Abstract

This report describes development studies on a two-stage slurry Fischer-Tropsch/ZSM-5 process for converting synthesis gas to high quality transportation fuels (gasoline and distillate). Successful gasoline-mode operation of a similar process was demonstrated under a previous DOE Contract (DE-AC22-80PC30022).

Three Fischer-Tropsch catalysts of $Fe/Cu/K_2CO_3$ type were evaluated for low methane + ethane (high reactor-wax) mode operation in eight separate runs. A total hydrocarbon production of 350 g/gFe was achieved, the only experimentally established number for this mode of operation. Various process studies were also performed including development of a continuous reactor-wax removal system and the testing of a new feed-gas distributor.

Bubble-column hydrodynamics were studied using two newly built tall, hot-flow columns. Data were acquired on gas holdup and bubble-flow patterns using sintered-metal-plate and orifice type feed-gas distributors. Actual reactor-waxes were used for the first time. Also the carbon-number distributions of the reactor-waxes were characterized up to C_{150} using the Field Ionization Mass Spectrometry.

Proprietary reactor-wax upgrading studies were carried out and are described in the Appendix-Restrictive Distribution of this report. Non-proprietary studies, including reactor-wax vacuum fractionation and thermal cracking of a Fischer-Tropsch reactor-wax vacuum bottom, were also carried out.

Finally, a conceptual process design and scoping cost estimate were developed. The design for the slurry Fischer-Tropsch and the ZSM-5 reactor sections is similar to that given in our previous DOE Contract. The design of the reactor-wax upgrading and product separation sections, as well as the scoping cost estimate are given in the Appendix-Restrictive Distribution

I. Objective and Scope of Work

The objective and scope of work given here are based on the original Statement of Work of the Contract.

The general objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H_2/CO ratio synthesis gas, of the type produced in a coal gasification system, into maximum yield of transportation fuels. To accomplish this objective, the following tasks will be undertaken.

Task 1 - Process Studies in Two-Stage Bench-Scale Unit

Operation of the bench-scale unit (BSU) will be directed toward production of hydrocarbons containing less than 8 wt % of methane plus ethane with high throughput, high conversion, and good catalyst stability. Together with Task 2, high quality liquid fuels, particularly the distillate, will be maximized. At least two tests shall be conducted using at least two different catalysts. Some of these catalysts may be provided by DOE's alternate energy development projects.

Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

Methods for upgrading reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated. These methods should include conventional refinery processes, such as Fluidized Catalytic Cracking, Hydrocracking, Catalytic Selective Cracking, Thermal Cracking, and Hydrodewaxing. Proprietary mathematical models and open literature information will be used to the extent possible for these process evaluations.

Means for separating the reactor-wax from the catalyst fines, if such a separation is needed prior to reactor-wax upgrading, shall be investigated.

Task 3 - Product Evaluation

The quality of the hydrocarbon liquid products from the two-stage unit and the reactor-wax upgrading processes shall be evaluated. Gasoline octane and distillate cetane quality, as well as pour points should also be determined.

Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

The effect of different feed-gas distributor designs on the slurry Fischer-Tropsch reactor performance will be investigated. Tests will be conducted in the bench-scale unit slurry reactor, or other bubble-column reactors, to provide

guidance for subsequent runs in Task 1 as well as for design and operation of the non-reacting models. For hydrodynamic studies, the design, construction, and operation of hot, non-reacting bubble-column models will be required.

Task 5 - Development of Conceptual Process Schemes

A conceptual process scheme to maximize gasoline and distillate yield using a combined system of slurry Fischer-Tropsch/ZSM-5 reactor plus reactor-wax upgrading will be developed. Scoping costs of the plant will be estimated.

II. Summary

A. Background

The Mobil two-stage slurry Fischer-Tropsch/ZSM-5 Process provides a novel route for the conversion of coal to high quality motor fuels. The Mobil design combines the slurry-phase Fischer-Tropsch (F-T) synthesis technology with a state-of-the-art fixed-bed ZSM-5 reactor which directly converts the vaporous F-T products from the first-stage slurry reactor into high quality gasoline.

Due to the unique features of a slurry F-T reactor, high single-pass H_2+CO conversion can be achieved using synthesis gas with H_2/CO molar ratios as low as 0.6 to 0.7, provided the F-T catalyst has water-gas shift reaction activity. These low H_2/CO ratio gases can generally be obtained from advanced coal gasification systems, such as the BGC (British Gas Corporation)/Lurgi Slagger, Texaco, Shell-Koppers, and Westinghouse gasifiers. These gasifiers have high thermal efficiencies and potentially lower costs than others (Shinnar and Kuo, 1980). Therefore, a combination of these advanced coal gasification systems with the two-stage technology constitutes a novel and lower-cost route for the conversion of coal to gasoline. In contrast, methanol synthesis routes stoichiometrically require synthesis gas of at least 2/1 H_2/CO ratio. The use of a low H_2/CO ratio synthesis gas for hydrocarbon synthesis plus a simple step for upgrading the F-T products into high quality gasoline in a single fixed-bed ZSM-5 reactor constitute two unique features of this two-stage technology.

Original development work on the two-stage process was done from 1980 to 1983 under DOE Contract No. DE-AC22-80PC30022. The specific objective was to develop the process in a bench-scale pilot plant consisting of a slurry F-T reactor (5.1 cm ID x 762 cm high) and a fixed-bed ZSM-5 reactor in series. The scope of work encompassed design and construction of the pilot plant, evaluation of F-T catalysts, process variable studies, characterization of the gasoline product, and a preliminary conceptual design and scoping economic study of a commercial-scale plant. That work focused on the maximization of the gasoline yield. The goal of this work, under Contract DE-AC22-83PC60019, is to demonstrate stable pilot plant operation while minimizing the yield of methane + ethane. This operation mode results in high yields of reactor-wax, which is the heavy C_{20}-C_{200} fraction of F-T products remaining in the first-stage reactor. Maximum gasoline + distillate yield can then be obtained by upgrading the reactor-wax to distillate and gasoline with minimum light gas yield.

B. Results

In process development studies, modification of the two-stage unit for high-wax mode operation began in July 1983. This included the development of a continuous catalyst/reactor-wax separator so that clean wax product could be efficiently removed from the reactor. Pilot-plant runs commenced in March, 1984 and eight separate runs were performed. Three F-T catalysts ($Fe/Cu/K_2CO_3$) were evaluated for low methane + ethane (high reactor-wax) mode operation. Two of the catalysts (designated I-C and I-D) were judged to be inferior to Catalyst I-B in long-term stability studies. Using Catalyst I-B, smooth operation at high H_2+CO conversions (80-85 mol %) and high reactor-wax yields (50-65 wt %) were demonstrated for 35 days, the longest such run in history. Process variable studies included the successful testing of a 1 mm single orifice as the feed-gas distributor in the bubble-column reactor.

The high-wax mode operation was achieved at about the similar synthesis conditions as those of a gasoline mode operation (Run CT-256-3) reported in our earlier DOE Contract (Kuo, 1983) using a F-T catalyst of same formulation. The only major difference was that the surface area of the new batch catalyst is reduced to about 40% of the old batch catalyst. In the gasoline mode operation, the catalyst aging observed after 45 DOS was mainly due to intrinsic activity loss and was compensated by raising the reaction temperature. In the high-wax mode operation, the total hydrocarbon production of 350 g/gFe was limited mainly due to catalyst settling at 35 DOS. Detectable activity loss may be observed if longer operation could be achieved.

The orifice feed-gas distributor was used for over 100 days and gave performances equivalent to that of the sintered-metal plate distributor which had been used previously. Orifice distributors are commercially superior to sintered-metal plates because they are easier to construct and have little or no plugging problems.

In other process studies, on-stream addition of fresh F-T catalysts were found not to be fully activated. This happened even with catalyst that would fully activate under on-stream synthesis conditions. Increases in H_2+CO conversion were achieved by on-stream addition of catalyst activated in another slurry reactor. Thus, it seems that a separate pretreatment step is essential for F-T catalyst activation. Also, a mathematical model was used to establish the minimum water-gas shift activity required to achieve high H_2+CO conversion with a low H_2/CO ratio synthesis gas. This critical shift activity can be obtained by either raising the catalyst temperature or varying the catalyst formulation. Lastly, the second-stage ZSM-5 reactor was used to satisfactorily convert the vaporous F-T product to gasoline, similar to what was demonstrated in our previous DOE Contract.

In scoping F-T reactor-wax upgrading studies, conventional refinery processes, including thermal cracking, hydrodewaxing, hydrocracking, and fluidized catalytic cracking were evaluated. A single-pass conversion of 46 wt % (of the C_{47}^+) of a reactor-wax vacuum bottom was achieved in a thermal cracking process. The unconverted fraction may be recycled to extinction in a scheme coupled with a vacuum distillation column. Results of upgrading using other processes are reported in the Appendix-Restrictive Distribution.

In product evaluation, three methods for analyzing reactor-waxes were evaluated. Gel Permeation Chromatography was judged to require extensive optimization to improve its resolution and was not pursued further. A modified Gas Chromatography technique was developed to improve the quantification of the total fraction heavier than C_{55}. Lastly, Field Ionization Mass Spectrometry was investigated and found to give the most complete carbon-number distribution, reaching as high as C_{150}. The new methods showed that in heavy reactor-waxes, as much as 75 wt % of the material is above C_{55}. New Schulz-Flory distributions, representing a single chain-growth probability mechanism, were prepared based on these results. The distributions showed that the amounts of the components larger than C_{18} are substantially higher than those predicted by a normal Schulz-Flory mechanism. This fact further confirms the observation from our previous DOE Contract that, in a slurry system, large molecules can reabsorb onto the active catalyst sites, allowing for further chain growth.

Two methods for analysing oxygenates in F-T reactor-wax were evaluated. Low Temperature Liquid Chromatography was useful for the waxes containing less than 5 wt % C_{60}^+; while High Temperature Liquid Chromatography was used for the heavier waxes. For a reactor-wax produced in a gasoline-mode operation (low reactor-wax mode), the oxygenate content was 13 wt %. A sample from a high reactor-wax mode operation shows 22 wt % oxygenates, though the total oxygen was only about 1.0 wt %.

In hydrodynamic studies, scoping work was done using two short hot-flow columns (3.2 and 5.3 cm ID x 1.9 m) to prepare the ground work for later studies in our two tall hot-flow columns (5.1 and 10.2 cm ID x 9.1 m). The work in the short columns revealed for the first time that different F-T waxes give very different gas holdups. Also, orifice distributors were shown to produce low gas holdups and non-uniform bubble sizes while sintered-metal plate distributors gave uniform small bubbles, resulting in large gas holdups and foam formation. Using a small bubble-column reactor (2.7 cm ID x 1.9 m), effects of pressure and diversely different gases on the gas holdup were found to be negligible. A literature review of past hydrodynamic work was conducted to provide guidelines for these studies and to confirm the non-existence of any data from studies using actual F-T reactor-waxes.

Construction work on the two tall hot-flow columns was completed in January 1984. Orifice feed-gas distributors were found to produce little or no foam and lower, but satisfactory, gas holdups than the sintered-metal plate distributors. A 1 mm orifice distributor was selected for use in the BSU bubble-column. The actual reactor-waxes gave substantially lower gas holdups than the FT-200 Vestowax(1) and produced no foam, consistent with experiences with the BSU bubble-column operation. This fact emphasizes the importance of using actual reactor-waxes in the hydrodynamic studies of F-T reactors. Four reactor-waxes produced at the high-wax mode operation behaved similarly with a 1 mm orifice though their viscosities and compositions were quite different. Varying the column diameter from 5.1 to 10.2 cm had negligible effects on the gas holdup in the FT-200 wax. It did, however, result in higher holdups in the reactor-wax due to a decreased effect of bubble slugging with the larger column. A column diameter somewhat larger than 10.2 cm may be needed to eliminate the wall effect. The average gas holdup varied substantially with liquid static height up to 4-5 m. In contrast to the sintered-metal plate distributors, orifice distributors gave higher gas holdups with increasing static height due to continuous bubble breakup along the column. Results of dynamic gas-disengagement experiments with two orifice distributors in the 5.1 cm ID column indicated the existence of small and large-size bubbles with distinct bubble-rise velocities. Finally, one experiment with 2 wt % catalyst in reactor-wax resulted in a 9% decrease in the gas holdup.

In a separate study using mathematical models, three or more continuous stirred-tank reactors (CSTR) in series were found to be sufficient to overcome the disadvantage of the gas- and liquid-phase backmixing in a CSTR system. The expected large benefit of higher catalyst loading in CSTRs over bubble-column reactor can only be quantified with proper experiments.

Lastly, based on our new process information, a conceptual design and a scoping cost estimate of a commercial-scale plant were developed. The design for the slurry F-T and the ZSM-5 reactor sections is similar to that given in our previous DOE Contract (Kuo, 1983). The design of the F-T reactor-wax upgrading and the product separation sections and the scoping cost estimate are given in the Appendix-Restrictive Distribution.

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(1)A F-T paraffinic wax from SASOL, with an average molecular weight of 600.

III. Introduction

In 1976, Mobil Research and Development Corporation (MRDC) announced a catalytic process for converting methanol to high octane gasoline in high yield (Meisel et al., 1976; Wise and Silvestri, 1976). Since commercial processes for the synthesis of methanol from coal-derived synthesis gas are known, this new technology provided a viable route for the conversion of coal to gasoline. The development of the fixed-bed MTG (Methanol-to-Gasoline) process was studied under an ERDA Contract, No. E(49-18)-1733 (Voltz and Wise, 1976). In 1978, under DOE Contract No. EX-76-C-01-2490, the conversion of methanol to high octane gasoline in a 4 BPD fluidized-bed pilot plant was demonstrated (Kam and Lee, 1978). A 14,000 BPD gasoline plant using fixed-bed MTG technology was started up in New Zealand in late 1985.

Another route for converting coal-derived synthesis gas to hydrocarbons involves the F-T reaction, which was first reported in 1923 and is named after its discoverers (Fischer and Tropsch, 1923). Excellent reviews on early F-T work have been given by Storch et al. (1951) and by Anderson (1956). SASOL in South Africa is currently operating three commercial plants producing transportation fuels using F-T technology Both fixed-bed tubular (Arge process) and fluidized entrained bed (Synthol process) reactor designs with Fe-based catalysts are used.

Both routes mentioned above require a synthesis gas of H_2/CO molar ratio greater than 2.0. In the case of methanol synthesis, this is required by stoichiometry. In the case of the conventional F-T technologies, the high H_2/CO ratio is required for minimizing carbon formation from the carbon monoxide and other problems. In the case of the fixed-bed tubular F-T process, use of a lower H_2/CO synthesis gas may require larger gas recycle for achieving satisfactory overall H_2+CO conversion and for controlling the catalyst temperature. It may also require higher reactor pressure to compensate the low H_2+CO partial pressure due to CO_2 accumulation in the recycle route. Furthermore, fixed-bed tubular reactors are expected to be costly. In the case of the fluidized entrained-bed F-T process, use of the high H_2/CO synthesis gas is essential to avoid the formation of waxy hydrocarbons, which causes the catalyst to lose fluidization. The process also produces high methane + ethane yield (about 16 wt % of total hydrocarbons produced).

In 1978, under DOE Contract No. EF-76-C-01-2447 (Schreiner, 1978), a research guidance study was carried out on coal-to-gasoline processes via both the MTG and SASOL type Synthol route. It was found that the predominant cost of a complete plant is associated with the gasification of the coal. Consequently, a study to identify potentially lower cost coal

gasification systems was carried out in 1978 under DOE Contract No. EF-77-C-01-2766 (Shinnar and Kuo, 1978). The majority of the advanced coal gasification systems that have high thermal-efficiency (and thus potentially lower-cost) produce low H_2/CO ratio synthesis gas (ranged from 0.35 to 1.0). This is a direct consequence of minimum steam usage during the gasification. Of course, the low H_2/CO ratio gases can be shifted to higher H_2/CO ratios in a separate water-gas shift unit and then used as feed-gases to either methanol synthesis or conventional F-T units. However, the major cost advantage from the advanced coal gasification is then negated. To maintain this advantage, a synthesis process, that can directly use a low H_2/CO ratio gas, is needed.

With Fe-based F-T catalysts which promote the water gas shift reaction under synthesis conditions, the following reactions take place simultaneously (as illustrated by formation of $[-CH_2]$ hydrocarbons):

$$CO + 2\ H_2 = [-CH_2] + H_2O \qquad \text{(III-1)}$$

$$H_2O + CO = H_2 + CO_2 \qquad \text{(III-2)}$$

The second reaction indicates that the Fe-based catalyst promotes "internal shift" by utilizing the water produced from the F-T reaction to make more H_2. By doing so, high single-pass synthesis gas conversion can be achieved with a low H_2/CO ratio synthesis gas. After this "internal shift" reaction, the overall F-T reaction becomes:

$$2\ CO + H_2 = [-CH_2] + CO_2 \qquad \text{(III-3)}$$

The high single-pass conversion greatly increases the process efficiency since it eliminates the equipment and penalties associated with any recycle operation.

The fact that very little water forms within the synthesis route further increases the process efficiency since the amount of water (or steam) moving through the process system is drastically reduced from that of any synthesis processes requiring high H_2/CO ratio synthesis gas. Since water has a very high latent heat, use of high H_2/CO ratio synthesis gas is always associated with very large movements of mass (water, steam, and others) and energy. Furthermore, the amount of waste water is also greatly reduced.

Reaction (III-3) is highly exothermic. Strict temperature control is essential. A slurry reactor provides excellent reaction temperature control and prevents excessive carbon formation by the following reaction:

$$2\ CO = CO_2 + C \qquad \text{(III-4)}$$

The rate of this undesirable reaction increases drastically with increasing temperature.

The products from all F-T processes, however, are highly nonselective. They include a wide range of hydrocarbons and oxygenates and require complicated refinery steps to upgrade them to marketable products. For example, the upgrading processes used at SASOL (Brink, 1985 and Kuo, 1984) include catalytic polymerization, catalytic isomerization, naphtha hydrogenation, Pt-forming, diesel hydrogenation, creosote hydrogenation, methane reforming, and separation and hydrogenation of water-soluble chemicals.

MRDC, however, developed a process using ZSM-5 which converts the F-T products into high-quality gasoline in a single step. By combining this benefit with benefits from the direct use of a low H_2/CO ratio synthesis gas, the conversion of coal derived synthesis gas to gasoline was made economically more attractive than other established routes. The potential of this two-stage technology was successfully demonstrated under our previous DOE Contract (DE-AC22-80PC30022) for a long-term gasoline (low reactor-wax) mode operation (see Kuo, 1983).

The new work described in this report was undertaken to establish long-term low methane + ethane (high reactor-wax) mode operations and to investigate the potential of existing refinery technologies to upgrade the reactor-wax product. Also, the hydrodynamics of bubble-column reactors was more throughly investigated in this study.

IV. Task 1 - Process Studies in Two-Stage Bench-Scale Unit

A. Bench-Scale Unit Modifications

A simplified flow-diagram of the existing two-stage Bench-Scale Unit (BSU) is shown in Figure IV-1. The details of this unit were given in the Final Report of an earlier DOE Contract (Kuo, 1983). The unit was modified for improved operation. The major modifications were:

- Improved on-line reactor-wax separation hardware.
- Improved DP-cell set-up for bubble-column hydrodynamic measurements.

The improved on-line F-T reactor-wax separation system enabled us to increase the flexibility and reduce the manpower requirement for the reactor-wax/slurry separation. A schematic of this system is shown in Figure IV-2. During normal operation, slurry is withdrawn continuously from the F-T reactor at the 610 cm level, and entrained gas is disengaged in a small disengager pot which is connected to the reactor-top. The gas-free slurry is passed through a dip-tube into a two-liter settling pot. The dip-tube length is designed to maintain 80% of the settling pot volume above its tip. The concentrated slurry exits the settling pot through a conical section, and is pumped back to the slurry reactor at the 305 cm level through a positive-displacement slurry pump. The pump is inverted, i.e., feed enters at the top and effluent exits at the bottom. This prevents catalyst settling in the feed line to the pump, but requires spring loading of the pump check valves. The clean reactor-wax is withdrawn from the top of the settling pot either semi-continuously by periodically opening a valve, or it can be withdrawn continuously by using a metering valve.

The new DP-cell set-up shown in Figure IV-3 consists of six purgeless DP-cells, with their high pressure sides contacting the reactor slurry. This eliminated the plugging which was previously experienced in the purged DP-legs, and also the nitrogen dilution effect. The low pressure sides of the DP-cells are equilibrated with the pressure at the reactor top. Thus, each DP-cell measures the static pressure of the slurry above it. The resulting small pressure prop across the cell membrane assures accurate DP-readings. Before installation of this new DP-system in the BSU, the concept was successfully demonstrated in Unit CT-225, a small (2.7 cm ID x 1.9 m height) bubble-column reactor.

Figure IV-1

SIMPLIFIED FLOW DIAGRAM OF TWO-STAGE PILOT PLANT FOR SYNTHESIS GAS CONVERSION

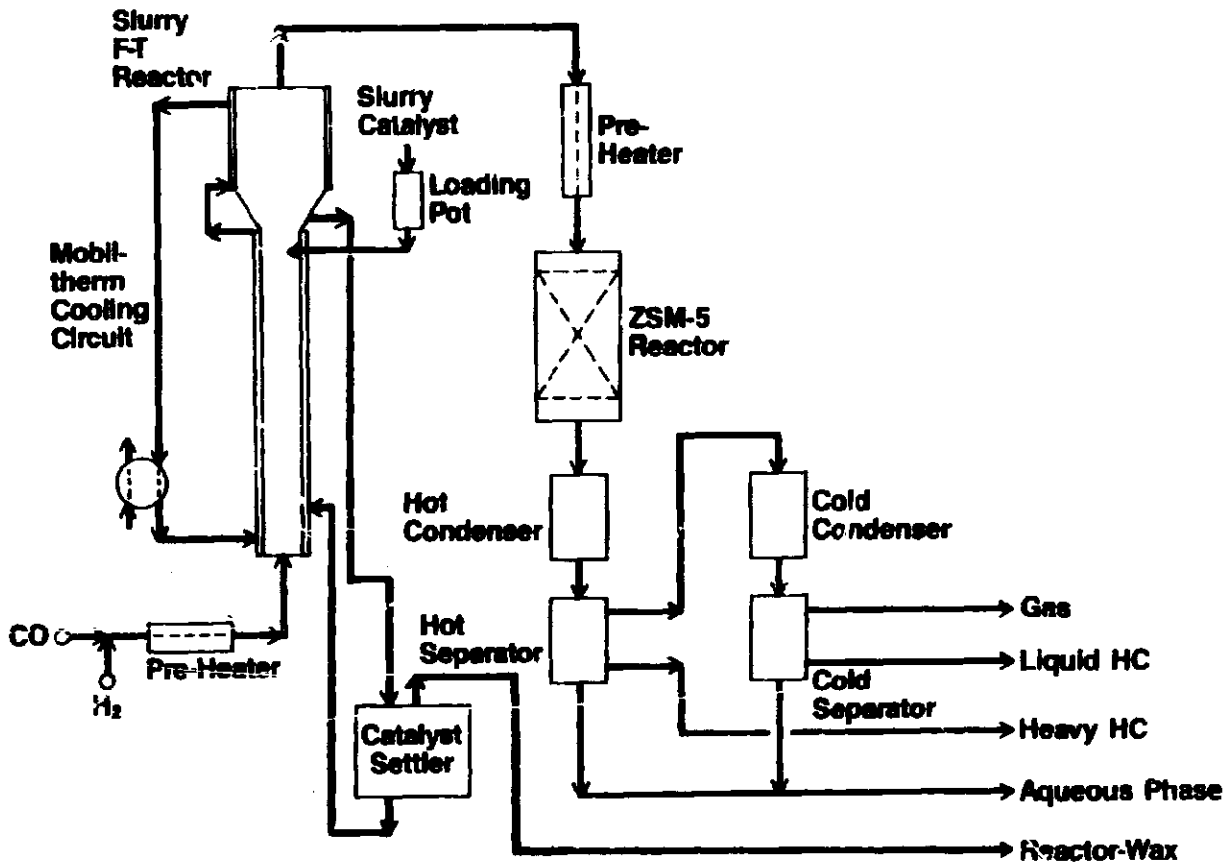


Figure IV-2

SCHEMATIC DIAGRAM OF
NEW CONTINUOUS SETTLING SYSTEM FOR
CATALYST/WAX SEPARATION

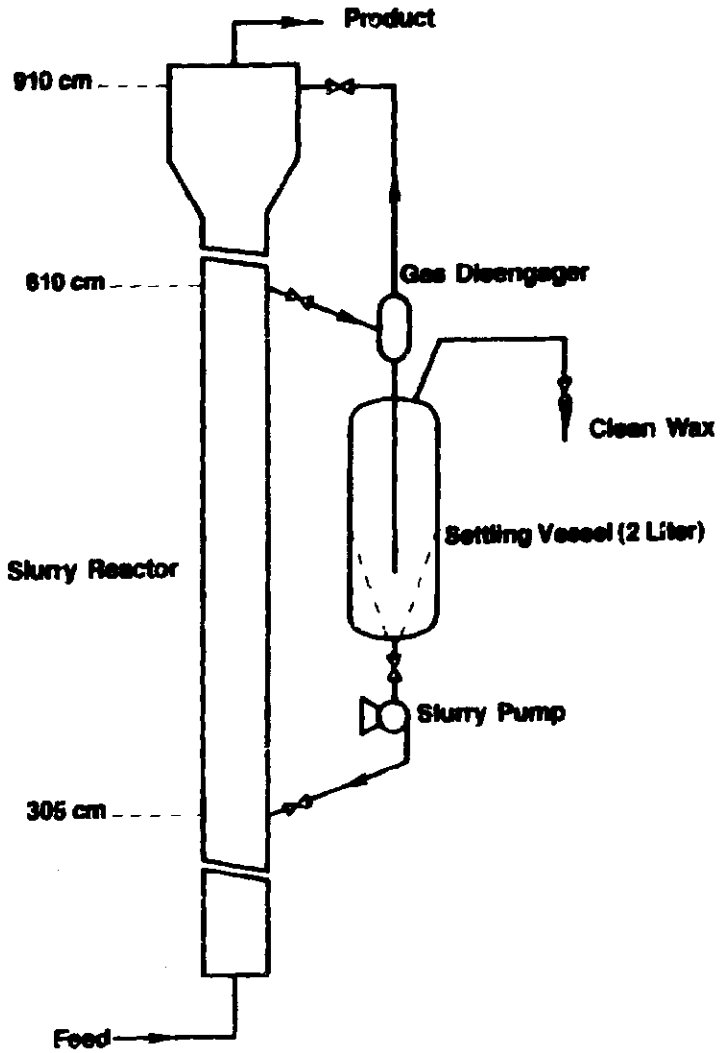
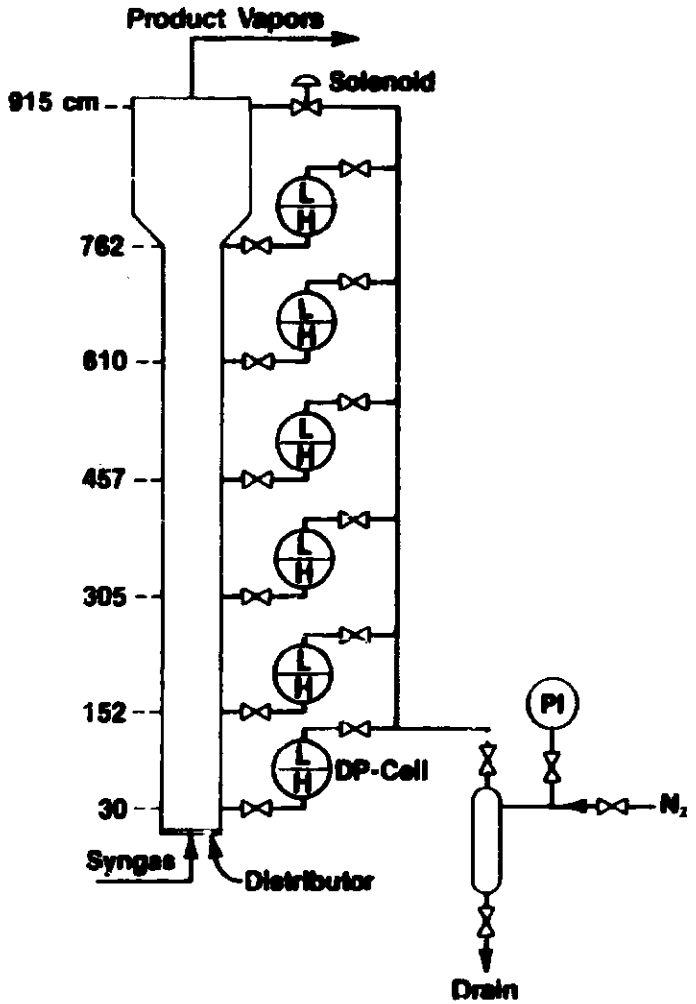


Figure IV-3

SCHEMATIC ARRANGEMENT OF NEW DP-CELLS FOR LIQUID LEVEL AND GAS HOLDUP MEASUREMENT



Immediately following modifications, the two-stage BSU was shaken down. The major action items were:

- Cold- and hot-pressure tested section by section with N_2 and H_2 at 2.86 MPa and fixed leaks.
- Calibrated Glycol Systems.
- Calibrated NDIR CO and CO_2 monitors.
- Tested new on-line reactor-wax separation and purgeless DP-system first with Mobil F-509[1] oil and then with the end-of-run CT-256-5 slurry.
- Tested and calibrated the on-line gas chromatograph system.

The Glycol systems are glycol displacement systems for periodical measurement of the feed H_2, CO, and H_2+CO flow rates. The NDIR CO and CO_2 monitors are NDIR Analyzers (Model 864) from Beckman Instrument Inc. and are used for monitoring the CO and CO_2 concentration in the off-gas of the unit.

B. Preliminary Evaluation of a New Fischer-Tropsch Catalyst in a Small Bubble-Column Reactor

B.1. Activation of Fischer-Tropsch Catalyst I-D Without a Separate Pretreatment Step

A new F-T catalyst, designated I-D (containing Fe/Cu/K_2CO_3), was evaluated using the 2.7 cm ID x 1.9 m tall bubble-column reactor (Unit CT-225). This unit does not contain a second-stage ZSM-5 reactor and is useful for scoping evaluations. No material balance data are reported. The run, designated as CT-225-112, was started on December 6, 1983 and concluded after sixteen days on-stream.

The following are major highlights of the run:

- The catalyst was activated at the same conditions as those for synthesis (250°C, 2.17 MPa). It is not certain that the activation was complete, due to catalyst loss.
- The ranges of operating conditions were:

Temperature, °C	250-255
Pressure, MPa	2.17
Feed H_2/CO, molar	0.67
Superficial Feed-Gas Vel., cm/s	0.9-1.8

- The H_2+CO conversion ranged from 23 to 58 mol % and the methane + ethane yield from 1.7 to 3.5 wt % of the hydrocarbons produced.

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(1) A proprietary high molecular weight paraffinic base stock.

- The reactor-wax yield was high, ranging from 60 to 80 wt % of the hydrocarbons produced.

- On-stream additions of fresh catalyst increased conversion, but less than the expected amounts. This may have been due to undetected catalyst losses.

Run CT-225-112 started with a slurry containing 136 g of Catalyst I-D and reactor-wax from Run CT-256-4. Aside from a general evaluation, it was desired to observe the catalyst performance at high pressures, where commercial reactors may operate. Also, it would be commercially desirable for a catalyst to be able to activate without a separate pretreatment step. For these reasons, the catalyst was brought on-stream at 2.17 MPa pressure and 250°C temperature. The space velocity was 4.5 NL/gFe-hr, which allows for a high gas throughput.

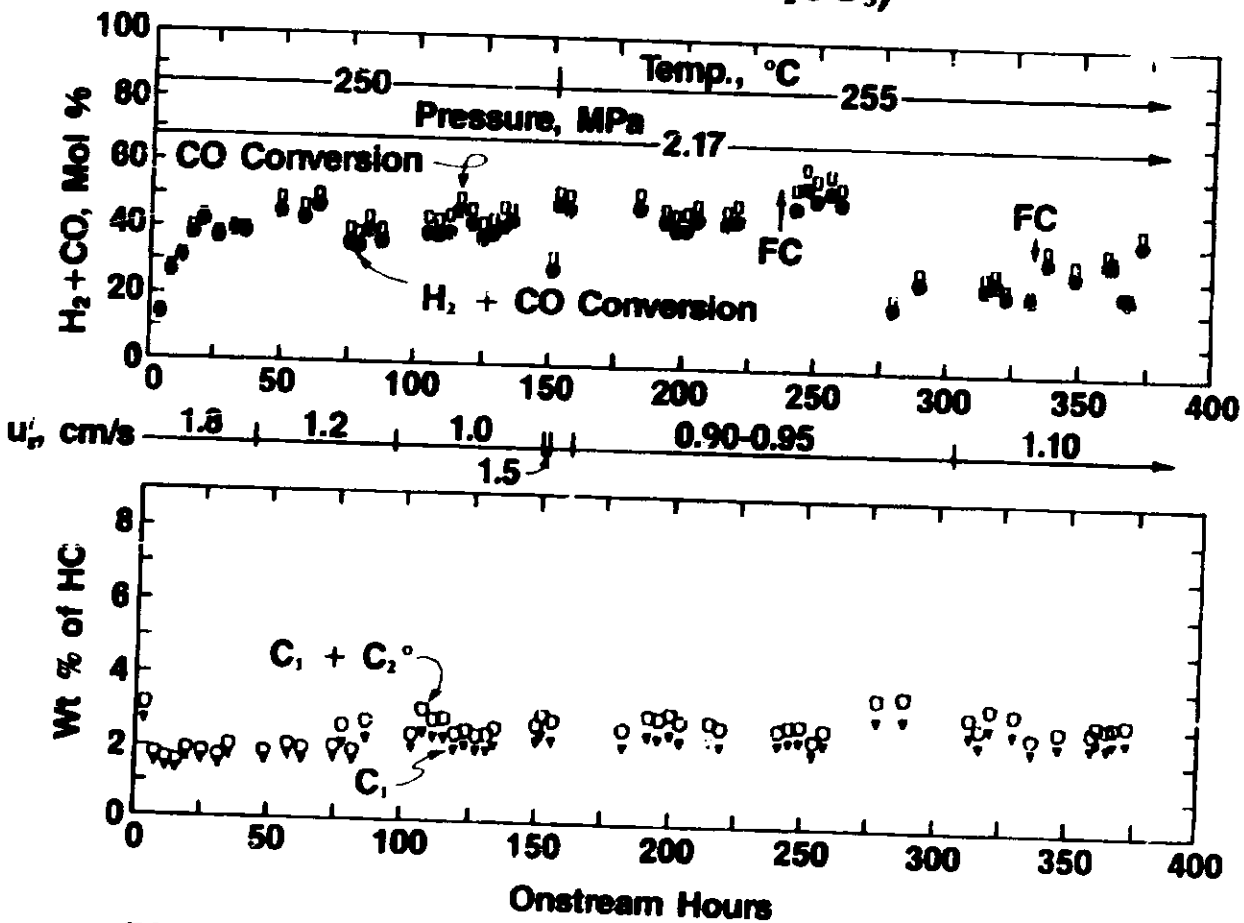
Figure IV-4 shows the conversion and methane + ethane selectivities for the run. Over the first 22 hours, the H_2+CO conversion rose to 41 mol %, while the methane + ethane selectivity was 2-3 wt % of the total hydrocarbons produced. At that point, the reactor-wax build-up necessitated its removal from the unit.

To remove reactor-wax from the Unit CT-225, a batch settling system similar to that used in Runs CT-256-4 and -5 was employed (see Kuo, 1983). The settling pot was a 300 cm^3 pressure-vessel with a dip-tube extending halfway down for decanting the wax. The pot was situated 30 cm below the level of the reactor bottom. Slurry was brought from a drain at the 1. m level to fill the pot. When settling was completed (usually 45 minutes), the upper layer of the wax was decanted and the remainder pressurized quickly back into the reactor bottom. A maximum of about 160 cm^3 of wax could be decanted in each batch, in contrast to the maximum reactor slurry capacity of about 1500 cm^3 (including the disengagement zone).

The first reactor-wax withdrawal at 22 HOS resulted in the accidental removal of 100 g of concentrated slurry from the settling pot. This was immediately placed back into the pot and pressurized into the reactor. Only 50 g of reactor-wax was decanted. However, some damage to the catalyst may have occurred due to its exposure to the air. This may explain the abrupt leveling-off of the H_2+CO conversion after 22 HOS or the catalyst may not have continued to activate, regardless. Later studies in the two-stage BSU (see Subsection IV.H) showed that full activation of a similar catalyst could not be reached at synthesis conditions.

Figure IV-4

SYNTHESIS GAS CONVERSION AND METHANE AND ETHANE YIELD (RUN CT-225-112; CATALYST I-D: PPTD Fe/Cu/K_2CO_3)



FC: Fresh Catalyst Added

Reactor-wax was withdrawn once every one to two days on the average. Figure IV-5 is a plot of the cumulative reactor-wax withdrawn. The slope of this curve, combined with the conversion data, indicates that the reactor-wax yield averaged from 60 to 80 wt % of the hydrocarbons produced. Solids analyses were done on each batch of wax removed.

Also, make-up fresh catalyst was added twice in-situ, at 238 and 333 HOS. On this basis the space velocity was determined. At the run's end, however, extensive solids analysis on the slurry and subsequent reactor rinses indicated that there was only about 40% of the original and added catalyst in the slurry. This leads to the possibility that the catalyst deposited in the settling pot or another part of the system undetected. In any case, this result made the space velocity a question mark for all but the very beginning of the run.

The difficulty we had in evaluating the activity of the catalyst in this small bubble-column is illustrated by the conversion at 20 and 200 HOS. Based on feed-gas flow rate and the estimated catalyst inventory obtained by deducting the catalyst loss in the withdrawn wax, the estimated space velocity at 200 HOS was 3.4 NL/gFe-hr or 75% of that at 20 HOS. In addition, the temperature was raised by 5°C. This should have resulted (based on a first-order kinetic estimate) in H_2+CO conversions of 65-75 mol % assuming 100 kJ/g-mol activation energy. The actual conversion (about 42 mol %) however, was roughly the same at both times.

The methane + ethane yield during the run, however, remained low, ranging from 1.7 to 3.5 wt % of hydrocarbons produced. This shows that the catalyst was aging very slowly, much the same as did Catalyst I-C in Run CT-256-5, which was also run at 250°C most of the time. During previous catalyst evaluations, we have observed that a drop in H_2+CO conversion due to catalyst aging is usually accompanied by a rise in the methane + ethane yield. This also supports the catalyst-loss hypothesis to explain the decreased H_2+CO conversion.

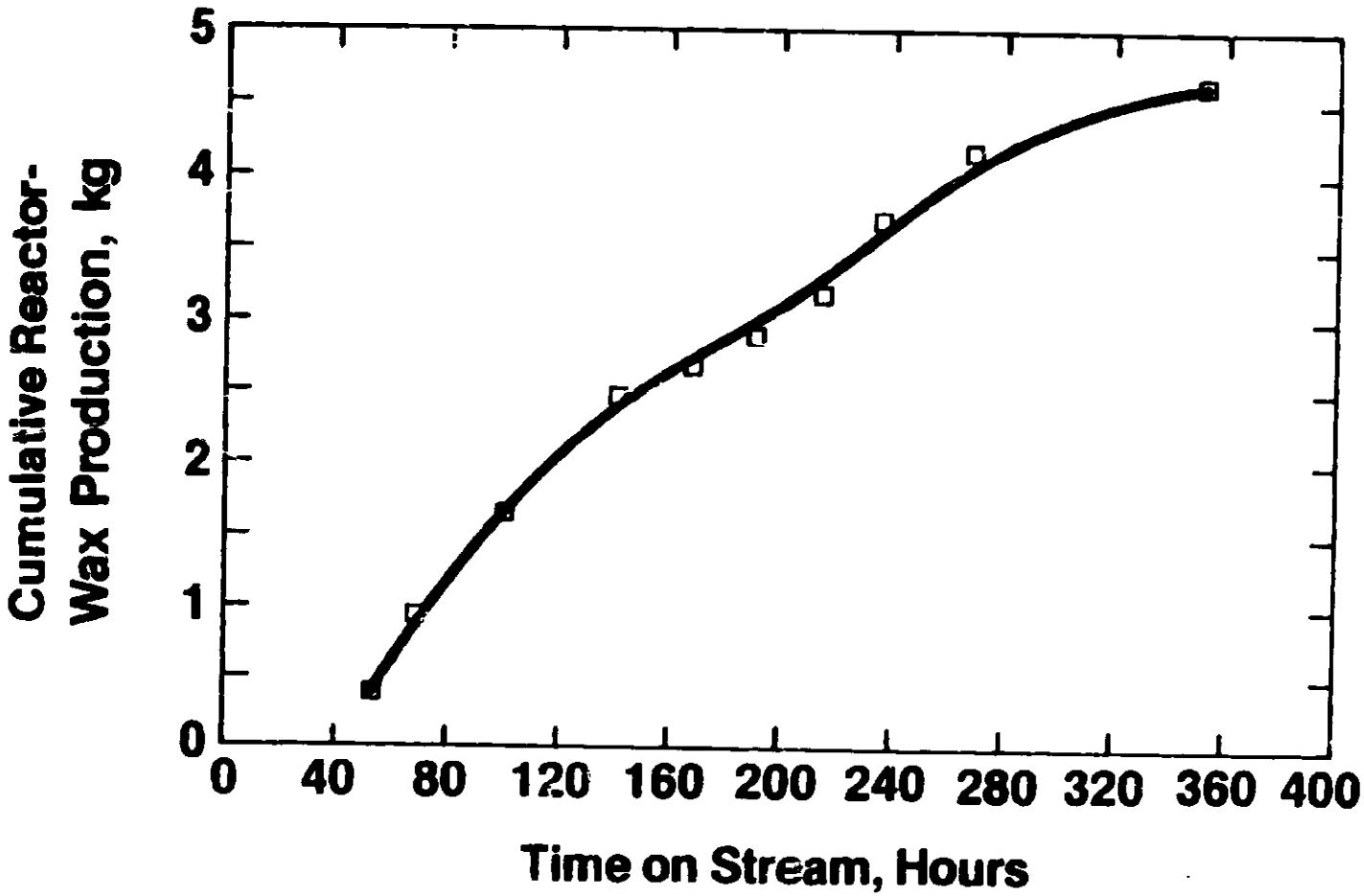
At 275 HOS, a large decrease in the H_2+CO conversion occurred. This was probably due to the following reasons:

- The conversion drop came after a series of five reactor-wax withdrawals which totalled nearly one-half the reactor contents. We have already seen that catalyst losses may have occurred during reactor-wax removals.

- After the fifth withdrawal, the concentrated slurry was accidently left in the settling pot for ten hours, possibly in contact with air for some of that time.

Figure IV-5

CUMULATIVE REACTOR-WAX PRODUCTION (RUN CT-225-112)



Previous experience has shown that F-T catalyst can deactivate under such conditions. The catalyst in the pot may have been 30% of the total catalyst in the reactor.

On-stream additions of fresh catalyst were carried out at 238 and 333 HOS. The following conclusions can be drawn:

- The H_2+CO conversion increased both times, the first time by 22% (63 g catalyst added) and the second time by 35% (50 g catalyst added). By comparison, conversion in Run CT-256-4 increased by only 5% after about a 50% increase in catalyst loading due to on-stream addition of fresh Catalyst I-B.
- The conversion increases were not as high as was expected based on the proportions of fresh catalyst added. The added catalyst may not be activated fully due to low H_2 and CO partial pressures.
- The methane + ethane yield was not significantly affected.

B.2. Activation of Fischer-Tropsch Catalyst I-D with a Separate Pretreatment Step

A second short evaluation was then done to study the effect of a standard pretreatment step on start-of-cycle performance of Catalyst I-D.

The run, designated as CT-225-113, lasted only one day, but the main objectives were accomplished, as the catalyst pretreated rapidly and produced excellent conversion and low methane + ethane selectivity. The pretreatment conditions were:

Temperature, °C	280
Pressure, MPa	1.14
Feed H_2/CO, molar	0.67
Space Velocity, NL/gFe-hr	3.0
Catalyst Loading, wt %	20
Duration, hrs.	4.0

The pretreatment was stopped when the molar gas contraction reached 50 vol %, which represents about a 75 mol % H_2+CO conversion (see Figure IV-6).

Figure IV-6

PRETREATMENT OF FISCHER-TROPSCH CATALYST I-D (RUN CT-225-113)