EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.1: Fischer-Tropsch Pilot Plant Confirmation

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Contributors:
David Storm (ChevronTexaco)
Govanon Nongbri (ChevronTexaco)
Steve Decanio (ChevronTexaco)
Ming He (ChevronTexaco)
Lalit Shah (ChevronTexaco)
Charles Schrader (ChevronTexaco)
Earl Berry (ChevronTexaco)
Peter Ricci (ChevronTexaco)
Belma Demirel (Rentech Inc.)
Charles Benham (Rentech Inc.)
Mark Bohn (Rentech Inc.)

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Texaco Energy Systems LLC
3901 Briarpark
Houston, Texas 77042

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

During Phase I, a design basis for the Fischer-Tropsch Synthesis section was developed based on limited experience with the specified feed gas and operating conditions. The objective of this Task in Phase II RD&T work was to confirm the performance of the F-T reactor at the set design conditions. Although much of the research, development, and testing work were done by TES outside of this project, several important issues were addressed in this phase of the project. They included Rejuvenation/Regeneration of the Fischer-Tropsch Catalyst, online Catalyst Withdrawal and Addition from the synthesis reactor, and the Fischer-Tropsch Design Basis Confirmation. In Phase III the results from these RD&T work will be incorporated in developing the engineering design package. This Topical Report documents the Phase II RD&T work that was completed for this task.

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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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I. 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.

In Phase I, 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). Several technical issues associated the Fischer-Tropsch (F-T) Synthesis reaction section were identified. These issues are addressed in the Phase II RD&T Task 2.1 Pilot Plant Confirmation. One of the issues is the handling and disposal of relatively large quantities of spent catalyst. It is important to obtain as much useful life from the catalyst as possible. If the catalyst is used on a once through basis, the operating cost of the F-T plant increases substantially. The operating cost can be reduced if the spent catalyst can be easily processed and recycled back to the reactor. Loss of activity in the unsupported precipitated iron catalyst can be due to wax deposits, composition change, and attrition. In Phase II RD&T, rejuvenation/ regeneration methods aimed at addressing deposits and composition change were explored. The program was carried out in Rentech's technology center in Denver, Colorado and ChevronTexaco's technology facility in Bellaire, Texas. Results showed that the deactivated catalyst did respond to the rejuvenation procedures. The in-situ regeneration treatment, however, did not significantly improve the deactivated catalyst performance.

Operation of a commercial slurry F-T reactor will require periodic on-line catalyst withdrawal and addition. This is necessary to replace catalyst lost with produced wax and to maintain reactor productivity as the catalyst deactivates. In Phase II RD&T, a catalyst withdrawal and addition system was successfully designed and implemented on Rentech's pilot-scale bubble column reactor (BCR). A test was conducted that demonstrated successful catalyst withdrawals and additions. The test also demonstrated the successful manipulation of the reactor performance by catalyst withdrawals and additions. This report describes tests to demonstrate both on-line catalyst withdrawal and addition from an operating F-T slurry reactor. Results of the testing show that catalyst can be withdrawn and added to an operating F-T reactor safely and that the reactor activity responds in direct proportion to the mass of catalyst added or withdrawn.

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

The final issue addressed in this Task was the design basis confirmation test. The main thrust of this work is to determine if a certain carbon monoxide (CO) conversion can be achieved at a specific space velocity and feed synthesis gas hydrogen (H_2) to CO ratio (H_2:CO) ratio and if the expected F-T subsystem feed gas carbon dioxide (CO_2) concentration of 5% will damage the catalyst. Tests were performed in the Rentech BCR in once-through mode in Denver, Colorado and demonstrated a conversion of a 97% of the desired conversion at 111% of the space velocity. Based on that result and an understanding of how the catalyst and reactor respond to space velocity changes, it appears that the design basis is feasible. In addition, it appears that 5% CO_2 in the feed gas is not detrimental to the catalyst.

II. 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. The objective of Phase I was to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

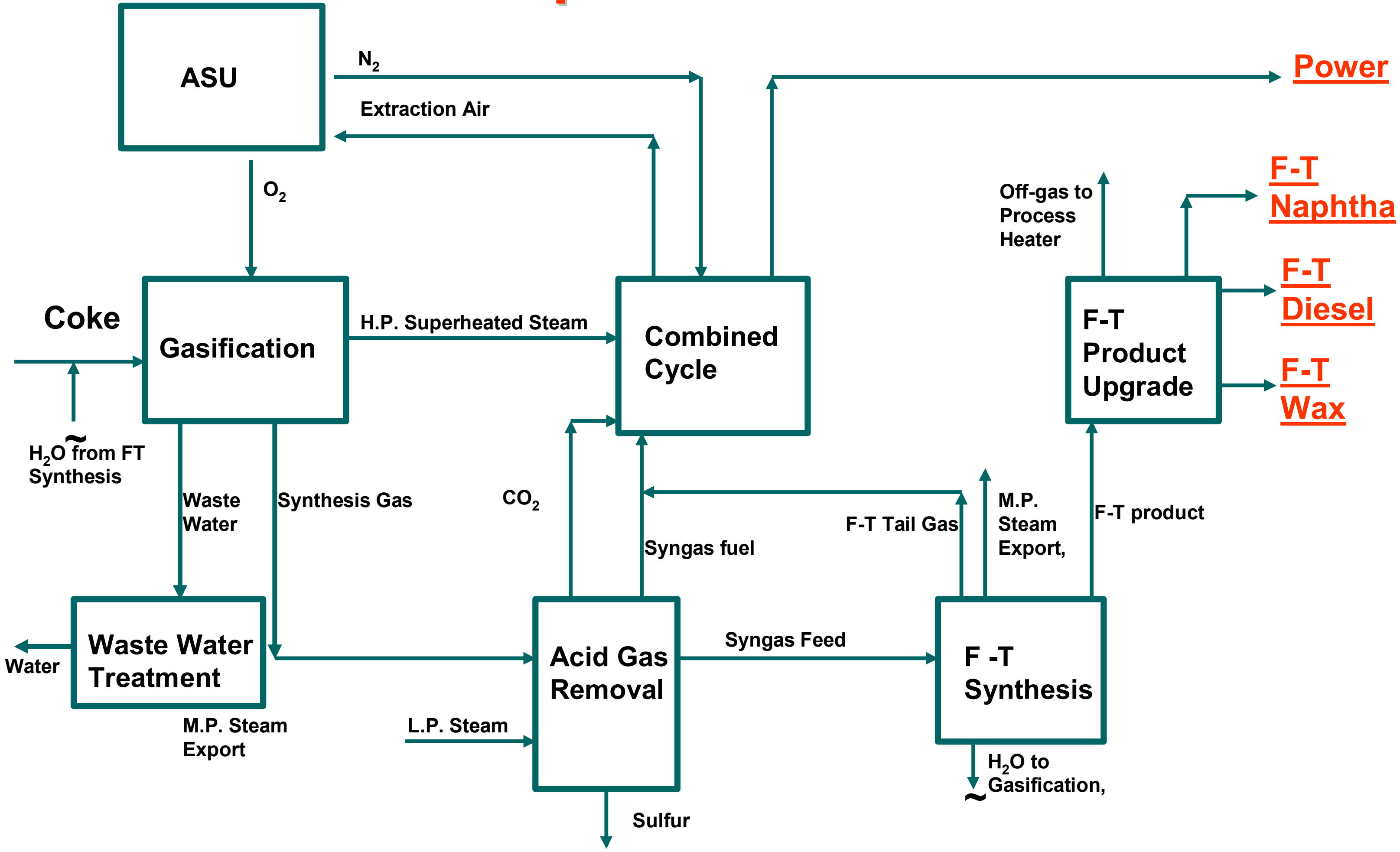
The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and consume approximately 1,120 metric tons per day (1,235 short tons per day) of petroleum coke. During Phase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

EECP Concept

The Overall Block Flow Diagram is shown below in 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 H_2, CO, water vapor (H_2O), and 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 from the ASU is compressed and sent to the gas turbine as a diluent stream, where its mass flow also helps increase the power production.

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,

Proposed EECP



Schematic 1 – EECP Concept

CO and H_2 react, aided by an iron-based catalyst, to form mainly heavy straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid, and light F-T liquid are sent to the F-T Product Upgrading Unit while F-T water, a reaction byproduct, is returned to the Gasification Unit and used in the slurrying process. 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, H_2 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 H_2 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.

Task 2.1

Phase II Task 2.1 addresses the engineering analysis, modeling, and experimental research and development issues associated with the F-T catalyst and reaction. The topics addressed in this task include catalyst rejuvenation/regeneration, catalyst withdrawal/addition from the reactor, and BCR confirmation of the design basis tests. These topics were identified to be important to the technical definition in the F-T Synthesis Section. They identify how that catalyst inventory will managed in a commercial plant. They also provide information for reactor design as well as confidence in the reactor performance. The catalyst/ wax separation is another critical issue to operability of the process. It is addressed in Task 2.3.

The F-T Synthesis Section is designed to convert synthesis gas (syngas) produced in the gasification section to liquid hydrocarbons using Rentech technology. The syngas is produced by gasifying petroleum coke using ChevronTexaco technology. The majority of the syngas from the gasification section is sent to a GE Frame 6FA gas turbine to produce electricity. Part of the syngas, after passing through a zinc oxide bed for hydrogen sulfide (H_2S) removal, is sent to the F-T Synthesis Section. The F-T Synthesis Section uses a slurry BCR. Hydrocarbon products from the F-T Synthesis Section are sent to the product upgrading section. Several issues associated with the F-T Synthesis Section were identified in Phase I as requiring further investigation. These include the following:

Catalyst Rejuvenation & Catalyst Regeneration

Catalyst Rejuvenation and Catalyst Regeneration are possible ways to address the catalyst disposal issue. If the catalyst can be effectively rejuvenated or regenerated, then the quantity of spent catalyst to be disposed can be reduced. Most of the laboratory work for the Catalyst Rejuvenation was completed in Rentech's laboratory facility in Denver, Colorado. The Catalyst Regeneration work was done in ChevronTexaco's laboratory facility in Bellaire, Texas. Since the work was done separately, the Catalyst Rejuvenation and the Catalyst Regeneration are presented in separate sections.

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

In order to evaluate various candidate techniques, it was necessary to have a supply of deactivated catalyst. Catalyst produced by a commercial vendor (Vendor A) for the TES-funded tests that were performed at the La Porte Alternative Fuels Development Unit (AFDU) was available. The La Porte AFDU is a 57.15 cm (22.5 inches) diameter by 8.7 meter (28.3 feet) high slurry bubble column reactor. This catalyst had undergone 30 days of testing. Rentech also produced two batches from Vendor B of used catalyst for testing. The catalysts were used in Rentech's 3.8 cm (1 ½ inch) diameter by 8 meter (26 feet) tall slurry bubble column reactor. In this manner, several hundred grams of catalyst were available for rejuvenation/regeneration work.

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

Testing of candidate techniques were carried out in the laboratory using deactivated catalyst. The approaches tried included: solvent extraction and reoxidation, H_2 reduction, and nitrogen gas stripping. Solvent extraction was carried out in the Rentech facility. The other approaches were carried out in ChevronTexaco's Bellaire facility.

Catalyst Withdrawal/Addition System

Development of an online catalyst withdrawal/addition system is critical in maintaining reactor productivity. Over time, the catalyst in the reactor may age and become less productive; it will need to be removed from the reactor. Fresh catalyst will need to be added to the reactor. In this task a system for catalyst withdrawal and addition was designed, fabricated and tested on the Rentech BCR. The system was designed to allow online catalyst withdrawal and addition without interrupting the reactor operations. During the test, unactivated catalyst was also added to the BCR to determine if it would activate sufficiently under operating conditions. The purpose of this experiment was to see if the activation step can be eliminated when adding catalyst to an operating reactor.

Pilot Test in a Bubble Column Reactor (BCR)

Since Phase I, TES and Rentech have done much testing outside of this program (outside of DOE funding) to investigate the kinetic effects of the feed gas on the F-T reaction. Based on those experiences and the mathematical model demonstrated in Task 2.2, the F-T Synthesis section design basis was revised. The revised design basis feed gas required testing to confirm that the feed H_2:CO ratio and the feed CO_2 concentration was technically feasible. This test was done at Rentech's BCR in Denver, Colorado. The successful confirmation of the design basis would not only provide more confidence in the reactor design in the next phase, but it will also validate the mathematical model as a design tool.

III. Catalyst Rejuvenation

Introduction

The selected "degenerated" catalysts, La Porte 18 (LP18), La Porte 19 (LP19), Rentech, Inc. 56 (RI56) and Rentech, Inc. 59 (RI59) were tested for baseline activity in an autoclave, and very low CO conversions were obtained. Dewaxing was the first step in the process of catalyst rejuvenation. In order to remove wax from the catalysts, each catalyst was extracted using tetrahydrofuran (THF) at 353-373 kelvins (K) (80-100 degrees Celsius [ºC]) and under supercritical fluid extraction conditions using hexane in a batch system. Supercritical fluid extraction using hexane exhibited better extraction power than the THF extraction at 353-373K (80-100ºC). However, there was still some wax left in the catalyst due to the batch extraction process and very high molecular weight of the wax components. Petroleum-based alkylation and reformate naphthas were also tested to determine their extraction power. Reformate naphtha showed better results to remove the wax compared to the other solvents used in this process. However this naphtha contains aromatics, which is not desirable. The extracted catalyst was then oxidized in a porcelain boat placed in a 25.4 millimeter (mm) (1 inch [in.])-diameter by 432 mm (17 inches)-long tubular reactor. Oxidation at 573K (300ºC) and higher oxidation gas flow rates seemed to sinter the catalysts. The optimized oxidation condition was determined to be 493K (220ºC) using 2% oxygen (O_2) in nitrogen (N_2) at the rate of 1.4 cubic meters per hour per kilogram of catalyst ($m^3h^{-1}kg\ cat^{-1}$). The oxidized catalysts were tested in an autoclave to determine their activity, and a significant improvement in conversion was seen relative to baseline activity. However, the chain-growth or the Shulz-Flory Distribution factor (alpha) was lower. This results in a shift in the product distribution towards the lighter materials. X-ray fluorescence analysis of some of the catalyst and wax samples showed that some potassium might have came out of the catalyst during the F-T synthesis reaction, and some was washed out during the extraction process. Although addition of potassium to the oxidized catalyst by impregnation method improved alpha, it was still lower than that of baseline test. Further studies on deactivated and rejuvenated catalysts are necessary to find out what causes lower alpha.

Experimental

Dewaxing

The first step in Catalyst Rejuvenation is dewaxing or removing the wax from the catalyst. The wax is solid at room temperature and is difficult to remove using conventional separation processes, such as filtration, centrifuging. To remove the wax from the catalyst, first, the slurry was heated to 353 K (80ºC) on a magnet to allow the catalyst to settle, and the wax above the catalyst layer was decanted. Once most of the wax was removed, a solvent is used to dissolve the remaining wax and extract it from the catalyst. Although many organic liquids can be used as solvents, the most practical solvent would be the naphtha produced in the F-T reaction. With the lack of F-T naphtha for testing, petroleum-based alkylation naphtha and reformate naphtha were used to give an indication of the potential efficiency of the extraction process F-T naphtha at supercritical conditions. In addition to naphtha, THF and hexane were selected from among other possible solvents due to their solubility, relatively higher boiling point, and ease of disposing.

Petroleum-based alkylation and reformate naphthas supplied by ChevronTexaco were tested to determine their extraction power under supercritical extraction conditions of 513 K (240ºC) and 3117 kPa (440 psig), and the reformate naphtha exhibited better extraction power compared to alkylation naphtha and hexane. For these tests, RI73 catalyst samples were used due to insufficient amounts of the selected samples, RI56, RI59, LP18 and LP19. However, naphtha contaminated the autoclave with sulfur, and the system had to be washed out using hexane. We still suspect some residual sulfur in the system based on a deactivation rate of fresh Rentech catalyst in the last test. The catalysts extracted with the petroleum-based alkylation and reformate naphthas were not tested for activity because the contaminated could have poisoned the catalysts and not offer any meaningful results. The purpose of this experiment was only to study the extraction power of the naphthas.

Solvent extractions were performed in two ways: THF extraction at 353-373 K (80-100ºC) and supercritical fluid extraction using hexane.

THF Extraction

THF extraction was accomplished by contacting the catalyst-wax mix with at 353-373 K (80-100ºC). The liquid was then decanted. This process was repeated until the liquid phase is clear at room temperature. The extracted catalyst was washed and dried.

Supercritical fluid extraction using hexane

Efficient separation of catalyst from the high molecular weight organics can be achieved by supercritical fluid extraction (SCFE). Supercritical fluids exhibit intermediate transport properties with lower viscosities than liquid and higher diffusivities than gases, and unique characteristics of supercritical hexane offers the following advantages: 1) more effective extraction of high molecular weight waxes from the catalyst surface and their transport out of the pores, 2) enhanced pore-transport of solvents to the catalyst surface, and 3) enhanced desorption of the dissolved compounds. SCFE is the most effective if it is carried out in a continuous system.

SCFE of LP18 and RI59 catalyst using hexane was performed in a batch autoclave, at 513 K (240ºC) and 3117 kPa (440 psig) for one hour, and repeated three times. Following extraction, the liquid was decanted. The extracted catalyst was dried. Results showed that SCFE was more effective compared to the THF extraction performed at 353-373 K (80-100ºC), however, some wax still remained in the catalyst due to the batch type of reactor used and high molecular weight hydrocarbons in wax.

Oxidation

After the dewaxing the catalyst, the next step in the catalyst rejuvenation is oxidation of the catalyst, returning the iron in the catalyst to its original state (ferrous oxide [Fe_2O_3]). An economical method is needed for returning the catalyst back to its initial oxide state without causing catalyst attrition or sintering. The oxidation step must be controlled to prevent overheating and sintering of the catalyst.

The presence of wax on the catalyst can cause carbon formation when limited oxygen is available during oxidation. Thus efficient and complete wax removal is the key to successful catalyst rejuvenation. Several oxidation procedures were tested.

The optimum oxidation condition was determined to be 493 K (220ºC) and 1.41 $m^3 \cdot h^{-1} kg\ cat^{-1}$ using 2% O_2 in N_2. The RI56, LP18, and LP19 were oxidized in the same manner. The RI56 and RI59 catalysts were impregnated with potassium carbonate to improve their performance, discussed in the next section. The oxidized catalysts were tested in an autoclave to determine their activity, and the results from these tests are discussed in the next section.

Activity Tests for Oxidized Catalysts

After the oxidation step, the catalyst is considered rejuvenated. It is then activated again and tested under operating conditions. The results are summarized in Table III-1.

Table III-1. Test results for regenerated catalysts.

	H_2:CO	Normalized Space Vel.	Normalize CO Conv.	Alpha
RI59[1]	0.77	1.05	0.35	0.790
RI59O	0.77	1.05	1.23	0.820
RI59OK[2]	0.77	1.05	1.83	0.763
RI56O[2]	0.77	1.05	1.82	0.705
	1.4		1.79	0.619
RI56OK[2]	0.77	1.05	1.59	0.809
LP18O[2]	0.77	1.05	1.85	0.749
			1.81	0.734
LP19O[2]	0.77	1.05	1.72	0.754

[1] Oxidized at 573 K

[2] Subsequent test revealed that actual reactor temperature was greater than the set reaction temperature. High temperature can elevate the CO conversion and reduce the Alpha.

RI59 oxidized slowly (RI59O) showed higher activity, and the normalized CO conversion increased to 1.23 and alpha to 0.82. The CO_2 and CH_4 selectivities obtained are 43.8 and 1.8%. The alpha was 0.846 when the original run was shut-down whereas it was 0.709 in the baseline test. Potassium is known as a chain growth promoter, and it is thought that potassium may have been washed out during the extraction process or it is also possible that potassium might have come out of the catalyst during F-T synthesis reaction. In addition, the catalyst may have been contaminated during the regeneration process. Considering all the possibilities, catalyst samples after oxidation and a wax sample, free of catalyst, were sent out for analysis by x-ray fluorescence (XRF) technique. The results showed that some potassium came off the catalyst and went into wax.

The RI59O was impregnated with potassium carbonate (K_2CO_3) (RI59OK), and tested in the autoclave to determine its activity. The normalized CO conversion increased to 1.83, and alpha was 0.763, which is higher than that from the baseline test but lower that that from the original run. The CO_2 and CH_4 selectivities were 42.9% and 3.2%.

The slowly oxidized RI56 (RI56O) was also tested in the autoclave and normalized CO conversion of about 1.82 and alpha of 0.705 were obtained at the H_2:CO ratio of 0.77. The CO_2 and CH_4 selectivities were 41.1% and 8.5%, respectively. The normalized CO conversion and alpha were 1.79 and 0.619 when the H_2:CO ratio was changed to 1.4. The alpha for this test was lower at both H_2:CO ratios than that for the baseline test. The XRF analysis revealed that the oxidized catalyst had very little potassium remaining. The RI56O was impregnated with potassium and tested in the autoclave. The potassium impregnated RI56 (RI56OK) gave a normalized CO conversion of 1.78 and alpha of 0.809. The CO_2 selectivity was 43.2% and the CH_4 selectivity decreased to 2.1%. The RI56OK gave better alpha when impregnated with potassium albeit those at the original and baseline tests were higher, 0.831 and 0.850 respectively. Further tests are necessary to explain why alpha is lower than that of the original test.

The oxidized LP18 catalyst (LP18O) gave a normalized CO conversion of 1.85, alpha of 0.749, CO_2 selectivity of 43% and CH_4 selectivity of 4.0%. The CO conversion decreased slightly to 1.8 and the alpha decreased to 0.734 when the operating pressure was dropped to the original operating pressure for testing LP18. The LP18O was not impregnated and tested due to an insufficient amount of this catalyst.

The oxidized LP19 was tested in the autoclave, and the normalized CO conversion was 1.72 times the standard baseline conversion and the alpha, CO_2 and CH_4 selectivities were 0.754, 43.4% and 3.4%, respectively. LP19O was not further evaluated due to an insufficient amount.

IV. Catalyst Regeneration

Introduction

In addition to the catalyst rejuvenation tests, a set of regenerative treatment experiments was carried out on the four batches of deactivated catalyst using stripping with N_2 or H_2 at elevated temperatures. The strategy here was to explore regeneration treatments that could be carried out in-situ (in the F-T synthesis reactor on-line) on working catalysts. Four treatments were individually tested on each of the deactivated catalysts: i.) a baseline treatment—wherein the catalyst was heated up in N_2 to 528K (255ºC) at a pressure of 205 kPa (15 psig), then pressured up to 415 psig and exposed to syngas; ii) N_2 stripping treatment—wherein the catalyst was heated to temperature under a nitrogen purge in the continuous stirred tank reactors (CSTR) reactor and held at temperature, 528K (255ºC), for 1 hour under a nitrogen purge prior to syngas exposure, and iii & iv) 1 and 3 hour H_2 reductions – wherein the deactivated catalysts were heated up to 528K (255ºC) in H_2 at 1032 kPa (135 psig) for 1 and 3 hours respectively and then re-activated with syngas. Treated catalysts were then tested for 48 hours at H_2:CO of 0.76 and a syngas rate of 2.08 standard liters per hour (slph).

The four deactivated catalysts were treated under the conditions described above and then tested under the standard F-T conditions to determine whether increases in CO conversion could be affected – particularly to determine if a stable catalyst was reactivated without changes in alpha. Data from N_2 and H_2 activation were compared to the baseline treatments. It was found that N_2 stripping, in some cases, improved catalyst activity as evidenced by elevated CO conversion rates. The H_2 reductive treatments did not enhance catalyst activity at all. The overall result from this part of the study is that in-situ treatments may not be effective in F-T catalyst regeneration. It should be noted, however, that literature work suggests that activation under H_2:CO and or CO atmospheres, under reaction temperature and pressure conditions may hold some promise for reactivation of precipitated iron, F-T catalysts.

Experimental

Catalyst Preparation and Reactor Testing: Samples of each of the four catalysts (RI56, RI59, LP18, and LP19) were subjected to in-situ regenerative treatments in CSTR. The catalyst/wax samples were mixed with Durasyn 164 oil to prepare a slurry. Each catalyst as removed from the BCR was made fluid by mixing with the lighter weight oil. Originally the catalyst was received as a catalyst/wax solid. The wax is solid at room temperature. After suspension, these materials were loaded into 300-cubic-centimeter (cc) CSTR's and tested under each of the four regeneration conditions. The catalyst/wax/Durasyn 164 slurry was added to a CSTR at elevated temperature of 373K (100ºC) in order to insure that the reactor stirrers and thermocouples had freedom of movement and remained undamaged.

Product slates were analyzed throughout the test periods and activity was measured primarily as CO conversion as a function of time (both syngas and H_2 conversions were tracked similarly to this).

Results and Discussion

The conditions used here to treat catalysts RI56, RI59, LP18, and LP19 were strategically focused on effecting wax removal and reactivating surface active sites on the iron. These regenerative treatments were all performed inside of the CSTR. The baseline treatment was used to bring each of the used catalysts up to the activity level (CO or syngas conversion) observed at the end of their original usage. This was necessary as exposure conditions varied between the materials when they were removed from the original reactor. As in the Catalyst Rejuvenation section, the CO conversions are presented as a normalized CO conversion to the standard baseline CO conversion.

The nitrogen stripping treatment was aimed at removing heavy wax from the surface of the iron particles. Wax deposition is one of the potential deactivating mechanisms that can occur on iron based F-T catalysts during the synthesis reaction. Some of the high molecular weight wax might cover the active iron sites and prevent carbide formation.

The H_2 treatments were aimed at restoring the iron surface to its original oxidation state. This would be particularly necessary if the surface were to be oxidized or changed in some fashion through the production of water and/or oxygenates during the F-T reaction. Like wax deposition, changes in the iron oxidation state is another potential deactivation mechanism.

After baseline treatment, the normalized CO conversions were variable among the four samples ranging from 0.38 to 1.35 (Figures IV-3 to IV-6). After 24 hours on stream all samples showed conversions of between 0.38 and 0.77 the activity of LP18 had degraded significantly after an initially higher value of 1.33 normalized CO conversion. These CO conversion values are somewhat similar to those obtained at the end of each original reactor test (Table III-1). This data shows clearly that the catalysts had lost a significant amount of activity during these original reactor testing.

The nitrogen stripping treatment was the only treatment that resulted in an increase in activity in sample LP19. The 0.77 to 0.96 normalized CO conversions observed in baseline operation increased to 1.35 to 1.54. The other three samples showed no significant improvement in activity. H_2 reductions at 1 and 3 hours were carried out for samples RI56 and RI59; reductions at 1 hour only were carried out on samples LP18 and LP19 due to sample size limitations. None of the H_2 reductions improved the catalyst activity. In each of the treated catalysts the F-T reactions showed similar CH_4 selectivity and alpha values that were within a close range to experimental values obtained in the baseline samples.

V. Catalyst Withdrawal & Addition

Introduction

Operation of a commercial F-T reactor will require periodic on-line catalyst withdrawal and addition. This is necessary to replace the catalyst lost with the produced wax and to maintain reactor productivity as the catalyst deactivates.

Objective of the Testing

The first objective of the test to demonstrate that catalyst can be added to and removed from the BCR at operating conditions in a safe and controlled manner. The second objective is to determine if catalyst activity can be maintained after withdrawal of spent catalyst by on-line addition of previously activated catalyst. The third objective is to evaluate whether fresh unactivated catalyst can be activated by synthesis gas at reactor conditions.

Experimental

Testing was conducted in the Rentech pilot-scale BCR located at the Rentech research and development (R&D) facilities in Denver, Colorado. Special equipment was designed, fabricated, and installed to allow the catalyst withdrawal and addition functions required for the test.

A batch of catalyst was activated in the BCR. This was used as the fresh activated catalyst for the catalyst addition operations. After the batch was activated it was purged with nitrogen and removed from the reactor. The batch was then segregated into several samples of uniform concentration solids by weight suitable for charging to the 1 liter slurry charge vessel for the catalyst addition tests.

Next, another batch of catalyst was activated in the same way as the first and then operated under the design basis conditions.

The BCR level was maintained by periodically removing wax through the primary wax/catalyst separation device, i.e. the normal method of maintaining reactor level. The removed slurry was assayed to determine the mass of catalyst removed.

After 1.5 days on stream (DOS) the reactor had reached steady operation and the first slurry withdrawal was conducted. This slurry was assayed to determine how much catalyst had been withdrawn. Twenty-four hours later, an equal mass of catalyst taken from the first catalyst activation step was added to the reactor. This cycle of withdrawal and addition was repeated 4 times.

Finally, an amount of oxide (unactivated) catalyst was added to the reactor and the behavior of the reactor was observed for an additional 24 hours.

Results and Discussion

Table V-1 gives the timing of the withdrawal and additions at each step. Figure V-1 shows the results of the entire test. The magenta trace shows the reactor catalyst loading as a fraction of the initial charge. This is calculated from the initial reactor loading minus the estimated quantity of catalyst in the primary separator loop, minus any catalyst removed from the primary separator, minus the catalyst removed by the withdrawal steps, plus catalyst added by the addition steps. This line has a slow downward trend due to the nearly continuous removal of catalyst from the primary separator and steps corresponding to the withdrawal and addition steps.

The blue line in figure V-1 shows the CO conversion normalized to the initial conversion. The CO conversion decreases rapidly just after activation is completed and the then quickly stabilizes. The reactor was operated for 1.5 days to allow it to stabilize. The conversion leveled off around 65% of the initial CO conversion value just before the first withdrawal at 1.54 DOS.

The first step down at 1.5 DOS is the first catalyst withdrawal. Subsequent withdrawals and additions can be seen as the steps up and down, respectively.

Table V-1 Summary of Catalyst Withdrawal and addition Steps

	time (DOS)
withdrawal #1	1.5
addition #1	2.5
withdrawal #2	3.3
addition #2	4.4
withdrawal #3	5.3
addition #3	6.4
withdrawal #4	7.3
addition #4	8.4
oxide addition	9.4

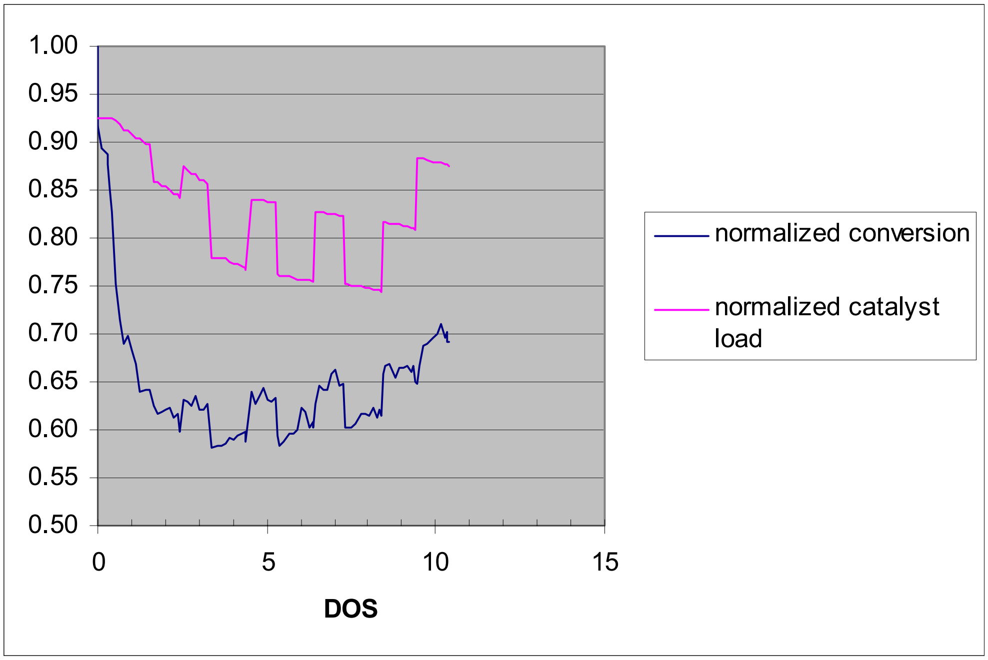


Figure V-1 **Performance Trends**

After the first withdrawal, conversion decreased. The first addition at 2.5 DOS brought the conversion almost all the way back to the value before the removal. Note that the mass of catalyst involved in the first withdrawal and addition were about half of the others. After seeing the noticeable but relatively small reactor response to the first withdrawal and addition we decided to double the quantity to be withdrawn and added in subsequent steps to make the response more obvious.

Catalyst addition steps were preceded by a fairly large removal of reactor wax via the primary separator in order to make room in the reactor for the wax/catalyst to be added in the addition step. Since these wax removals contained small amounts of catalyst, a small down step in the conversion is seen just before each addition. The size of each of these down steps decreases with each addition because the wax removed from the primary separator becomes cleaner during the run so the impact on the removal just before the addition is less each time.

In order to determine how this removal affected the reactor independent of the effect of an addition step immediately following, at 5.79 DOS, 759 grams of wax was removed at a rate of 30 grams a minute (g/min) from the primary wax/catalyst separation unit. CO conversion increased for a short time around 6.0 DOS and then returned to the original trend value. It is estimated that the 759 grams of wax contained about half the amount catalyst in the first withdrawal, therefore a change about half of that from the first withdrawal is expected. In addition to appearing that the CO conversion increased rather than decreased, the size of the change is larger than that for the first removal. Thus, it seems reasonable that the brief excursion in conversion was not related to the removal of 759 grams of wax from the primary separator and that the removal did not impact the reactor at all.

The next withdrawal (3.3 DOS) decreased the normalized conversion to about 58% and the corresponding addition (4.2 DOS) increased it back to about 63%. Subsequent withdrawals and additions continued to decrease the conversion and then increase the conversion by about 5 percentage points.

After 5.2 DOS there is a general upward trend in the conversion, separate from the sudden changes due to the withdrawals and additions. It is believed that this upward trend may be due to the relatively large fraction of fresh catalyst that had been added to the reactor at that time, and the fact that freshly activated catalyst requires several days of operation to become fully active.

Twenty-four hours after the last addition of active catalyst, the normalized conversion appears to have stabilized at 66%. At this point an addition of oxide (unactivated) catalyst was made. In the following 24 hour period the normalized conversion increased by about 5 percentage points just as it had with each addition of active catalyst, although much more slowly. From this one could conclude that the addition of oxide catalyst to an operating reactor may increase reactor activity over about a 24-hour period. It remains to be seen how long the conversion stays at this increased level. The last few measurements seen in the graph show a continuous decline in conversion.

Other critical reactor operating parameters seem to change little with the catalyst withdrawal and addition. Methane productivity, defined as the production of methane divided by the CO conversion, exhibited little response to the withdrawal and addition. This seems reasonable as the quantity of catalyst in the reactor should not affect the chain growth or water gas shift activity.

The results described above show clearly that ability to safely add and withdraw catalyst from the operating reactor which was the first objective of the test was demonstrated. All four withdrawals and five additions were accomplished without incident. In each operation, improvements were made to the operating procedure and suggestions were made on improvements to the hardware. What is less clear is whether this hardware can or should be scaled up for use with a larger reactor. Operations of the withdrawal and addition systems for this test were completely manual and required a great deal of labor to execute. Typically, the addition step required two people plus the normal control system operator for about 2 hours while the withdrawal step required 1 hour. Although the basic principles valid, considerable thought would need to go into scale-up.

The second objective of the test was to determine if catalyst activity can be maintained after withdrawal of spent catalyst by on-line addition of previously activated catalyst. In a commercial reactor, decline in reactor activity will be due to catalyst aging as well as catalyst that is lost with wax removed by the primary wax/catalyst separator. In this test these two decline mechanisms were simulated by withdrawing catalyst from the reactor. Results described in this section show clearly the loss of activity after a withdrawal and a similar increase in activity after an equivalent quantity of activated catalyst is added to the reactor which strongly suggests that reactor activity can be maintained with this operation. A more difficult task is to determine the quantities of catalyst that need to be withdrawn and added to an operating reactor to maintain steady productivity and selectivity.

The third objective of the test was to add oxide catalyst (unactivated) to the operating reactor and determine whether that catalyst becomes active. Results presented in this section strongly suggest that, at least in the short-term, the catalyst does become active. It remains to be proven whether that activity is sustained.

VI. F-T Confirmation Test

Objective of the Testing

The first objective of this activity was to determine whether a CO conversion target can be achieved at the proposed EECP design basis conditions. The second objective was to determine whether there are any negative effects of 5% volume CO_2 in the feed gas.

Experimental

Testing was conducted in the Rentech pilot-scale BCR located in Denver, Colorado.

The first objective was accomplished by adding activated catalyst during the test, gradually reducing space velocity to the design basis value, and then determining the CO conversion at that point. Due to the constraints of the pilot-scale BCR, the amount of catalyst require to achieve the design basis specified space velocity could not be activate in one batch. Therefore online catalyst addition was required. Three batches of Rentech (RI) catalyst were activated. The first two batches were set aside and the third batch was used as the initial inventory for the initial test designated as RI74a. After lining out test RI74a for 3.5 days, catalyst from the first two activated batches was added once per day for 5 days according to the schedule in Table VI-1

	time (DOS)
addition #1	3.54
addition #2	4.54
addition #3	5.51
addition #4	6.52
addition #5	7.51

Table VI-1 Summary of Catalyst Additions

Sufficient reactor wax was removed via the Rentech Dynamic Settler prior to each addition to make room in the reactor for the total mass added for each addition.

After these additions were completed, CO_2 was introduced (RI74b) for two days to determine if the CO_2 would create any problems such as catalyst deactivation. RI74a conditions were then resumed for one day for further confirmation on performance after CO_2 exposure.

Finally, the test was conducted with an isothermal slurry temperature profile, RI74c, for 4 days. The purpose of that test period was to determine the conversion with operating conditions closer to that of a commercial reactor. Typical BCR operation involves a uniform temperature above the 6 feet level and lower temperatures below that. It has been observed that extended operation of the BCR with an isothermal temperature distribution can lead to rapid catalyst deactivation due to limited mixing in the small-diameter reactor. Since a commercial reactor will not have this limitation, RI74c was intended to get a more realistic estimate of CO conversion.

Results and Discussion

Performance

The CO conversion reached a maximum of 93% of the design basis value just after the fifth catalyst addition. There was a small increase in CO_2 productivity, which is defined as the production of CO_2 divided by the CO conversion, as the CO conversion increased.

Figure VI-1 shows the performance plot for RI74b. Two days of operation with 5% by volume CO_2 in the feed gas showed no significant negative effect. The normalized CO conversion decreased by about 4 percentage points over the two-day run, a trend similar to RI74a at 9.5 DOS (before CO_2 was started).

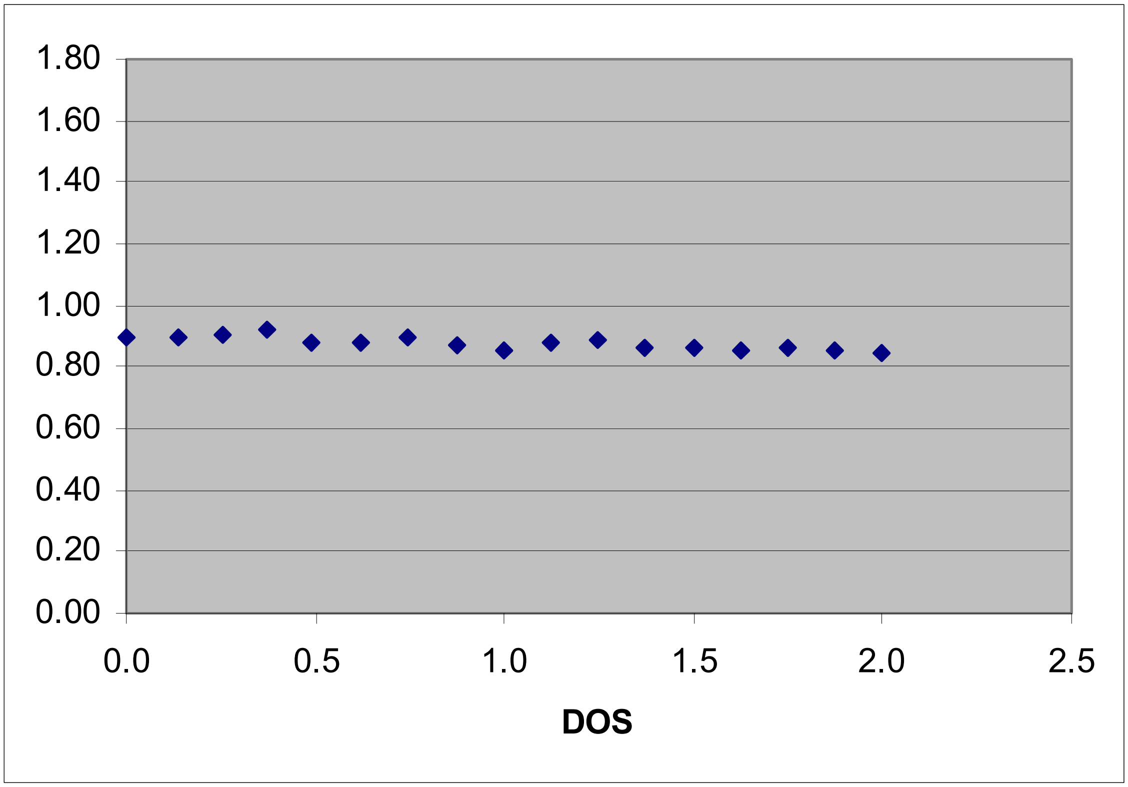


Figure VI-1 Normalized CO Conversions for RI74b

Figure VI-2 shows the performance of RI74c. At zero DOS, the set points of the lowest three reactor heater zones were increased to make a uniform slurry temperature profile. The normalized CO conversion increased from 85% to about 97%. At about 0.4 DOS, a substantial drop in conversion was observed before operation was returned to the non-isothermal temperature profile. CO Conversion then began to recover and leveled out at about 83%.

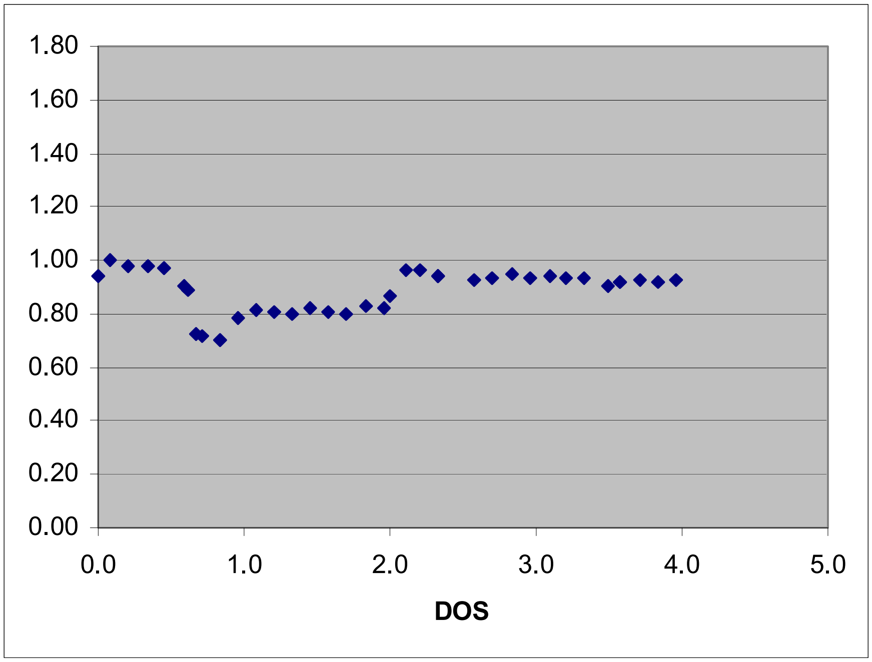


Figure VI-2. Normalized CO Conversions for RI74c

At two DOS the uniform temperature profile was resumed. The normalized CO conversion increased from 83% to about 96% and CO_2 productivity increased slightly as well. The test period continued without problems until four DOS when the run was ended. At that point, the CO conversion was 93%.

The highest CO conversion measured was 97% of the design basis value. Space velocity at this conversion was 111% of the design basis value. It is expected that operation at the design basis space velocity will result in a CO conversion of at least the design basis value.

Productivity

Figure VI-3 shows the production rate of collected products for the entire run. Collected non-aqueous condensate (naq) shows an increase as catalyst is added. Aqueous condensate (aq) production declines slightly during the test. Wax production is erratic because of the necessity of lowering reactor level before each addition.

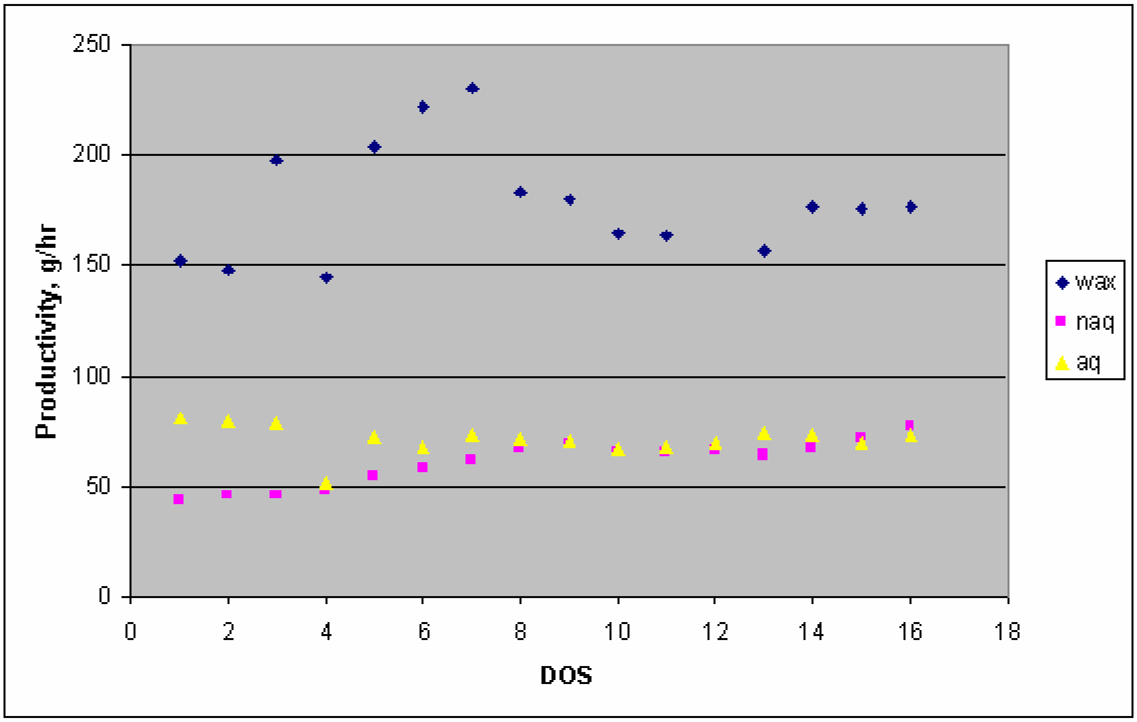


Figure VI-3. Productivity of Collected Products

VII. Conclusions

Much effort was invested in each of the topics addressed in this task. The information collected will all contribute to the final design and operation of a commercial F-T reactor.

Catalyst Rejuvenation

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

Catalyst Regeneration

Catalyst regeneration involves in-situ treatment of the spent catalyst in order to restore its activity. Nitrogen stripping and H_2 reduction were the two methods tested in this task. Nitrogen stripping was found to be effective in one case on one catalyst. The H_2 treatment tests did not show any improvements. Literature surveys indicate that the H_2 reductions may have been too harsh for effective regeneration of these catalysts. Further investigations might utilize nitrogen stripping followed by CO or syngas regeneration. If a successful regenerative treatment is found, it would provide an inexpensive method for maintaining the catalyst activity a prolonging the catalyst life. This would contribute to the overall reduction of the catalyst cost.

Catalyst Withdrawal and Addition

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

Bubble Column Confirmation Test

The test confirmed the F-T synthesis performance at the set design basis feed gas H_2:CO ratio, temperature, pressure, and space velocity. Since the design basis and performance were developed with the mathematical model (Task 2.2), the results of this test give confidence to the model as a design and scale-up tool. The test also demonstrated that the presence of up to 5% volume CO_2 in the feed gas does not adversely affect the performance. This result indicated that in a commercial plant, the Acid Gas Removal Section before the F-T Synthesis section would be able to allow up to 5% CO_2 in the syngas without adversely affecting the F-T reaction. This can lead to a reduction in cost of the AGR Section.

VIII. Appendices

A. Literature Survey of Catalyst Rejuvenation and Regeneration

Rejuvenating and regenerating iron-based F-T catalysts is becoming important due to increasing concerns over disposal of industrial wastes in landfills from both economic and environmental aspects. The catalyst rejuvenation process generally involves removing the wax from the catalyst (or dewaxing) and oxidizing the catalyst back to its oxide state. Dewaxing can be achieved by solvent extraction after filtering the catalyst from most of the wax in the slurry. The oxidation step plays an important role in the process, and must be controlled to prevent overheating and sintering of the catalyst. Dewaxing and oxidation (and surface reactivation, where appropriate) can be carried out externally to the reactor or in-situ. The advantage, in the former case, is that catalyst surface and bulk changes can be more easily and completely controlled. The re-activated catalyst can be prepared under a much wider variety of conditions. In situ rejuvenation, on the other hand, often allows for simpler, less costly process options. Both types of reactivation processes can be applied commercially provided they show promise and can be effectively scaled up. Both external and in-situ rejuvenation schemes were examined in this report.

Catalyst Regeneration as used in this report refers to the processes for recovering the catalyst activity without returning the catalyst to its oxide state. These processes involve stripping the catalyst wax slurry with gas or chemically reducing the catalyst.

There are several potential mechanisms of deterioration of iron-based F-T catalysts. In addition to reduction in activity, some iron-based catalysts undergo a shift in selectivity toward production of lighter products with time on stream. Compositional change of the catalyst, crystallite growth due to sintering, and contamination of active sites by a carbon layer are the primary suspected mechanisms.

As stated by Soled et al in US Patent No. 5,397,806 (1), “In virtually any catalytic process, catalyst activity decreases as run length increases due to a variety of factors: deposition of coke or carbon on the catalyst as a result of cracking, hydrogenolysis, or polymerization, buildup of poisons in the feed such as sulfur or nitrogen compounds, etc. In hydrocarbon synthesis reactions carbon tends to build up or grow (by complex polymerization mechanisms) on the surface of the catalyst, thereby shielding the catalytic metals from the reactants. Activity decreases and at some pre-set level of activity (as defined by conversion or selectivity or both), the process becomes sufficiently uneconomical to continue and the catalyst is either replaced or regenerated. In either case, downtime results and in the former, significantly increased catalyst costs are incurred.”

In US Patent 2,620,347 (2) Rottig describes an iron-based catalyst, an operating regime, and a solvent extraction procedure to produce a catalyst which converts about 70 % of the water gas (H_2:CO =1) to substantial amounts of hydrocarbon products boiling above 573K (300°C). One of the catalysts described was prepared by soda precipitation of iron and copper nitrates, washed, impregnated with potassium phosphate and dried. The catalyst precursor was then reduced in H_2 at 503K (230°C). The reduced catalyst was treated with water gas at a temperature of 423K (150°C) and atmospheric pressure. Over a period of 48 hours the temperature was increased to

463K (190^{o}C) at which point the CO plus H_2 conversion reached 85%. During the next 48 hours, the conversion dropped to 27% by reason of catalyst adsorption of paraffin material. The exhausted catalyst was then thoroughly extracted at a temperature between 443K (170^{o}C) and 468K (195^{o}C) with 5 times its volume of hydrogenated diesel oil fraction having a boiling point between 493K and 533K (220-260^{o}C). The catalyst was again subjected to water gas at 423K (150^{o}C) as before. In this case the H_2 plus CO conversion was about 45%. After 72 hours the conversion dropped to 40% due to catalyst adsorption of paraffin material. The synthesis and treatment cycles were repeated several times until the CO plus H_2 conversion stabilized at about 70%. The catalyst had a useful life of several thousand hours with an average conversion rate of about 70%. During this period, extractions were carried out at first every 5-6 days and subsequently every 10-14 days.

In US Patent 2,632,015 (3) Kratzer describes a novel regeneration process using ethanol. The procedure is directed toward removing carbon from an iron catalyst which has operated at high temperatures in a fluidized-bed F-T reactor. The carbon on the catalyst or perhaps the carbon in iron carbide reacts with ethanol in a fluidized-bed reactor at a pressure between 1034 kiloPascal (kPa) (150 pounds per square inch [psi]) and 4137 kPa (600 psi) and a temperature between 623 K (350^{o}C) and 633 K (360^{o}C) to produce acetone. The ethanol is separated from the acetone and recycled to the reactor. Additional treatment of the catalyst is described whereby H_2 or a mixture of H_2 and steam is introduced into the fluidized-bed at a temperature between 643 K (370^{o}C) and 753 K (480^{o}C) for a period of time between eight and fifteen hours.

It is thought that the removal of surface contaminants from the active sites is a very complex phenomenon in precipitated iron-based catalysts. In several studies (4, 5) Dataye, et. al., it was found that severe H_2 reduction at temperatures of 543 K (270^{o}C) resulted in inactive catalysts. Much more active materials were obtained after mild H_2 reductions or with CO reductions. It was postulated that hematite crystals are converted to magnetite, which favors carbide formation, after mild reductive treatments. Conversely, more severe reduction was believed to lead to the formation of metallic iron. Formation of this phase was believed to have resulted in: i) catalytic activity loss; ii) catalyst attrition, and iii) tendencies toward poisoning by trace impurities such as sulfur. The implication of this study is that the surface chemistry of the precipitated iron catalyst is crucial for its effective activity, and that this surface chemistry is very sensitive to pretreatment. This sensitivity of the active sites to pretreatment has been observed frequently. Successful regeneration schemes must: i) remove light and heavy surface wax from the catalyst; and ii) result in the restoration of surface iron environments which favor iron carbide formation. In addition, the effective regeneration cycle will limit iron crystal changes that can result in catalyst attrition.

The attrition phenomenon is well known among those working with precipitated catalysts, particularly precipitated iron catalysts (6-8). Additives such as silica and alumina were often found to prevent attrition. Typically catalyst activity was found to be lowered as well. Most likely this was due to changes of the active iron sites which resulted from the additive. The implication here then, is that effective control of the iron surface chemistry may be more effective at preventing attrition than additive use.

McBrayer, Jr. et al in US patent 6,121,179 (9) describe a process for removing organic contaminants from adsorbent materials using supercritical water. The organic contaminants are destroyed in a second stage by oxidation.

US patents 6,114,399 and 6,217,830 (10, 11) were issued to Roberts and Kilpatrick for their methods and apparatus respectively of using supercritical organic solvents to effect catalyst/wax separation for a F-T slurry reactor. In this patent, the solvent and catalyst/wax slurry are mixed to dissolve wax in the solvent, and the wax-laden solvent is separated from the catalyst-laden wax which is returned to the F-T reactor. The solvent and wax are separated via one or more stages of flash separation. The recovered solvent is recycled to the mixer and the wax is collected as product. The procedures described in these patents do not provide a wax- and contaminant-free catalyst.

In US Patent 2,487,867 (12) L. I. Griffin, Jr. describes a process for purifying catalyst particles used in a fluidized-bed F-T reactor. A slipstream of catalyst and H_2 are fed to a hydrogenation reactor wherein waxy and oily deposits are destructively hydrogenated to form volatile products and to lower the molecular weight and viscosity of the oily material remaining on the catalyst. The catalyst is then fed to a second vessel for washing with a solvent. After drying, the catalyst is returned to the fluidized-bed reactor. For an iron-based catalyst, Griffin recommends that the hydrogenator be operated at a temperature of 503 K (230^{o}C) to 673K (400^{o}C) and at a pressure of 247 kPa (25 psig) to 2515 kPa (350 psig). The solvent can be naphtha, gasoline, or liquefied petroleum gases.

A. Voorhies, Jr. was issued US Patent 2,533,072 (13) for a method of decarbonizing a F-T catalyst used in a fluidized-bed reactor by H_2 treatment. Since the decarbonizer must operate at a higher temperature (808-923 K (535-650^{o}C)) than the F-T reactor (588-673 K (315-400^{o}C)), sufficient CO is fed along with the H_2 fed to the decarbonizer to provide an exothermic reaction to heat the decarbonizer to the required temperature. Sufficient carbon is removed from the catalyst to maintain the carbon content of the catalyst in the F-T reactor below 20 percent by weight.

In US Patent 5,817,701 (14) Leviness and Mitchell describe a process for regenerating a partially deactivated catalyst used in a three-phase bubble column F-T reactor (BCR). The synthesis gas flow into the F-T reactor is interrupted and replaced with a H_2 rich regenerating gas. The regenerating gas is recycled back to the reactor after water scrubbing to remove deactivating species. The regenerating gas was specified to contain at most 5-10% volume CO and to have a H_2:CO ratio of at least 3-5. In one embodiment of the invention, CO_2 was present in the regenerating gas in sufficient amount to suppress the water gas shift reaction.

Maretto et al in US Patent 6,162,754 (15) describe the use of a draft tube situated inside a F-T slurry BCR for regenerating catalyst. Catalyst flows from the top of the draft tube downward between the draft tube and reactor wall. A regenerating gas, preferably H2, is introduced into this annular region for contact with the catalyst. After a period of time, the H_2 flow is stopped and circulation of slurry from the draft tube into the annular region resumes thereby displacing the regenerated catalyst into the draft tube where the F-T reaction takes place. This sequence is repeated without having to interrupt the F-T reaction.

In US Patent 6,022,755 (16) Kinnari and Schanke describe a novel method of regenerating a catalyst used in a slurry BCR. In order to provide a H_2-rich gas for regeneration, the space velocity is lowered to a level whereby the outlet gas composition is low in CO and high in H_2. In this mode of operation, the CO conversion is high, the H_2:CO ratio is high, the CO_2 selectivity is high, and the C_5+ selectivity is low. The resulting effect of the new reaction mode is a regenerative gas mixture. Therefore, it is not necessary to change the synthesis gas composition for regeneration.

When an iron-based catalyst has deactivated irreversibly, oxidation may be the only way to remove the deactivating species and allow salvaging the catalyst. In this case reactivating the resulting iron oxide (hematite) is necessary. The difficulty in oxidizing the precipitated iron catalyst is preventing overheating and sintering of the catalyst. The converse is true as well, although heat treatments under neutral or reductive environments may effect wax removal, severe reduction results in catalyst surface changes to alpha iron, which is inactive. Iron carbide formation does not occur on this species. The overall picture then that emerges is of a catalyst with surface sensitivity that is adversely affected by either oxidations or reductions which are too extreme. This reveals that catalyst surface rejuvenations or regenerations of the type described here (whether by dewaxing and oxidationor in-situ gas treatment) must be carried out under very controlled conditions in order to recover catalyst activity.

In US Patent 2,661,338 (17) W. C. Lanning describes a procedure for rejuvenating an iron-based F-T catalyst used in a fluidized-bed reactor. In this case carbonaceous deposits are oxidized in a combustion reactor and iron oxide is melted as it falls through the combustion zone. Solid iron oxide particles are formed as the droplets move down through the cooling zone of the reactor. Particles which have agglomerated are broken up by grinding. The fused iron particles are reduced in H_2 and returned to the F-T reactor. This method is not applicable to a precipitated iron catalyst.

Kölbel and Ralek (18) mentioned the successful rejuvenation of a precipitated iron catalyst used in a slurry BCR by controlled oxidation. However, no details were given.

B. Selection of Catalysts for Regeneration/Rejuvenation Studies

Four samples of “deactivated” catalysts were selected for both catalyst regeneration and catalyst rejuvenation studies at Rentech, Inc., and ChevronTexaco Inc.: La Porte 18 (LP18), La Porte 19 (LP19), Rentech, Inc. 56 (RI56) and Rentech, Inc. 59 (RI59). These catalysts were all used catalysts and showed very low activity. The Rentech catalysts, RI56 and RI59 had used in a 41mm (1.6 in.) diameter x 26 ft high BCR located at the Rentech facility. The La Porte catalysts, LP18 and LP19 had been used in a 22.5 in. x 20 ft high BCR at the DOE La Porte Alternative Fuels Development Unit (AFDU) that is operated by Air Products and Chemicals, Inc (APCI).

Baseline Tests

In order to determine the effects of catalyst regeneration/rejuvenation, baseline autoclave tests were first performed on each of the four selected catalysts. The baseline catalysts were tested without any pretreatment in order to determine their activity to end-of-run activity. All of the baseline runs were done at a single space velocity. The results from the baseline tests are summarized in Table VIII.B-1.

Table VIII.B-1. Test Results performed in autoclave for the selected catalysts.

	Catalyst Manufacturer	H_2:CO	Normalized Space Vel.	Normalized CO Conv. (normalized to baseline)	Alpha
RI[1]	Vendor B	0.77	1	1	0.889
LP18	Vendor A	0.84	1.79	0.21	0.892
			1.05	0.29	0.865
LP19	Vendor A	0.84	1.05	0.58	0.824
RI56	Vendor B	0.77	1.05	0.58	0.850
RI59	Vendor A	0.77	1.05	0.47	0.709

[1] Fresh Rentech catalyst, activated prior to test; Standard

A standard baseline test was performed with fresh Rentech catalyst which was activated prior to the test. All of the other tests were compared to this baseline. All of the results are presented relative to the standard baseline test. The space velocities and CO conversions are shown as normalized values to the space velocity and CO conversion of this standard baseline test. It is shown in the first row of Table VIII.B-1.

C. Experimental Reports

1. Catalyst Rejuvenation

Introduction

The selected "degenerated" catalysts, La Porte 18 (LP18), La Porte 19 (LP19), Rentech, Inc. 56 (RI56) and Rentech, Inc. 59 (RI59) were tested for baseline activity in an autoclave, and very low CO conversions were obtained. Dewaxing was the first step in the process of catalyst rejuvenation. In order to remove wax from the catalysts, each catalyst was extracted using tetrahydrofuran (THF) at 353-373 kelvins (K) (80-100 degrees Celsius [ºC]) and under supercritical fluid extraction conditions using hexane in a batch system. Supercritical fluid extraction using hexane exhibited better extraction power than the THF extraction at 353-373K (80-100ºC). However, there was still some wax left in the catalyst due to the batch extraction process and very high molecular weight of the wax components. Petroleum-based alkylation and reformate naphthas were also tested to determine their extraction power. Reformate naphtha showed better results to remove the wax compared to the other solvents used in this process. However this naphtha contains aromatics, which is not desirable. The extracted catalyst was then oxidized in a porcelain boat placed in a 25.4 millimeter (mm) (1 inch [in.])-diameter by 432 mm (17 inches)-long tubular reactor. Oxidation at 573K (300ºC) and higher oxidation gas flow rates seemed to sinter the catalysts. The optimized oxidation condition was determined to be 493K (220ºC) using 2% oxygen (O_2) in nitrogen (N_2) at the rate of 1.4 cubic meters per hour per kilogram of catalyst ($m^3h^{-1}kg\ cat^{-1}$). The oxidized catalysts were tested in an autoclave to determine their activity, and a significant improvement in conversion was seen relative to baseline activity. However, the chain-growth or the Shulz-Flory Distribution factor (alpha) was lower. This results in a shift in the product distribution towards the lighter materials. X-ray fluorescence analysis of some of the catalyst and wax samples showed that some potassium might have came out of the catalyst during the F-T synthesis reaction, and some was washed out during the extraction process. Although addition of potassium to the oxidized catalyst by impregnation method improved alpha, it was still lower than that of baseline test. Further studies on deactivated and rejuvenated catalysts are necessary to find out what causes lower alpha.

Experimental

Selection of Catalysts For Regeneration/Rejuvenation Studies

Four samples of "deactivated" catalysts were selected for catalyst regeneration/rejuvenation studies at Rentech, Inc., and ChevronTexaco Inc.: La Porte 18 (LP18), La Porte 19 (LP19), Rentech, Inc. 56 (RI56) and Rentech, Inc. 59 (RI59). These catalysts showed very low activity at the end of individual runs. Test conditions and characteristic test results of each catalyst are summarized in Table VIII.C.1-1. RI56 and RI59 were prepared in a 41mm (1.6 in.) diameter x 26 ft high BCR located at the Rentech facility. LP18 and LP19 were prepared in a 22.5 in. x 20 ft high BCR at the DOE La Porte Alternative Fuels Development Unit (AFDU) that is operated by Air Products and Chemicals, Inc (APCI).

Table VIII.C.1-1. Performance of the Four Selected Catalysts at the End of Each Run.

	Catalyst Manufacturer	H_2:CO	Normalized CO Conv. (normalized to RI[1])	Alpha
RI56	Vendor B	0.77	0.33	0.831
RI59	Vendor A	0.77	0.73	0.846
LP18	Vendor A	0.84	0.92	0.892
LP19	Vendor A	0.84	0.66	0.890

[1] Fresh Rentech catalyst, activated prior to test; Standard

Preliminary tests were performed in an autoclave before starting catalyst regeneration/rejuvenation studies. Fresh Rentech catalyst was used for the procedure development and tested at each stage, i.e., baseline test, dewaxing, oxidizing, and activity test for rejuvenated catalyst. Samples of the same materials were used for the nitrogen and H_2 in-situ catalyst regeneration studies.

Dewaxing

Dewaxing these catalysts is a troublesome operation. The wax materials with high-boiling points will form a solid material at room temperature, and create difficulties in separation processes, such as filtration, centrifuging. However, if sufficient solvent is present to maintain wax materials in solution, separation can be easier. There are a number of methods for dewaxing in the petroleum industry, i.e., centrifuging, cold settling, pressing and sweating, solvent dewaxing. The use of the first three methods has been very costly to refiners. Almost all plants employ solvents for dewaxing, and acetone, benzene, toluene, and methyl ethyl ketone are the most common solvents used in these processes. Solvent dewaxing is a typical solvent extraction process, and the term "solvent extraction" will be used in this report. However, this term may be confusing, because it also applies to the leaching of a soluble substance from a solid. Because of its variety of applications, leaching is known as extraction, solid-liquid extraction, percolation, washing, and decantation-settling. In the case of separation of wax from catalysts, wax is the soluble constituent, and catalyst is the insoluble mass with pores.

Before the solvent extraction process, catalyst must be separated from most of the wax to minimize solvent consumption. Slurry was heated to 353 K (80ºC) on a magnet to allow the catalyst to settle, and the wax above the catalyst layer was decanted. The catalyst-rich wax was then assayed for baseline tests.

Although many organic liquids can be used as solvents, the most practical solvent would be the naphtha produced in the F-T reaction. The naphtha can be used either as a normal solvent or under supercritical conditions. Other potential solvents include hexane, acetone, toluene, benzene, and tetrahydrofuran (THF). Among those, THF and hexane were selected for the extraction due to their solubility, relatively higher boiling point, and ease of disposing. Petroleum-based alkylation naphtha and reformate naphtha were also used to determine the efficiency of the extraction process at supercritical conditions.

Solvent extractions were performed in two ways: THF extraction at 353-373 K (80-100ºC) and supercritical fluid extraction using hexane.

THF Extraction

THF extraction was accomplished by contacting the catalyst-wax mix with THF in a beaker on a hot plate. THF was added to catalyst-rich wax, melted, and the mix was heated up to 353-373 K (80-100ºC) stirring continuously to increase the solubility of wax. The mix was then put on a magnet to allow catalyst to settle and the wax dissolved in THF to be separated by decanting. This process was repeated until the liquid phase is clear at room temperature. Some wax is expected to remain in the catalyst because solvent extraction is generally least effective on very high molecular weight organics. The extracted catalyst was transferred into an evaporating dish and washed with acetone at room temperature to wash out the THF, and then dried at room temperature by mixing it continuously to prevent the catalyst particles from sticking together. The catalyst was also dried in an oven at 333 K (50ºC) overnight to evaporate and remove the remaining solvents. A picture of a typical extracted catalyst is shown in Figure VIII.C.1-1. RI56, RI59, LP18 and LP19 were THF extracted before oxidation. Catalyst loss during extraction was very low for RI56 and RI59, and relatively higher for LP18 and LP19 due to their fine particle sizes.

Figure VIII.C.1-1. THF Extracted Catalyst

Supercritical fluid extraction using hexane

Efficient separation of catalyst from the high molecular weight organics can be achieved by supercritical fluid extraction (SCFE). Supercritical fluids exhibit intermediate transport properties with lower viscosities than liquid and higher diffusivities than gases, and unique characteristics of supercritical hexane offers the following advantages: 1) more effective extraction of high molecular weight waxes from the catalyst surface and their transport out of the pores, 2) enhanced pore-transport of solvents to the catalyst surface, and 3) enhanced desorption of the dissolved compounds. SCFE is the most effective if it is carried out in a continuous system.

SCFE of LP18 and RI59 catalyst using hexane was performed in a batch autoclave, at 513 K (240ºC) and 3117 kPa (440 psig) for one hour, and repeated three times. Following extraction, the catalyst was allowed to settle in the bottom of the container on a magnet and the solute, wax, dissolved in hexane was separated from the catalyst by decanting. The extracted catalyst was first dried at room temperature by mixing continuously to prevent particles sticking together, and then at 323 K (50ºC) in an oven overnight. Results showed that SCFE was more effective compared to the THF extraction performed at 353-373 K (80-100ºC), however, some wax still remained in the catalyst due to the batch type of reactor used and high molecular weight hydrocarbons in wax.

Petroleum-based alkylation and reformate naphthas supplied by ChevronTexaco were tested to determine their extraction power under supercritical extraction conditions of 513 K (240ºC) and 3117 kPa (440 psig), and the reformate naphtha exhibited better extraction power compared to alkylation naphtha and hexane. For these tests, RI73 catalyst samples were used due to insufficient amounts of the selected samples, RI56, RI59, LP18 and LP19. However, naphtha contaminated the autoclave with sulfur, and the system had to be washed out using hexane. We still suspect some residual sulfur in the system based on a deactivation rate of fresh Rentech catalyst in the last test.

Baseline Tests

In order to determine the effectiveness of catalyst regeneration/rejuvenation, baseline autoclave tests were performed on each of the four selected catalysts, and compared with the regenerated catalysts. The baseline catalysts were tested without any pretreatment to determine their activity to end-of-run activity. All of the baseline runs were done at a single space velocity. The results from the baseline tests are summarized in Table VIII.C.1-2.

Table VIII.C.1-2. Test Results performed in autoclave for the selected catalysts.

	Catalyst Manufacturer	H_2:CO	Normalized Space Vel.	Normalized CO Conv. (normalized to baseline)	Alpha
RI[1]	Vendor B	0.77	1	1	0.889
LP18	Vendor A	0.84	1.79	0.21	0.892
			1.05	0.29	0.865
LP19	Vendor A	0.84	1.05	0.58	0.824
RI56	Vendor B	0.77	1.05	0.58	0.850
RI59	Vendor A	0.77	1.05	0.47	0.709

[1] Fresh Rentech catalyst, activated prior to test; Standard

A standard baseline test was performed with fresh Rentech catalyst which was activated prior to the test. All of the other tests were compared to this baseline. All of the results are presented relative to the standard baseline test. The space velocities and CO conversions are shown as normalized values to the space velocity and CO conversion of this standard baseline test. It is shown in the first row of Table VIII.C.1-2.

The first baseline test for LP18 was carried out with a feed H_2:CO ratio of 0.84 and a normalized space velocity of 1.79, which correspond to those at the end of the test performed at the La Porte AFDU. The normalized CO conversion was about 0.21, and alpha was 0.892. The next test for this catalyst was performed at the normalized space velocity of 1.05 due to the very low CO conversion at higher space velocity. However, the CO conversion was a low at 0.29.

Since CO conversion at higher space velocity is expected to be lower, other catalysts for baseline tests were carried out at the same normalized space velocity 1.05. The other conditions for LP19 were selected to be the same operating conditions as those at the end of the test: feed H_2:CO ratio of 0.84. The normalized CO conversion and alpha were about 0.58 and 0.824. The CO_2 selectivity was close to 40% and the methane (CH_4) selectivity reached 1.8% at the time of the shut-down.

A baseline test for RI56 was performed with a feed H_2:CO ratio of 0.77 and a normalized space velocity of 1.05. Results showed that the normalized CO conversion was 0.58 and alpha 0.850 , and CO_2 and CH_4 selectivities were 41% and 1.25%, respectively.

The baseline test for RI59 showed that the normalized CO conversion and alpha were 0.47 and 0.709, and CO_2 and CH_4 selectivities were about 55% and 3.5%, respectively. This test was performed with a feed H_2:CO ratio of 0.77 and a normalized space velocity of 1.05.

Oxidation

The extracted catalysts must be oxidized to return the iron in the catalyst to its original state (ferrous oxide [Fe_2O_3]). Some methods have been proposed which rejuvenate iron-based catalysts for a short period of time, but an economical method is needed for returning the catalyst back to its initial oxide state without causing catalyst attrition or sintering. The oxidation step must be controlled to prevent overheating and sintering of the catalyst.

The presence of wax on the catalyst can cause carbon formation when limited oxygen is available during oxidation. Thus efficient and complete wax removal is the key to successful catalyst rejuvenation.

Determination of Oxidation Condition:

As a preliminary test, the THF extracted Rentech catalyst was oxidized at 623 K (350ºC) in an oven in air for about eight hours. The catalyst particles had to be ground at the end of the oxidation because of particle agglomeration. This indicated that the wax in the extracted catalyst might have been overheated the catalyst during the oxidation. The oxidized catalyst was then tested to determine its activity at the same baseline test conditions. The catalyst showed only 0.29 normalized CO conversion during the catalyst activation, and the CO_2 and CH_4 selectivities were 90% and 2.5%, respectively. The data indicated that the catalyst may have been sintered due to very high oxidation temperatures, possibly on the surface of the catalyst because of the wax remaining in the catalyst. The test was terminated without changing to operating conditions since activity was low during the activation condition.

Oxidation experiments were continued by using the THF extracted RI59 catalyst because there was more of it available. First oxidation tests for the THF extracted RI59 were performed in a vertical tubular reactor, 12.7 mm (½ in.) diameter by 432 mm (17 in.) high. The catalyst was mixed with glass beads to prevent overheating during oxidation, and placed between the supports, glass fibers, at the inlet and exit lines. The oxidizing gas of 0.342 $m^3 \cdot h^{-1} kg\ cat^{-1}$ (18% O_2 in N_2 by volume) were passed through the catalyst bed at 473 to 573 K (200 to 300ºC) for sufficient time to oxidize the catalyst.

The oxidized RI59 catalyst was tested in an autoclave to determine its activity. After activation, the oxidized RI59 was tested with a feed H_2:CO ratio of 0.77 and a normalized space velocity of 1.05. The normalized CO conversion was only 0.35, alpha was 0.79, CO_2 and CH_4 selectivities were 25-30% and 3%. Very low activity of RI59 catalyst indicates that catalyst was sintered. This is probably due to high oxidation temperature and high oxygen flow rate.

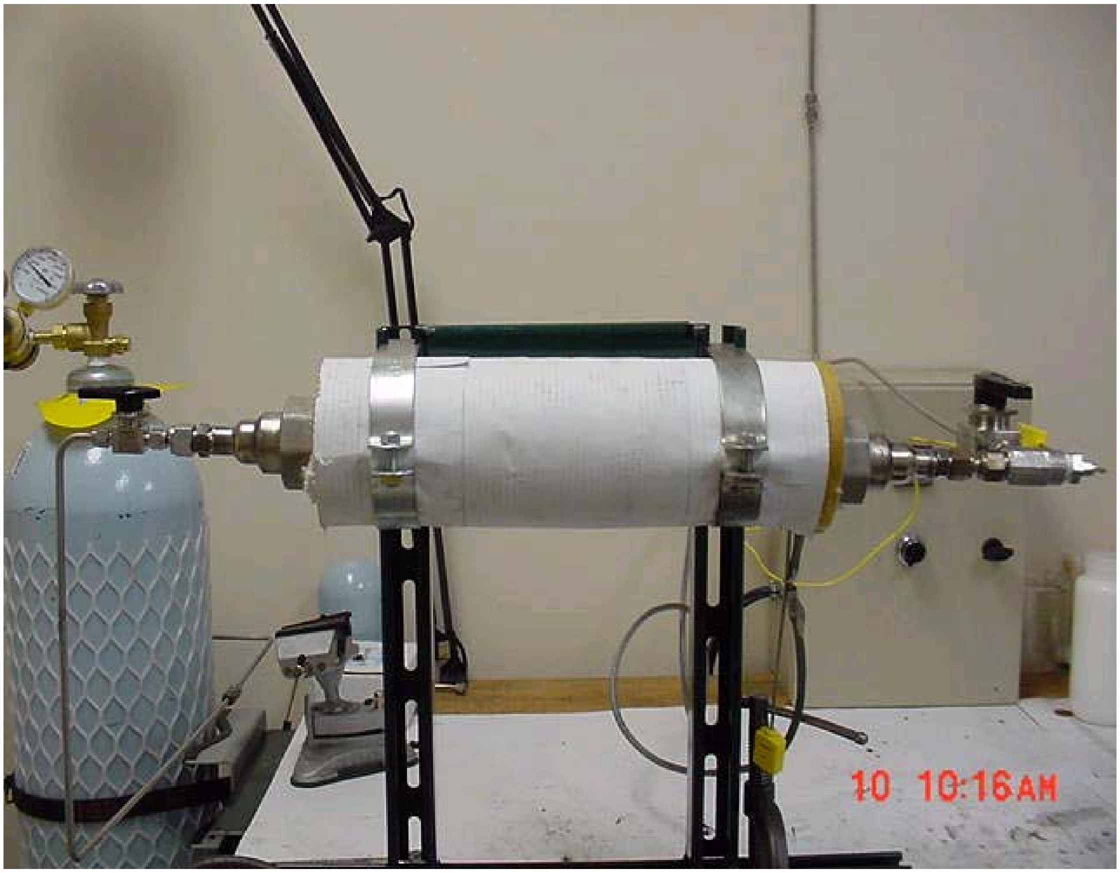


Figure VIII.C.1-2 Oxidation Reactor

The vertical tubular reactor for oxidation was problematic for this operation due to pressure drop across the catalyst bed, and sample loss from each oxidation. A new horizontal oxidation reactor was built with the dimensions of 25.4 mm (1 in.) diameter by 432 mm (17 in.) long, (see Figure VIII.C.1-2). A weighed amount of RI59 catalyst was put in a porcelain boat and placed into the reactor. Temperature was slowly increased to 473 K (200ºC), and the oxidation gas (2% O_2 in N_2 by volume) flow was started at a rate that would oxidize the catalyst in 24 hours, which was typically 1.41 $m^3 \cdot h^{-1} kg\ cat^{-1}$. The reactor was cooled to 293 K (20ºC) to check if the oxidation was complete. The catalyst was not completely oxidized after 24 hours, because it had black particles from iron carbide. This material was put back to the oxidation reactor, and heated up to 493 K (220ºC), and kept there until the color was red. At the end of this process, the catalyst was completely oxidized. The optimum oxidation condition was determined to be 493 K (220ºC) and 1.41 $m^3 \cdot h^{-1} kg\ cat^{-1}$ using 2% O_2 in N_2. The RI56, LP18, and LP19 were oxidized in the same manner. The RI56 and RI59 catalysts were impregnated with potassium carbonate to improve their performance, discussed in the next section. The oxidized catalysts were tested in an autoclave to determine their activity, and the results from these tests are discussed in the next section.

Activity Tests for Oxidized Catalysts

A number of tests were performed for the oxidized catalysts to select an activation procedure. Each oxidized catalyst was then tested in an autoclave to determine its performance. Activation and reaction conditions for the tests are listed below. The results are summarized in Table VIII.C.1-3.

Table VIII.C.1-3. Test results for regenerated catalysts.

	H_2:CO	Normalized Space Vel.	Normalize CO Conv.	Alpha
RI59[1]	0.77	1.05	0.35	0.790
RI59O	0.77	1.05	1.23	0.820
RI59OK[2]	0.77	1.05	1.83	0.763
RI56O[2]	0.77	1.05	1.82	0.705
	1.4		1.79	0.619
RI56OK[2]	0.77	1.05	1.59	0.809
LP18O[2]	0.77	1.05	1.85	0.749
			1.81	0.734
LP19O[2]	0.77	1.05	1.72	0.754

[1] Oxidized at 573 K

[2] Subsequent test revealed that actual reactor temperature was greater than the set reaction temperature. High temperature can elevate the CO conversion and reduce the Alpha.

RI59 oxidized slowly (RI59O) showed higher activity, and the normalized CO conversion increased to 1.23 and alpha to 0.82. The CO_2 and CH_4 selectivities obtained are 43.8 and 1.8%. The alpha was 0.846 when the original run was shut-down whereas it was 0.709 in the baseline test. Potassium is known as a chain growth promoter, and it is thought that potassium may have been washed out during the extraction process or it is also possible that potassium might have come out of the catalyst during F-T synthesis reaction. In addition, the catalyst may have been contaminated during the regeneration process. Considering all the possibilities, catalyst samples after oxidation and a wax sample, free of catalyst, were sent out for analysis by x-ray fluorescence (XRF) technique. The results showed that some potassium came off the catalyst and went into wax.

The RI59O was impregnated with potassium carbonate (K_2CO_3) (RI59OK), and tested in the autoclave to determine its activity. The normalized CO conversion increased to 1.83, and alpha was 0.763, which is higher than that from the baseline test but lower that that from the original run. The CO_2 and CH_4 selectivities were 42.9% and 3.2%.

The slowly oxidized RI56 (RI56O) was also tested in the autoclave and normalized CO conversion of about 1.82 and alpha of 0.705 were obtained at the H_2:CO ratio of 0.77. The CO_2 and CH_4 selectivities were 41.1% and 8.5%, respectively. The normalized CO conversion and alpha were 1.79 and 0.619 when the H_2:CO ratio was changed to 1.4. The alpha for this test was lower at both H_2:CO ratios than that for the baseline test. The XRF analysis revealed that the oxidized catalyst had very little potassium remaining. The RI56O was impregnated with potassium and tested in the autoclave. The potassium impregnated RI56 (RI56OK) gave a normalized CO conversion of 1.78 and alpha of 0.809. The CO_2 selectivity was 43.2% and the CH_4 selectivity decreased to 2.1%. The RI56OK gave better alpha when impregnated with potassium albeit those at the original and baseline tests were higher, 0.831 and 0.850 respectively. Further tests are necessary to explain why alpha is lower than that of the original test.

The oxidized LP18 catalyst (LP18O) gave a normalized CO conversion of 1.85, alpha of 0.749, CO_2 selectivity of 43% and CH_4 selectivity of 4.0%. The CO conversion decreased slightly to 1.8 and the alpha decreased to 0.734 when the operating pressure was dropped to the original operating pressure for testing LP18. The LP18O was not impregnated and tested due to an insufficient amount of this catalyst.

The oxidized LP19 was tested in the autoclave, and the normalized CO conversion was 1.72 times the standard baseline conversion and the alpha, CO_2 and CH_4 selectivities were 0.754, 43.4% and 3.4%, respectively. LP19O was not further evaluated due to an insufficient amount.

Conclusion

The four selected "degenerated" catalysts, LP18, LP19, RI56 and RI59, were tested for baseline activity and very low conversions were obtained. Wax from each catalyst was removed by solvent extraction using THF at 353-373 K (176-212°F) and hexane at supercritical hexane extraction conditions. Almost all of the wax was removed from the catalysts using multiple batch extractions. In a commercial process, continuous extraction would be used. The extracted catalysts were oxidized in an oxidation reactor at 493 K (428°F) and a rate of 1.41 $m^3 \cdot h^{-1} kg\ cat^{-1}$ using 2% O_2 in N_2 by volume. The oxidized catalysts tested in an autoclave showed significant improvements. The CO conversion reached 1.83 times the baseline conversion value and the chain growth, i.e. alpha, was lower than that in the baseline tests. However, it was found that the high CO conversions and low alphas were due mainly to higher actual temperatures than desired set-point temperatures. The low alpha was attributed to high temperature and potassium loss during extraction, and possibly during F-T synthesis reaction. Addition of potassium to two of the catalysts after oxidation improved alpha significantly.

2. Catalyst Regeneration

Introduction

In addition to the catalyst rejuvenation tests, a second set of regenerative treatments was carried out on the four batches of deactivated catalyst using stripping with N_2 or H_2 at elevated temperatures. The strategy here was to explore regeneration treatments that could be carried out in-situ in the F-T synthesis reactor on-line, on working catalysts. Four treatments were individually tested on each of the deactivated catalysts: i.) a baseline treatment—wherein the catalyst was heated up in N_2 to 528K (255ºC) at a pressure of 205 kPa (15 psig), then pressured up to 415 psig and exposed to syngas; ii) N_2 stripping treatment—wherein the catalyst was heated to temperature under a nitrogen purge in the continuous stirred tank reactors (CSTR) reactor and held at temperature, 528K (255ºC), for 1 hour under a nitrogen purge prior to syngas exposure, and iii & iv) 1 and 3 hour H_2 reductions – wherein the deactivated catalysts were heated up to 528K (255ºC) in H_2 at 1032 kPa (135 psig) for 1 and 3 hours respectively and then re-activated with syngas. Treated catalysts were then tested for 48 hours at H_2:CO of 0.76 and a syngas rate of 2.08 standard liters per hour (slph).

The four deactivated catalysts were treated under the conditions described above and then tested under the standard F-T conditions to determine whether increases in CO conversion could be affected – particularly to determine if a stable catalyst was reactivated without changes in alpha. Data from N_2 and H_2 activation were compared to the baseline treatments. It was found that N_2 stripping, in some cases, improved catalyst activity as evidenced by elevated CO conversion rates. The H_2 reductive treatments did not enhance catalyst activity at all. The overall result from this part of the study is that in-situ treatments may not be effective in F-T catalyst regeneration. It should be noted, however, that literature work suggests that activation under H_2:CO and or CO atmospheres, under reaction temperature and pressure conditions may hold some promise for reactivation of precipitated iron, F-T catalysts. As a consequence, in-situ treatments other than those attempted here might be useful in iron F-T catalyst regeneration.

Experimental

Catalyst Preparation and Reactor Testing: Samples of each of the four catalysts (RI56, RI59, LP18, and LP19) were subjected to in-situ regenerative treatments in CSTR. The catalyst/wax samples were mixed with Durasyn 164 oil to prepare a slurry. Each catalyst as removed from the BCR was made fluid by mixing with the lighter weight oil. Originally the catalyst was received as a catalyst/wax solid. This was their form after removal and cooling from the BCR. Figures VIII.C.2-1 and VIII.C.2-2 are photos of two of the representative iron based catalysts. After suspension, these materials were loaded into 300-cubic-centimeter (cc) CSTR's and tested under each of the four regeneration conditions. The catalyst/Durasyn 164 slurry was added to a CSTR at elevated temperature of 373K (100ºC) in order to insure that the reactor stirrers and thermocouples had freedom of movement and remained undamaged.

Figure VIII.C.2-1. Hydrocarbon (Durasyn)/Used Catalyst; Feed Mix – RI59.

Figure VIII.C.2-2. Hard Wax – used catalyst wax mixture as received, prior to suspension or regeneration – LP18

After sealing in the CSTR's, the loaded samples were pressure tested under nitrogen and H_2 and then subjected to one of the four pretreatment conditions shown below:

A. BASELINE TREATMENT
  - Heat up in nitrogen at 205 kPa (15 psig) with a flowrate of 0.036 standard cubic meters per hour (sm^3/h) for 2-3 hours
  - Switch to syngas (H_2:CO ratio 0.76) at a flowrate of 0.125 sm^3/h at reaction temperature of 528K (255ºC)
  - Pressure up to 2960 kPa (415 psig) and run for 48 hours
  - Stirrer speed at 1800 rotation per minute (rpms)

B. NITROGEN STIPPING
  - Heat up in nitrogen at 205 kPa (15 psig) with a flowrate of 0.36 sm^3/h for 2-3 hours
  - Strip with nitrogen a flowrate of 0.036 sm^3/h at reaction temperature of 528K (255ºC) for 1 hour
  - Cut in Syngas (H_2:CO ratio 0.76) at a flowrate of 0.125 sm^3/h and pressure up to 2960 kPa (415 psig) and run for 48 hours.
  - Stirrer speed at 1800 rpms

C. HYDROGEN REDUCTION – 1 HOUR
  - Heat up in H_2 at 1030 kPa (135 psig) at a flowrate of 0.036 sm^3/h for 2-3 hours up to 528 K (255ºC)
  - Reduce for **one** hour with H_2 at 0.036 sm^3/h
  - Reactivate Catalyst
  - Run with syngas with a H2:CO ratio: 0.76 At a temperature of 528K (255ºC) and pressure of 2960 kPa (415 psig) and run for 48 hours
  - Maintain stirrer speed at 1800 rpms

D. HYDROGEN REDUCITON – 3 HOURS
  - Heat up in H_2 at 1030 kPa (135 psig) at a flowrate of 0.036 sm^3/h for 2-3 hours up to 528K (255ºC)
  - Reduce for **three** hours with H_2 at 0.036 sm^3/h
  - Reactivate Catalyst
  - Normal startup procedure (as indicated above in C) run for 48 hours
  - Maintain stirrer speed at 1800 rpms

Product slates were analyzed throughout the test periods and activity was measured primarily as CO conversion as a function of time (both syngas and H_2 conversions were tracked similarly to this).

Results and Discussion

The conditions used here to treat catalysts RI56, RI59, LP18, and LP19 were strategically focused on effecting wax removal and reactivating surface active sites on the iron. These regenerative treatments were all performed inside of the CSTR. The baseline treatment was used to bring each of the used catalysts up to the activity level (CO or syngas conversion) observed at the end of their original usage. This was necessary as exposure conditions varied between the materials when they were removed from the original reactor. As in the Catalyst Rejuvenation section, the CO conversions are presented as a normalized CO conversion to the standard baseline CO conversion.

The nitrogen stripping treatment was aimed at removing heavy wax from the surface of the iron particles. Wax deposition is one of the potential deactivating mechanisms that can occur on iron based F-T catalysts during the synthesis reaction. Some of the high molecular weight wax might cover the active iron sites and prevent carbide formation.

The H_2 treatments were aimed at restoring the iron surface to its original oxidation state. This would be particularly necessary if the surface were to be oxidized or changed in some fashion through the production of water and/or oxygenates during the F-T reaction. Like wax deposition, changes in the iron oxidation state is another potential deactivation mechanism.

After baseline treatment, the normalized CO conversions were variable among the four samples ranging from 0.38 to 1.35 (Figures VIII.C.2-3 to VIII.C.2-6). After 24 hours on stream all samples showed conversions of between 0.38 and 0.77 the activity of LP18 had degraded significantly after an initially higher value of 1.33 normalized CO conversion. These CO conversion values are somewhat similar to those obtained at the end of each original reactor test (Table VIII.C.1-1). This data shows clearly that the catalysts had lost a significant amount of activity during these original reactor testing.

The nitrogen stripping treatment was the only treatment that resulted in an increase in activity in sample LP19. The 0.77 to 0.96 normalized CO conversions observed in baseline operation increased to 1.35 to 1.54. The other three samples showed no significant improvement in activity. H_2 reductions at 1 and 3 hours were carried out for samples RI56 and RI59; reductions at 1 hour only were carried out on samples LP18 and LP19 due to sample size limitations. None of the H_2 reductions improved the catalyst activity. In each of the treated catalysts the F-T reactions showed similar CH_4 selectivity and alpha values that were within a close range to experimental values obtained in the baseline samples.

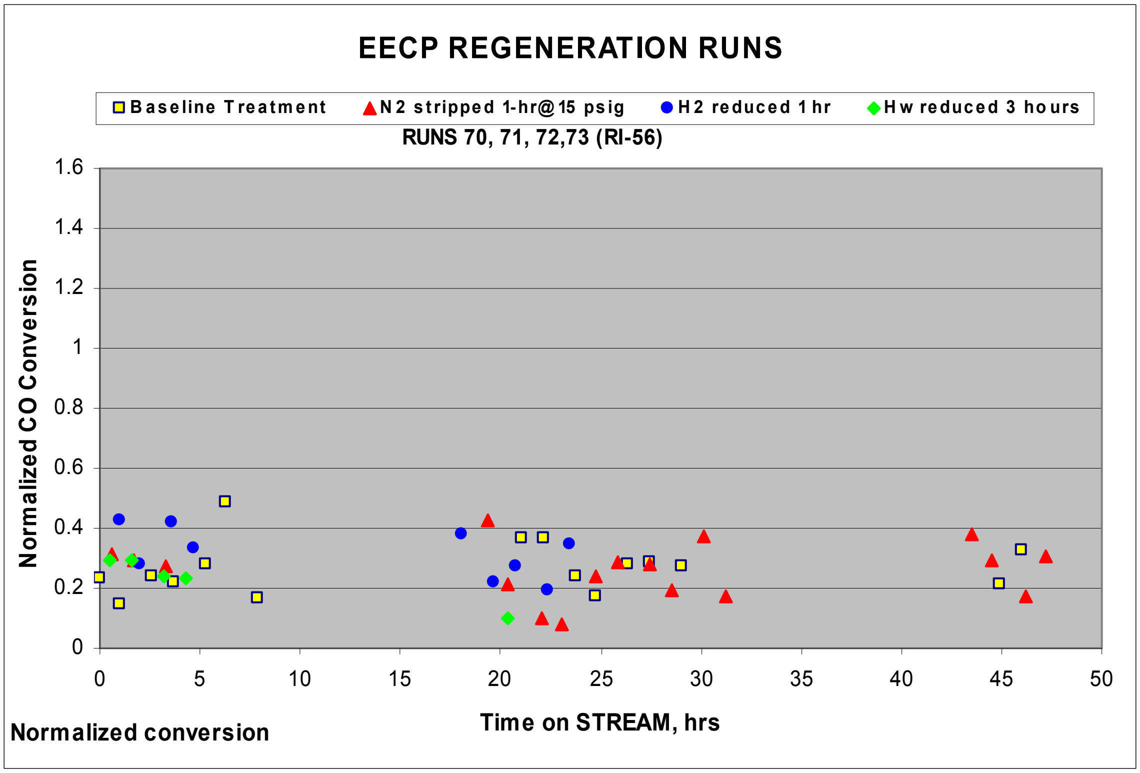


Figure VIII.C.2-3 Regeneration results for the RI56 used iron catalyst.

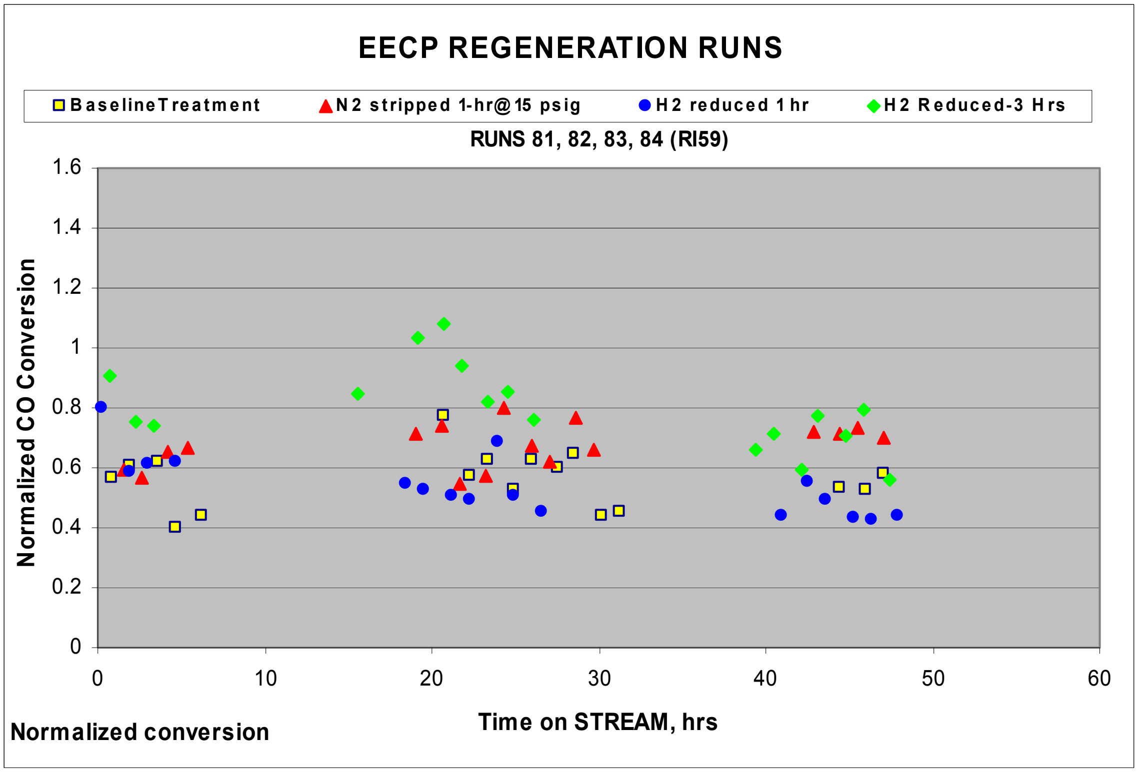


Figure VIII.C.2-4 CO conversion showing the results of regeneration of the RI59 used catalyst.

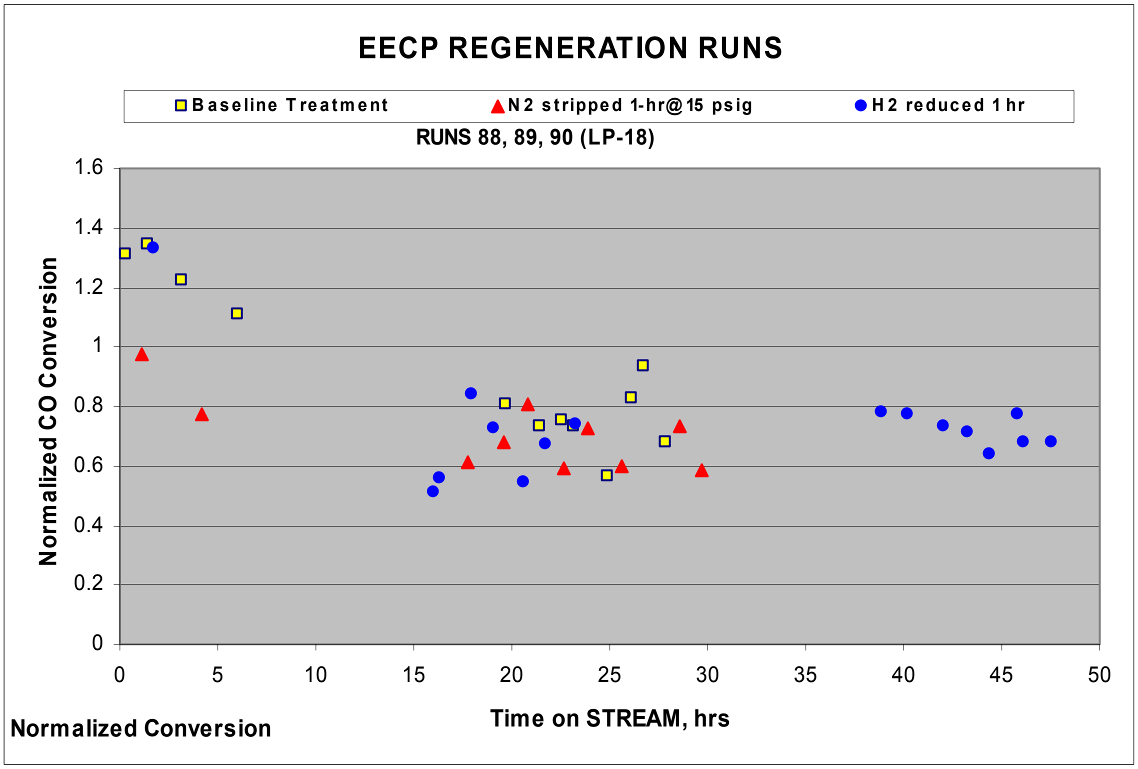


Figure VIII.C.2-5 Regeneration results for the LP18 used iron catalyst.

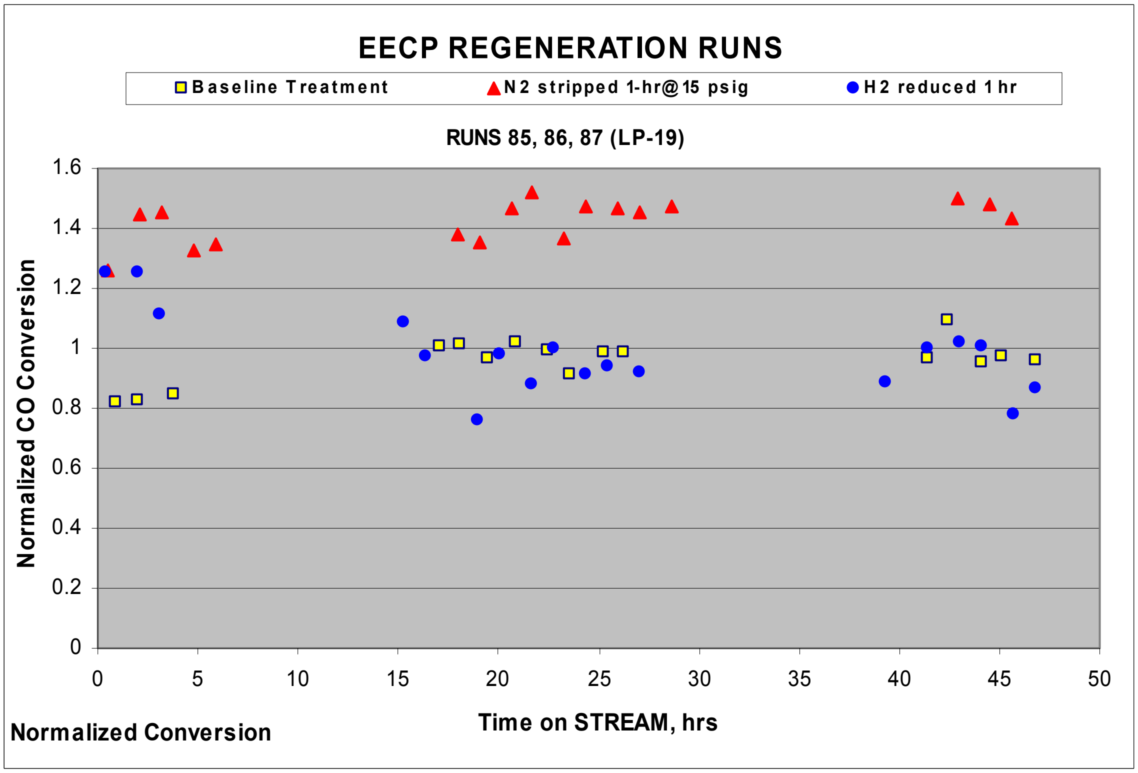


Figure VIII.C.2-6 CO conversion results after regeneration of the used LP19 precipitated iron catalyst.

Conclusions

The four selected catalysts were subjected to a series of regeneration treatments in order to determine the difficulty of regenerating these catalysts on-line, during the processing of synthesis gas. Samples were subjected to baseline, nitrogen stripping, and H_2 reduction treatments. The nitrogen stripping was found to be effective in one case, and the H_2 reductions were found to be ineffective. It is likely that the nitrogen stripping results in wax removal from the catalyst surface, but the H_2 treatment does not result in regeneration of the active sites. Literature results indicate that the H_2 reductions may have been too harsh for effective regeneration of these catalysts. Further investigations might utilize nitrogen stripping followed by CO or syngas regeneration.

3. Catalyst Withdrawal & Addition

Introduction

Operation of a commercial F-T reactor will require periodic on-line catalyst withdrawal and addition. This is necessary to replace the catalyst lost with the produced wax and to maintain reactor productivity as the catalyst deactivates. If the rate of catalyst deactivation is low enough, catalyst that is added to the reactor to replace catalyst lost with wax production will be sufficient to maintain reactor productivity. In this case it will only be necessary to add catalyst, not remove it. If catalyst deactivation rate is greater than the catalyst lost with wax production, it will be necessary to add and remove catalyst. Since the catalyst deactivation rate has not yet been quantified, it is necessary to demonstrate both on-line catalyst withdrawal and addition in case both capabilities are needed for the commercial reactor.

Objective of the Testing

The first objective of the test to demonstrate that catalyst can be added to and removed from the BCR at operating conditions in a safe and controlled manner. The second objective is to determine if catalyst activity can be maintained after withdrawal of spent catalyst by on-line addition of previously activated catalyst. The third objective is to evaluate if fresh unactivated catalyst can be activated by synthesis gas at reactor conditions.

Experimental

Testing was conducted in the Rentech pilot-scale BCR located at the Rentech research and development (R&D) facilities in Denver, Colorado. Special equipment was designed, fabricated, and installed to allow the catalyst withdrawal and addition functions required for the test. Figures VIII.C.3-1 through VIII.C.3-4 show the piping and instrumentation diagrams for both the withdrawal and addition units as well as photographs of the installed hardware.

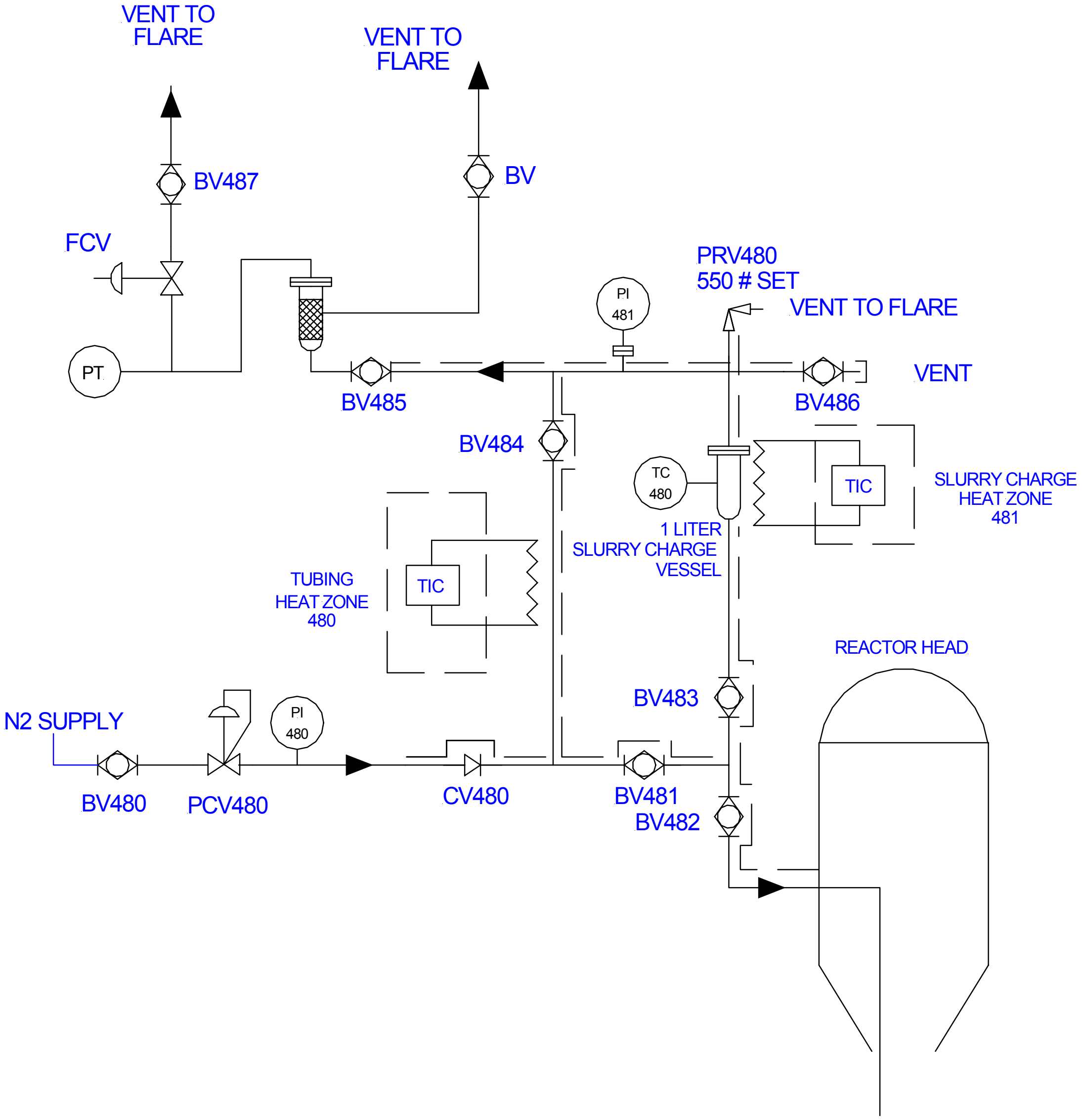


Figure VIII.C.3-1. Piping and Instrumentation Diagram, Catalyst Addition System

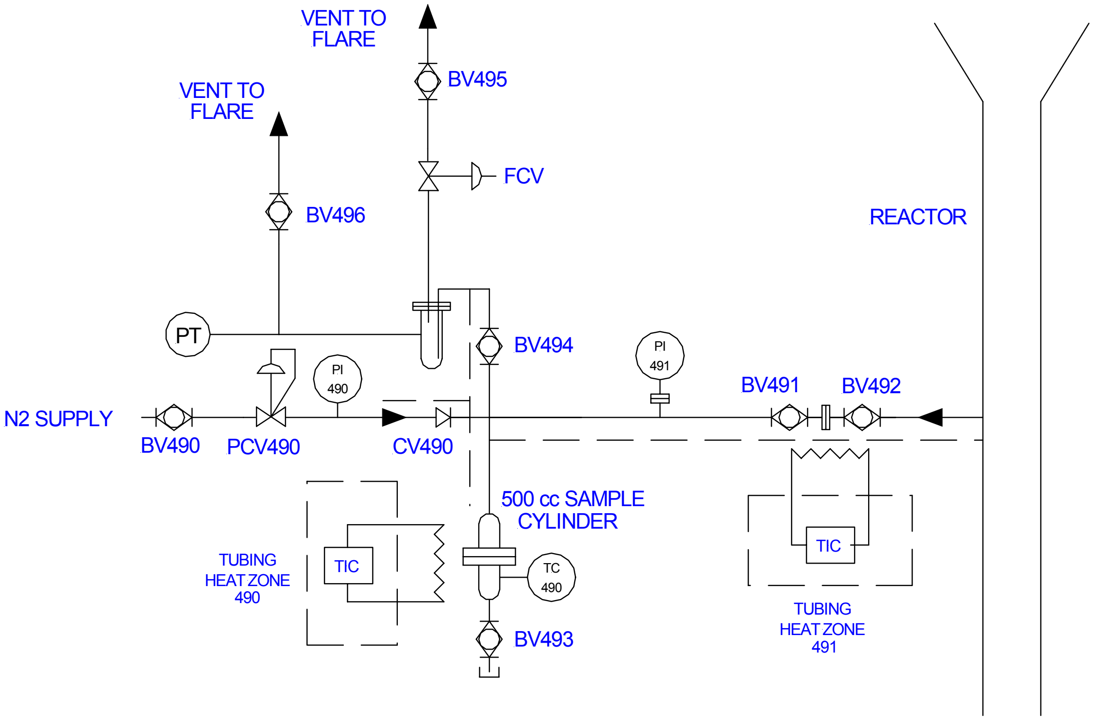


Figure VIII.C.3-2. **Piping and Instrumentation Diagram, Catalyst Withdrawal System**

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Figure VIII.C.3-3. **Catalyst Addition System Hardware before Insulation**

Figure VIII.C.3-4. Catalyst Withdrawal System before Insulation

A batch of catalyst was activated in the BCR. This was used as the fresh activated catalyst for the catalyst addition operations. After the batch was activated it was purged with nitrogen and removed from the reactor. The batch was then segregated into several samples of uniform concentration solids by weight suitable for charging to the 1 liter slurry charge vessel for the catalyst addition tests.

Next, another batch of catalyst was activated in the same way as the first and then operated under the design basis conditions.

The BCR level was maintained by periodically removing wax through the primary wax/catalyst separation device, i.e. the normal method of maintaining reactor level. The removed slurry was assayed to determine the mass of catalyst removed.

After 1.5 days on stream (DOS) the reactor had reached steady operation and the first slurry withdrawal was conducted. This slurry was assayed to determine how much catalyst had been withdrawn. Twenty-four hours later, an equal mass of catalyst taken from the first catalyst activation step was added to the reactor. This cycle of withdrawal and addition was repeated 4 times.

Finally, an amount of oxide (unactivated) catalyst was added to the reactor and the behavior of the reactor was followed for an additional 24 hours.

Results and Discussion

Table VIII.C.3-1 gives the timing of the withdrawal and additions at each step. Figure VIII.C.3-5 shows the results of the entire test. The magenta trace shows the reactor catalyst loading as a fraction of the initial charge. This is calculated from the initial reactor loading minus the estimated quantity of catalyst in the primary separator loop, minus any catalyst removed from the primary separator, minus the catalyst removed by the withdrawal steps, plus catalyst added by the addition steps. This line has a slow downward trend due to the nearly continuous removal of catalyst from the primary separator and steps corresponding to the withdrawal and addition steps.

The blue line in figure VIII.C.3-5 shows the CO conversion normalized to the initial conversion. The CO conversion decreases rapidly just after activation is completed and the then quickly stabilizes. The reactor was operated for 1.5 days to allow it to stabilize. The conversion leveled off around 65% of the initial CO conversion value just before the first withdrawal at 1.54 DOS.

The first step down at 1.5 DOS is the first catalyst withdrawal. Subsequent withdrawals and additions can be seen as the steps up and down, respectively.

Table VIII.C.3-2 Summary of Catalyst Withdrawal and addition Steps

	time (DOS)
withdrawal #1	1.5
addition #1	2.5
withdrawal #2	3.3
addition #2	4.4
withdrawal #3	5.3
addition #3	6.4
withdrawal #4	7.3
addition #4	8.4
oxide addition	9.4

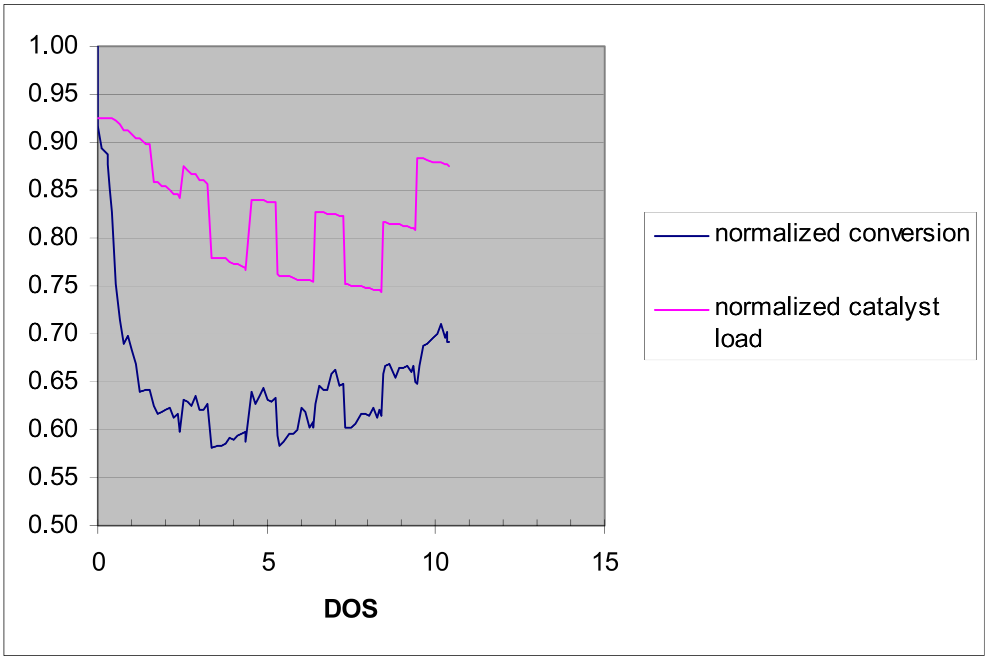

Figure VIII.C.3-5 Performance Trends

After the first withdrawal, conversion decreased. The first addition at 2.5 DOS brought the conversion almost all the way back to the value before the removal. Note that the mass of catalyst involved in the first withdrawal and addition were about half of the others. After seeing the noticeable but relatively small reactor response to the first withdrawal and addition we decided to double the quantity to be withdrawn and added in subsequent steps to make the response more obvious.

Catalyst addition steps were preceded by a fairly large removal of reactor wax via the primary separator in order to make room in the reactor for the wax/catalyst to be added in the addition step. Since these wax removals contained small amounts of catalyst, a small down step in the conversion is seen just before each addition. The size of each of these down steps decreases with each addition because the wax removed from the primary separator becomes cleaner during the run so the impact on the removal just before the addition is less each time.

In order to determine how this removal affected the reactor independent of the effect of an addition step immediately following, at 5.79 DOS, 759 grams of wax was removed at a rate of 30 grams a minute (g/min) from the primary wax/catalyst separation unit. CO conversion increased for a short time around 6.0 DOS and then returned to the original trend value. It is estimated that the 759 grams of wax contained about half the amount catalyst in the first withdrawal, therefore a change about half of that from the first withdrawal is expected. In addition to appearing that the CO conversion increased rather than decreased, the size of the change is larger than that for the first removal. Thus, it seems reasonable that the brief excursion in conversion was not related to the removal of 759 grams of wax from the primary separator and that the removal did not impact the reactor at all.

The next withdrawal (3.3 DOS) decreased the normalized conversion to about 58% and the corresponding addition (4.2 DOS) increased it back to about 63%. Subsequent withdrawals and additions continued to decrease the conversion and then increase the conversion by about 5 percentage points.

After 5.2 DOS there is a general upward trend in the conversion, separate from the sudden changes due to the withdrawals and additions. It is believed that this upward trend may be due to the relatively large fraction of fresh catalyst that had been added to the reactor at that time, and the fact that freshly activated catalyst requires several days of operation to become fully active.

Twenty-four hours after the last addition of active catalyst, the normalized conversion appears to have stabilized at 66%. At this point an addition of oxide (unactivated) catalyst was made. In the following 24 hour period the normalized conversion increased by about 5 percentage points just as it had with each addition of active catalyst, although much more slowly. From this one could conclude that the addition of oxide catalyst to an operating reactor may increase reactor activity over about a 24-hour period. It remains to be seen how long the conversion stays at this increased level. The last few measurements seen in the graph show a continuous decline in conversion.

Other critical reactor operating parameters seem to change little with the catalyst withdrawal and addition. Methane productivity exhibited little response to the withdrawal and addition. This seems reasonable as the quantity of catalyst in the reactor should not affect the chain growth or water gas shift activity.

Mass balance reports are not presented in this report. Typically a BCR run is allowed to reach steady operation and then mass balance reports are produced for two or more 24-hour periods during which no operating conditions are changed and no significant upsets occur. Obviously, in the present test significant changes were made to the reactor catalyst loading. These changes were made at the beginning or end of each 24-hour mass balance period but the mass balance period clearly includes a transient period during which the reactor adjusts to the new catalyst loading. Figure VIII.C.3-5 shows that the conversion adjusts within 6 hours but changes in the collected hydrocarbon production rate and characteristics may be slower. For this reason the mass balance reports were not included.

Figure VIII.C.3-6 extracts critical information from the mass balance reports and shows trends.

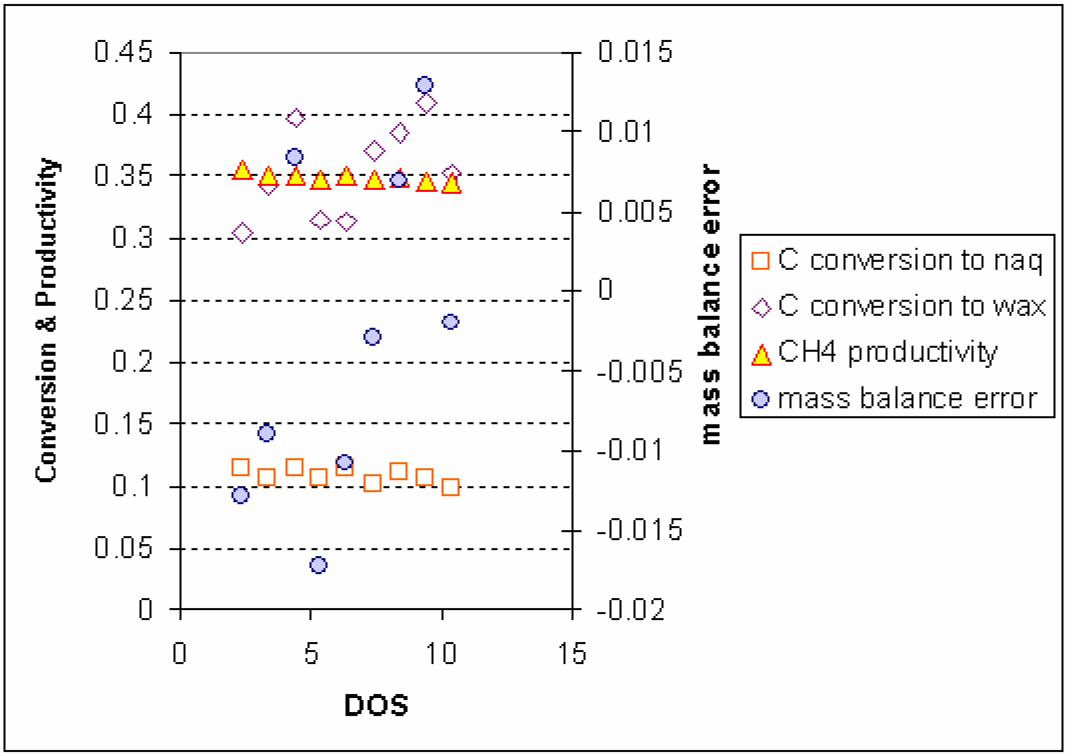

Figure VIII.C.3-6. Mass Balance Data

Mass balance errors are quite small ranging from +1.25% to –1.75%. Typically most mass balance reports do not have positive mass balance errors. It is suspected that this is related to the previous discussion regarding the effect of the large wax removal/addition on the mass balances.

Data in Figure VIII.C.3-6 have a poor correlation with the withdrawal and addition steps. Only the carbon conversion to wax shows any significant change and this is due to the large quantities of wax that were manually removed from the reactor prior to the addition steps and that added with the addition steps. Previous tests have shown that the carbon conversion to wax is very consistent among mass balance periods as long as the wax removal from the primary separator is allowed to proceed within its normal reactor level control loop. Downward trends in the methane productivity and the collected non-aqueous condensate (naq) are consistent with one another and could reflect the addition of fresh catalyst to the reactor.

The results described above show clearly that ability to safely add and withdraw catalyst from the operating reactor which was the first objective of the test was demonstrated. All four withdrawals and five additions were accomplished without incident. In each operation, improvements were made to the operating procedure and suggestions were made on improvements to the hardware. What is less clear is whether this hardware can or should be scaled up for use with a larger reactor. Operations of the withdrawal and addition systems for this test were completely manual and required a great deal of labor to execute. Typically, the addition step required two people plus the normal control system operator for about 2 hours while the withdrawal step required 1 hour. Although the basic principles in Figures VIII.C.3-1 and VIII.C.3-2 are probably valid, considerable thought would need to go into scale-up.

The second objective of the test was to determine if catalyst activity can be maintained after withdrawal of spent catalyst by on-line addition of previously activated catalyst. In a commercial reactor decline in reactor activity will be due to catalyst aging as well as catalyst that is lost with wax removed by the primary wax/catalyst separator. In this test these two decline mechanisms were simulated by withdrawing catalyst from the reactor. Results described in this section show clearly the loss of activity after a withdrawal and a similar increase in activity after an equivalent quantity of activated catalyst is added to the reactor which strongly suggests that reactor activity can be maintained with this operation. A more difficult task is to determine the quantities of catalyst that need to be withdrawn and added to an operating reactor to maintain steady productivity and selectivity.

The third objective of the test was to add oxide catalyst (unactivated) to the operating reactor and determine whether that catalyst becomes active. Results presented in this section strongly suggest that, at least in the short-term, the catalyst does become active. It remains to be proven whether that activity is sustained.

Conclusion

These tests have shown that it is possible to safely add and withdraw catalyst from an operating reactor and that the reactor activity responds accordingly. This suggests that a commercial reactor could be operated at a steady-state productivity and selectivity using methods demonstrated in this test. Unactivated oxide catalyst added to the operating reactor appeared to become active.

4. F-T Confirmation Test

Objective of the Testing

The first objective of this activity was to determine whether a CO conversion target can be achieved at the proposed EECP design basis conditions. The second objective was to determine whether there are any negative effects of 5% volume CO_2 in the feed gas.

Experimental

Testing was conducted in the Rentech pilot-scale BCR located in Denver, Colorado.

The first objective was accomplished by adding activated catalyst during the test, gradually reducing space velocity to the design basis value, and then determining the CO conversion at that point. The reduction in space velocity was achieved by adding activated catalyst to the BCR using a catalyst addition system. Three batches of Rentech (RI) catalyst were activated. The first two batches were set aside and the third batch was used as the initial inventory for the initial test designated as RI74a. After lining out test RI74a for 3.5 days, catalyst from the first two activated batches was added once per day for 5 days according to the schedule in Table VIII.C.4-1

	time (DOS)
addition #1	3.54
addition #2	4.54
addition #3	5.51
addition #4	6.52
addition #5	7.51

Table VIII.C.4-1 Summary of Catalyst Additions

Sufficient reactor wax was removed via the Rentech Dynamic Settler prior to each addition to make room in the reactor for the total mass added for each addition.

After these additions were completed, CO_2 was introduced (RI74b) for two days to determine if the CO_2 would create any problems such as catalyst deactivation. RI74a conditions were then resumed for one day for further confirmation on performance after CO_2 exposure.

Finally, the test was conducted with an isothermal slurry temperature profile, RI74c, for 4 days. The purpose of that test period was to determine the conversion with operating conditions closer to that of a commercial reactor. Typical BCR operation involves a uniform temperature above the 6 feet level and lower temperatures below that. It has been observed that extended operation of the BCR with an isothermal temperature distribution can lead to rapid catalyst deactivation due to limited mixing in the small-diameter reactor. Since a commercial reactor will not have this limitation, RI74c was intended to get a more realistic estimate of CO conversion.

Results and Discussion

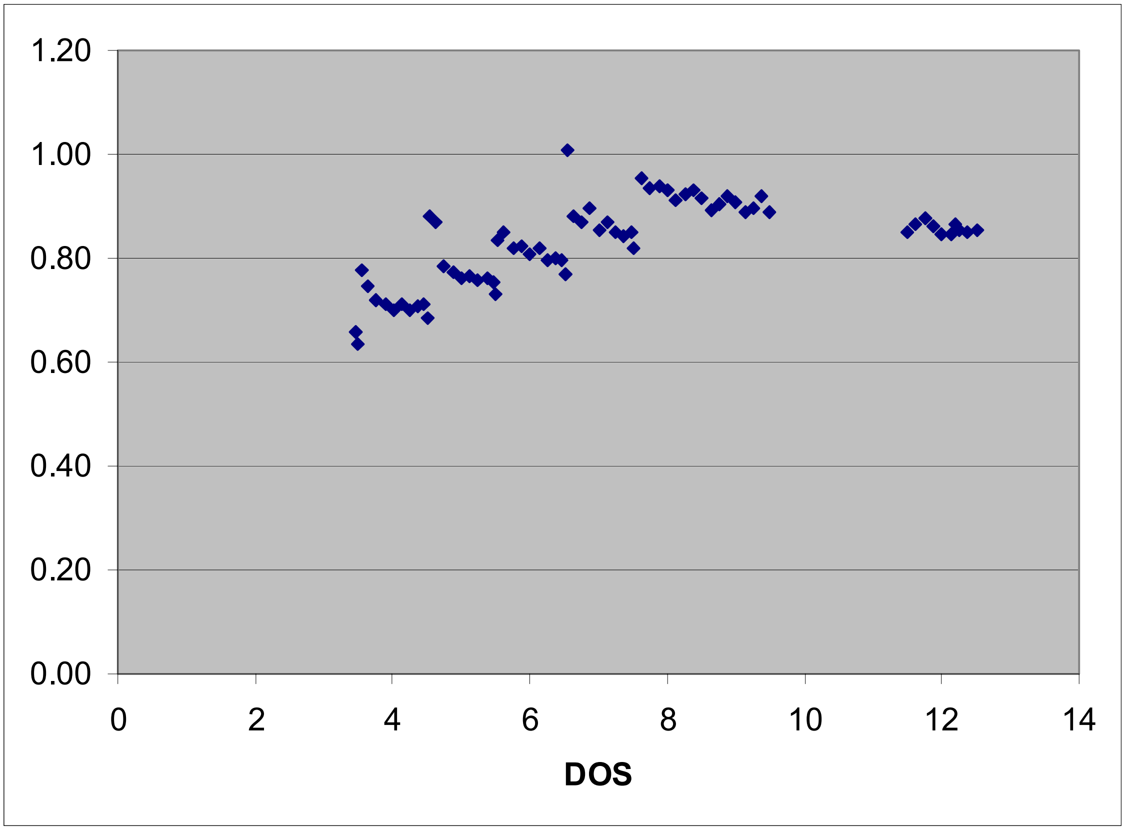

Figure VIII.C.4-1 Normalized CO Conversions for RI74a

Performance

Figure VIII.C.4-1 shows the CO conversions, normalized by the design basis values for both parts of RI74a. (The period from 9.5 to 11.5 DOS is RI74b). The times of the five catalyst additions can be seen on Figure VIIII.C.4-1 at the five discontinuities. The slight decrease in conversion just before each addition is due to the removal of about 1 kg wax (with some catalyst) to make room in the reactor for the subsequent addition. The CO conversion reached a maximum of 93% of the design basis value just after the fifth catalyst addition. There was a small increase in CO_2 productivity as the CO conversion increased.

Figure VIII.C.4-2 shows the performance plot for RI74b. Two days of operation with 5% by volume CO_2 in the feed gas showed no significant negative effect. The normalized CO conversion decreased by about 4 percentage points over the two-day run, a trend similar to RI74a at 9.5 DOS (before CO_2 was started).

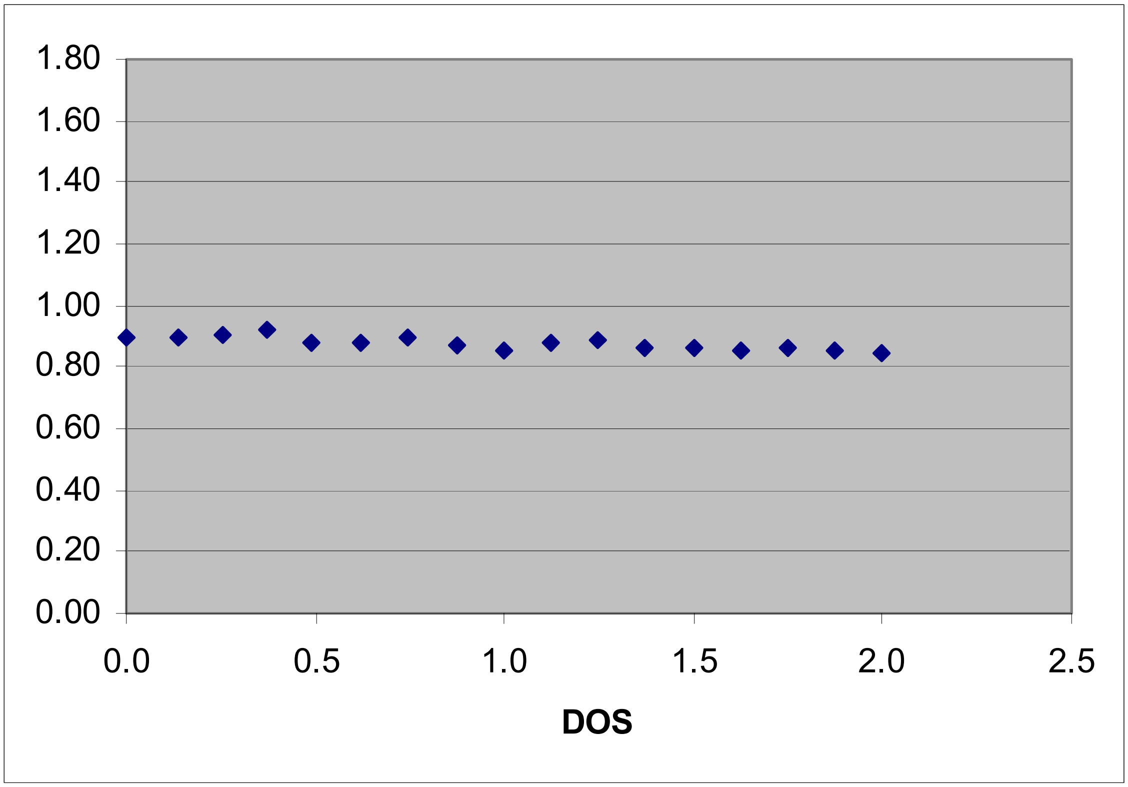

Figure VIII.C.4-2 Normalized CO Conversions for RI74b

Returning to Figure VIII.C.4-1, the last day of RI74a completed after RI74b, also shows no ill effect of the CO_2 present in RI74b. Trends established at 9.5 DOS in RI74a continue for the last day, 11.5 to 12.5 DOS. From this, it was concluded that two days of exposure of the catalyst to 5% volume CO_2 in the feed gas is not harmful.

Figure VI-3 shows the performance of RI74c. At zero DOS, the set points of the lowest three reactor heater zones were increased to make a uniform slurry temperature profile. The normalized CO conversion increased from 85% to about 97%. At about 0.4 DOS, a substantial drop in conversion was observed before operation was returned to the non-isothermal temperature profile. CO Conversion then began to recover and leveled out at about 83%.

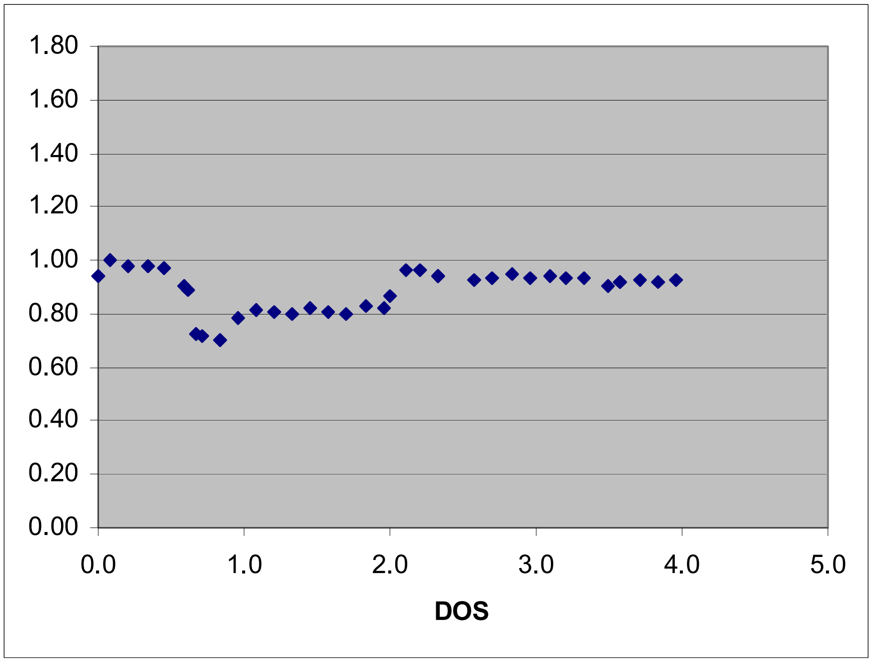

Figure VIII.C.4-3. Normalized CO Conversions for RI74c

At two DOS the uniform temperature profile was resumed. The normalized CO conversion increased from 83% to about 96% and CO_2 productivity increased slightly as well. The test period continued without problems until four DOS when the run was ended. At that point, the CO conversion was 93%.

The highest CO conversion measured was 97% of the design basis value. Space velocity at this conversion was 111% of the design basis value. It is expected that operation at the design basis space velocity will result in a CO conversion of at least the design basis value.

Productivity

Figure VIII.C.4-4 shows the production rate of collected products for the entire run. Collected non-aqueous condensate (naq) shows an increase as catalyst is added. Aqueous condensate (aq) production declines slightly during the test. Wax production is erratic because of the necessity of lowering reactor level before each addition.

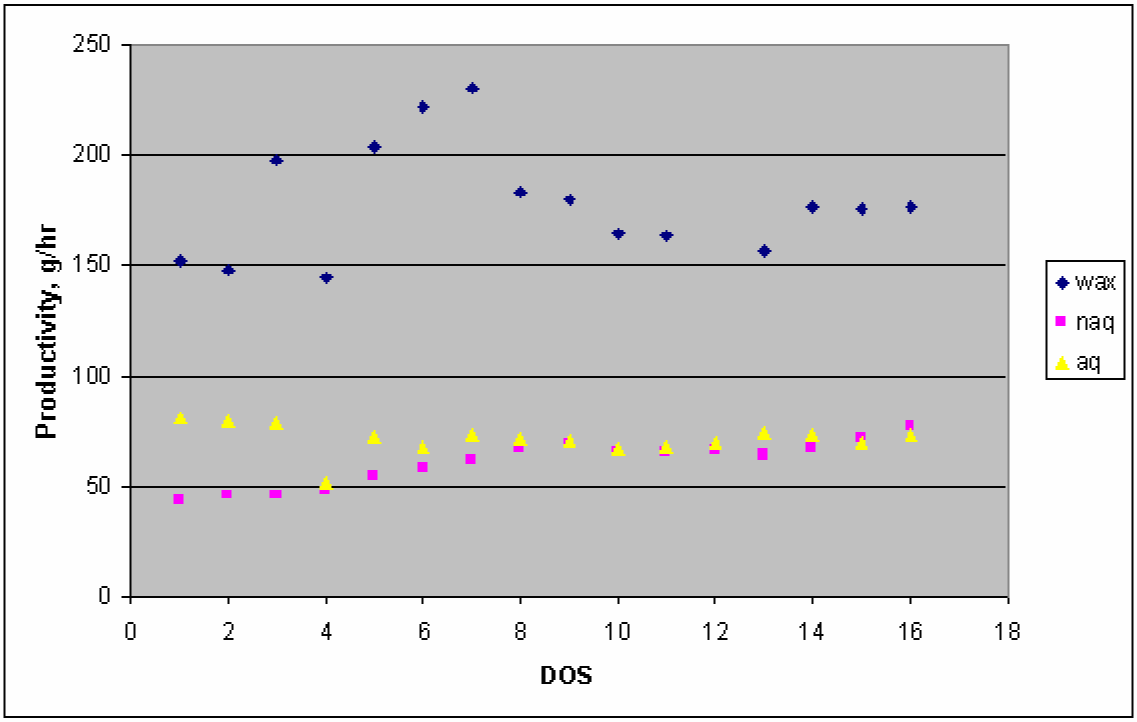

Figure VIII.C.4-4. Productivity of Collected Products

Mass Balance Reports

Due to the large wax removal just before each catalyst addition and because the system was not allowed to stabilize after the catalyst additions, the mass balance reports can not be expected to give very meaningful data. Figure VIII.C.4-5 shows the more important data extracted from the mass balance reports.

Most of the mass balance errors were in the –4% to –5% range. Two reports that were strongly impacted by the transient nature of the tests gave –8% errors. Methane productivity was very stable at 0.007 (moles of methane (CH_4) produced per mole of CO converted). Usage ratio (moles of hydrogen (H_2) converted per mole of CO converted) varied from 0.67 to 0.77. Carbon conversion to naq (moles of carbon in naq per mole of carbon in CO converted) started at 0.1 and increased slowly during the run to about 0.13. Carbon conversion to wax varied from 0.3 to 0.46 and is much more erratic than is typical.

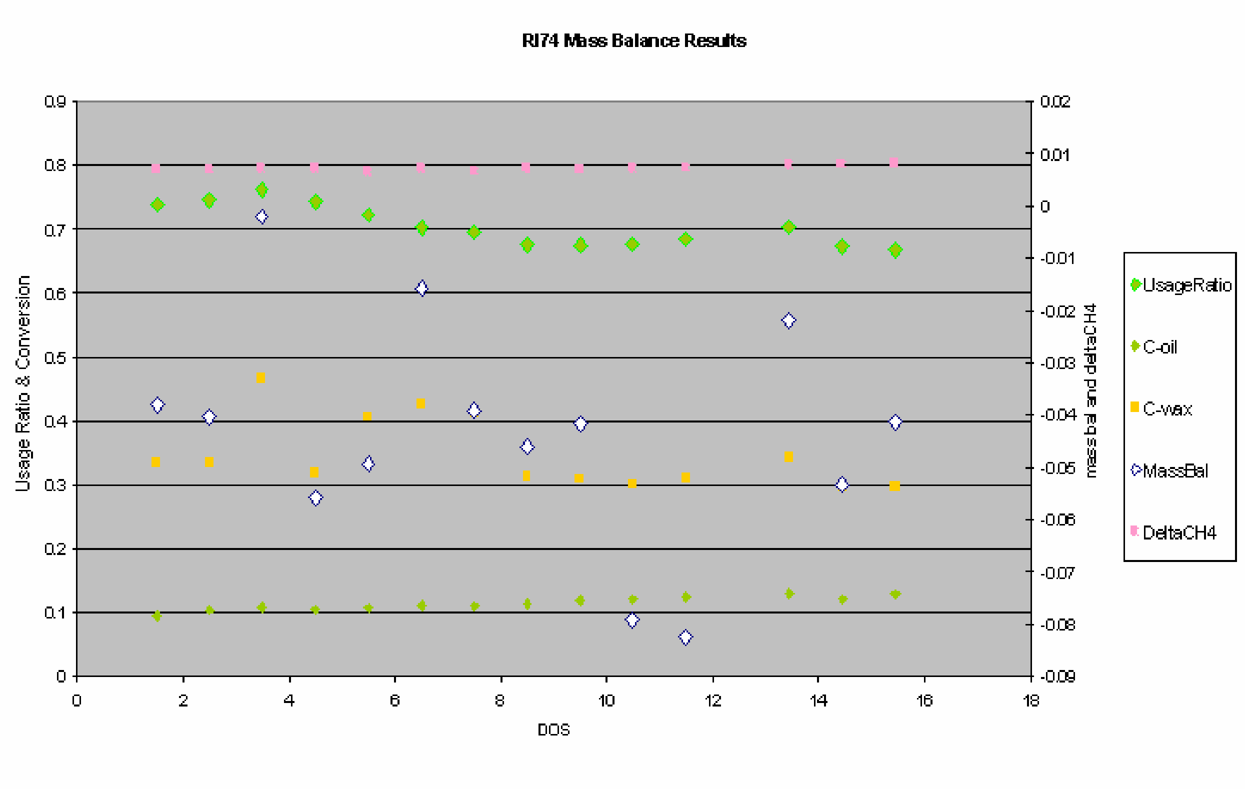

Figure VIII.C.4-5 Mass Balance Results

Conclusions

Catalyst additions resulted in an increase in CO conversion. The highest normalized CO conversion achieved was 97% at 111% of the design basis space velocity. Although it is not definitive proof, these results indicate that at the design space velocity, the desired CO conversion should be achievable.

The presence of 5 volume % CO_2 in the feed gas did not adversely affect the performance of the catalyst over a two-day period.

The main uncertainty in this test is the measurement errors associated with determining the reactor catalyst loading and the impact of that on the space velocity. A direct measure of reactor catalyst loading is not possible during a test. It is only possible to assay the reactor loading at the end of a test to determine the catalyst loading at that point. Even that measurement has associated errors. An additional uncertainty is that the target space velocity was not achieved, so it is necessary to extrapolate the CO conversion to determine its value at the target space velocity.

IX. List of Acronyms and Abbreviations

°C	degree(s) Celsius
AFDU	Alternative Fuels Development Unit
aq	aqueous condensate
BCR	Bubble Column Reactor
BV	ball valve
$C_{\#}$+	hydrocarbons with more than # (number of) carbons
cat	catalyst
cc	cubic centimeter(s)
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
C-oil	carbon conversion to non-aqueous condensate
conv.	conversion
CSTR	continuous stirred tank reactor
CV	control valve
C-wax	carbon conversion to wax
DOE	Department of Energy
DOS	day(s) on stream
EECP	Early Entrance Coproduction Plant
FCV	flow control valve
ft	feet
F-T	Fischer-Tropsch
GE	General Electric
gm	gram(s)
h	hour(s)
H_2	hydrogen
H_2S	hydrogen sulfide
hr(s)	hour(s)
in.	inch(es)
K	Kelvin
K_2CO_3	potassium carbonate
KBR	Kellog Brown and Root
kg	kilogram(s)
kPa	kilopascal(s)
LP	La Porte
m	meter(s)
min	minute(s)
mm	millimeter(s)
N_2	nitrogen
naq	non-aqueous condensate
O_2	oxygen
PI	pressure indicator
PRV	pressure relief valve
psi	pound(s) per square inch
psig	pound(s) per square inch gauge
RD&T	Research, Development and Testing
RI	Rentech, Inc.
rpms	rotations per minute
SCFE	supercritical fluid extraction
slph	standard liter per hour
sm3	standard cubic meter(s)
TES	Texaco Energy Systems
THF	tetrahydrofuran
TIC	temperature indicating controller
U.S.	United States
US	United States
vel.	velocity
XRF	X-ray fluorescence

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