile with a diminishing increase in flux per pound per square inch (psi) at higher pressures. These results can suggest a higher concentration of finer solids in BCR wax than in LaPorte wax.

Figure 11. TES - BCR and LaPorte Waxes
Flux vs. Concentration



Data Corrected to:
T=250C
V=20fps
TMP=30psi

Note: Bounds on data points show the correction from actual data.

Figure 11 shows a near-continuous curve when corrected flux data are normalized to suspended solids. This graph illustrates the strongest indication that LaPorte wax can be used as an analog for BCR in future tests as long data are interpreted with a wide band of uncertainty when operating conditions are not as shown in the plot.

Figure 12 shows widely divergent effects of velocity on flux. The reasons for these effects are not well understood. These uncertainties and mystery point to the need for care in extrapolating velocity effects from LaPorte wax results to BCR wax.

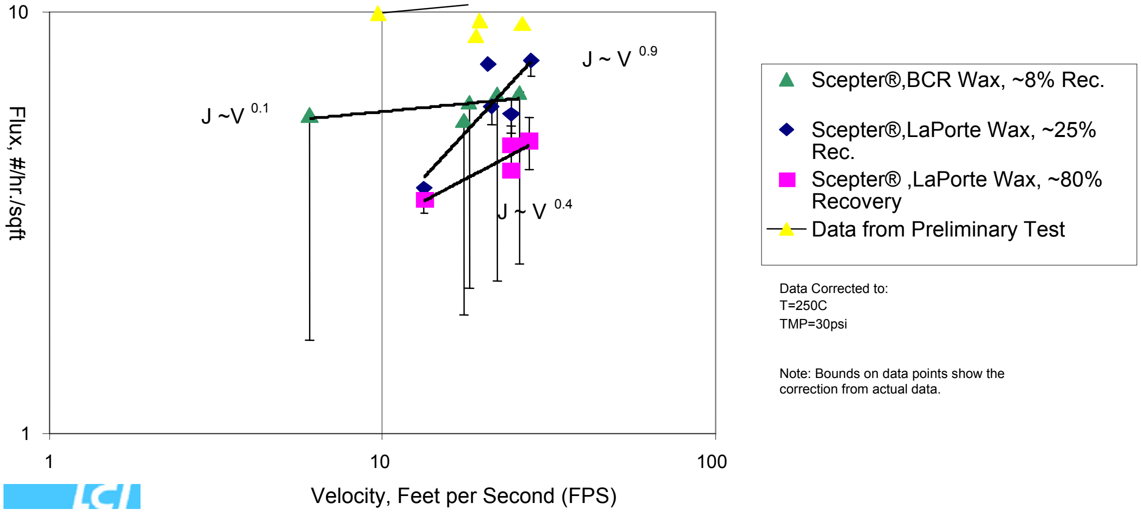


Figure 12. TES - BCR and LaPorte Waxes
Flux vs. Velocity

Data Corrected to:
T=250C
TMP=30psi

Note: Bounds on data points show the correction from actual data.

The temperature response to flux for the Scepter® microfilter processing both BCR and LaPorte waxes is as expected. The higher the F-T wax temperature, the higher the observed flux. The pressure response of flux was similar at similar conditions for both waxes. The Specter® Microfiltration system was able to meet the EECP goal of 10 ppmw with both slurry feeds (see Figure 13).

Additionally, when the flux data is normalized for suspended solids, it becomes apparent that the LaPorte wax can be used as an analog for the BCR in future tests. This will allow for parametric testing in Task 3.0 (Additional RD&T).

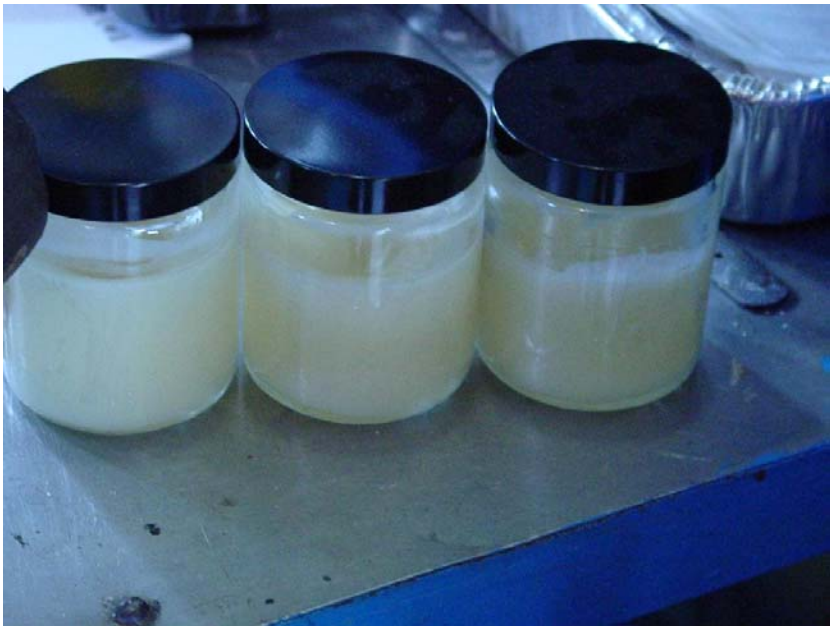


Figure 13. F-T Wax (< 10 ppmw solids) Collected Using the LCI Scepter® Microfiltration System

Based on results from these tests, LaPorte wax appears to be suitable as analog material for BCR testing. While quite different in appearance, it performed similarly in sequential test with the same test module. While performance variations did occur in the shapes of response to pressure and temperature, flux versus suspended solids at similar operation conditions revealed a continuous curve (see figure 3).

LCI recommended that further parametric testing be initiated with LaPorte AFDU wax to further determine longer-term effects of operation on flux and on separation capability. This testing will be performed and the results of these tests will be reported in the Task 3.0 Additional RD&T Topical Report.

Conclusions

Based on successful testing at Rentech (outside of DOE funding) at smaller scale and difficulties in finalizing an agreement to demonstrate magnetic separation, TES selected the Rentech Dynamic Settler as a main primary catalyst/wax separation method. Testing has shown the Dynamic Settler is capable of producing filtrate meeting the proposed EECP primary catalyst/wax separation goal of 0.1 wt%. Additional testing with a larger-scale Rentech Dynamic Settler should be considered before utilizing in a full commercial-scale F-T operation.

Secondary F-T catalyst/wax separation is a crucial step in producing cleaned F-T products. Of the three technologies tested, the LCI Scepter® Microfiltration system appeared to be best suited for producing a filtrate that met the EECP standards of 10 ppmw solids in F-T wax for downstream F-T product upgrading section. The other technologies, magnetic separation and electrostatic separation tested shows promising results and, were able to reduce the solids concentrations in the filtrate, but not to the required EECP level. With further testing and optimization, the magnetic and electrostatic separation devices may be able to meet the EECP standard. However, since the Scepter® Microfiltration system met the 10 ppmw standard with all slurry samples, the team recommended the LCI system for parametric testing in Task 3.0 (Additional RD&T).

Overall, the EECP team feels the risk outlined in the Phase II RD&T Plan has been mitigated by conducting Task 2.3: Fischer-Tropsch Catalyst/Wax Separation. Successful catalyst/wax separation to the 10 ppmw solids level will allow the proposed EECP to produce high-value food grade wax.

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List of Acronyms and Abbreviations

#/hr/sqft	pounds per hour per square feet
AFDU	Alternative Fuels Development Unit
AGR	Acid Gas Removal
ASU	Air Separation Unit
CO	carbon monoxide
CO_2	carbon dioxide
FCC	Fluid Catalytic Cracking
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
FPS	feet per second
GE	General Electric
H_2	hydrogen
H_2O	water
H_2S	hydrogen sulfide
HRSG	heat recovery steam generator
KBR	Kellogg Brown & Root
MDEA	methyldiethanolamine
NOx	nitrogen oxides
ppmw	parts per million (weight)
PSI	pound per square inch
RFCC	Resid Fluid Catalytic Cracking
RD&T	Research, Development, and Testing
SO_2	sulfur dioxide
SRU	sulfur recovery unit
SWS	sour water stripper
TES	Texaco Energy Systems LLC
wt%	weight percent