PROJECT REVIEW ON

DOE CONTRACT NO. DE-AC22-80PC30022
"TWO-STAGE SLURRY FISCHER-TROPSCH/ZSM-5
PROCESS OF CONVERTING SYNGAS TO HIGH OCTANE GASOLINE"

By

J. C. W. Kuo
T. M. Leib
K. M. Gupte
J. Smith

MOBIL RESEARCH AND DEVELOPMENT CORPORATION
PAULSBORO, NJ 08066

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TWO-STAGE SLURRY FISCHER-TROPSCH/ZSM-5 PROCESS

J. C. W. Kuo, T. M. Leib, K. M. Gupte and J. Smith

MOBIL RESEARCH AND DEVELOPMENT CORPORATION

Paulsboro, New Jersey 08056

Abstract

We have recently completed the initial phase of development studies for conversion of synthesis gas to high octane gasoline via a two-stage slurry F-T/ZSM-5 process. A slurry F-T catalyst ($Fe/Cu/K_2CO_3$) showed high activity and long-term stability and produced 815 gHC/gFe in eighty-six days. Effects of feed H_2/CO ratio, pressure, and feed-gas velocity were studied. The addition of a potassium-salt to reduce methane + ethane yield was also demonstrated. A second-stage ZSM-5 catalyst performed well, converting the F-T products into high quality gasoline in one step. It accumulated eighty-seven days on-stream-time with two regenerations. The gasoline product showed satisfactory oxidation stability.

Methane + ethane selectivities as low as 2-5 wt % for the F-T synthesis were demonstrated by using either higher pressure and/or lower temperature or a new catalyst. The liquid hydrocarbon yield was maximized in this case; however, reactor-wax yields as high as 85 wt % were obtained. An on-line settling method was demonstrated to effectively separate a low solid-content reactor-wax from the catalyst slurry.

A conceptual process design and scoping cost estimate for a battery-limit 27,000 BPSD gasoline plant from clean synthesis gas was conducted.

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J. C. W. Kuo, T. M. Leib, K. M. Gupte, and J. Smith
Mobil Research and Development Corporation
Paulsboro, New Jersey 08066

I. Introduction

The title of the contract is "Slurry Fischer-Tropsch/ Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline." This contract began on October 1, 1980 and ended on April 30, 1983. The overall objective of the contract was to develop a two-stage slurry F-T/ZSM-5 process for direct conversion of a low H_2/CO ratio synthesis gas to high octane gasoline (Slide #1). To achieve this objective, specific tasks were the design, construction, and operation of a two-stage bench-scale pilot plant, and the acquisition of necessary process information for the evaluation of the technical and economic potential of the process. Altogether, more than 220 days' operation of the pilot plant has been accumulated. In last year's project review meeting, completion and smooth operation of the pilot plant was reported. This time, the remaining aaccomplishments of the project will be reported.

II. Status of the Project

The contract is now complete, and all required work has been fulfilled.

Slides #2 and #3 summarize the status of this project up to the completion of the contract. In last year's meeting, evaluation of a slurry F-T catalyst, designated as I-A ($Fe/Cu/K_2CO_3$), was reported. Two more slurry F-T catalysts, designated as I-B and I-C ($Fe/Cu/K_2CO_3$), have since been evaluated using the pilot plant. Catalyst I-B demonstrated high activity and long-term stability and produced 815 gHC/gFe in eighty-six days. This hydrocarbon production far exceeded the argeted production of 450 gHC/gFe, suggested by Professor H. Koelbel. A second-stage ZSM-5 catalyst accummulated eighty-seven days on-stream-time with two regenerations. It satisfactorily converted the F-T products into high octane gasoline. The raw gasoline samples from the pilot plant were tested and showed satisfactory oxidation stability. In the latter period of the long-term stability test of the catalyst I-B, a process variable study of feed H_2/CO ratio, pressure, and feed-gas velocity for the slurry F-T reactor was conducted. Addition of a pottassium-salt to reduce the methane + ethane yield was also demonstrated.

During the course of the pilot plant operation, some hydrodynamic data were also collected. In addition, simple bubble-column hydrodynamic studies were carried out with two existing short, hot and cold glass bubble-columns. A summary of this hydrodynamic information will be presented by T. M. Leib later today. A complex analytical scheme for characterizing F-T products was also developed. Details of the scheme were given in DOE reports and will not be given here.

A conceptual process design for a commercial scale plant of producing 27,000 BPSD gasoline from clean synthesis gas was completed. A scoping cost based on this design was also estimated.

To maximize the liquid fuel yield, ways to minimize the methane + ethane yield in the F-T operation were examined. We have found that by using either catalyst I-B at higher pressures and/or slightly lower temperatures or a new F-T catalyst (I-C), methane + ethane selectivities as low as 2-5 wt % were obtained. However, reactor-wax yields as high as 85 wt % were also obtained due to a shift in hydrocarbon distribution to higher carbon-numbered compounds. To effectively withdraw the reactor-wax from the slurry reactor without losing too much catalyst, an on-line settling method was demonstrated.

III. The Slurry Fischer-Tropsch/ZSM-5 Two-Stage Pilot Plant Operation

The next three slides (Slides #4, 5, and 6) summarize the highlights of the three runs of the two-stage pilot plant concluded since last year's meeting. Run CT-256-3 was reported at that time as having accumulated forty days time-on-stream. This run was completed after eighty-six days of operation. The first three items shown here were included in the earlier status slide. The next item concerns the operation of the second-stage ZSM-5 reactor. To compensate for catalyst aging due to coking, a policy of gradually increasing the reactor inlet temperature for maintaining a constant operational severity of the bed was established. During this run, we also discovered that the conversion activity was greatly reduced and the methane + ethane yield increased when the F-T catalyst was exposed to the air. It was speculated that the state of the catalyst was altered.

Run CT-256-4 achieved two objectives. The first was to evaluate if the F-T catalyst I-B used in Run CT-256-3 could produce less methane + ethane under higher pressure and/or lower temperature conditions. A 3-5 wt% methane + ethane yield was achieved. However, the reactor-wax yield was increased greatly to more than 50 wt%. In addition, the F-T hydrocarbon liquid and aqueous phase had higher acid numbers indicating higher oxygenate yields under these operating conditions. The other objective was to test several means of separating the reactor-wax from the catalyst slurry. An on-line settling method was successfully demonstrated. The total on-stream time of this run was

thirty-seven days.

Run CT-256-5 also achieved two objectives. The first was to evaluate a new F-T catalyst (I-C) which produced a methane + ethane yield of less than 4 wt%. In achieving this, reactor-wax yields as high as 85 wt% were obtained. High acid numbers were also obtained for the F-T hydrocarbon liquid and aqueous phase. The other objective was to demonstrate that the F-T catalyst could be activated without the use a separate pretreatment step, which could be cumbersome in commercial application. The run was terminated voluntarily after thirteen days of on-stream-time.

Slides #7 and 8 summarize the conditions and results of Run CT-256-3, the longest and most important run to date. The results shown here demonstrate a very stable operation with high catalyst loading, high synthesis gas throughput, and high synthesis gas conversion. The F-T catalyst pretreatment was described in the last meeting and will not be repeated here. The wide range of results mainly reflects the process variable studies conducted during the latter part of the run. During the long-term aging operation (first sixty-one days), the target carbon monoxide conversion was 90%, the feed H_2/CO ratio 0.7, and the pressure 1.48 MPa (200 psig). After sixty-one days, process variable studies were carried out. Details of this operation are given in the following.

Slide #9 mainly shows the operation of the first-stage slurry F-T reactor. The whole run can be divided into two periods. The long-term stability test was carried out in the first sixty-one days, followed by a period of twenty-five days of process variable studies. The important features during the first period were the high synthesis gas conversion and the relative stability of the methane + ethane yield. The CO conversion was maintained at 90% and higher. The ethane yield was very stable and increased only slightly over the first sixty-one days; while the increase in the methane yield is more pronounced (from 6 to 9 wt %). The average methane + ethane yields were about 10 wt %. The synthesis operation was very smooth except for two-minor and one major interruptions, which were caused either by a false alarm or by leakage at the flanges of the bubble-column reactor. In the two minor interruptions, the reactor was immediately purged with nitrogen and was brought back to synthesis operation as soon as the emergency problems were resolved. However, in both cases a slight drop in the synthesis gas conversion was observed after the restart. To restore the synthesis gas conversion to the same level as before the interruptions, the feed-gas velocity was decreased by 4% in both cases with a slight increase on methane yield. A major interruption occurred at sixty-one days on-stream-time due to a leakage at the bottom flange of the slurry reactor. The catalyst slurry was withdrawn from the reactor into an open container and was reloaded after fifty hours. A substantial decrease in H_2 +

CO conversion (from 87 to 70%) and an increase in the methane + ethane selectivity (from 13 to 19 wt%) were observed. This demonstrated that exposure to air was detrimental to the performance of this catalyst.

After sixty-five days of on-stream-time we began to vary the operation conditions of the slurry reactor, including the feed H_2/CO ratio, the pressure, and the superficial feed-gas velocity. The feed H_2/CO ratio of 0.6 was used for about twenty days. We did not observe any significant changes in the catalyst aging rate over this period. No conclusion of its effect on the catalyst activity and selectivity could be drawn due to the large change in catalytic activity and selectivity after the major interruption. Pressures from 1.48 MPa (200 psig) to 2.51 MPa (350 psig) were used for about eighteen days. Some detailed results from the process variable studies will be given later. At about eighty-one days of on-stream-time, a potassium-salt was added to the slurry reactor, and an instant decrease of the methane + ethane selectivity from 13 to 8 wt% with little change on synthesis gas conversion was observed. This demonstrated a means of reducing methane + ethane selectivity as previously reported by Koelbel and Ackerman (1951) and Koelbel and Ralek (1980). Unfortunately, a "Hydrodynamic Upset" occurred about twelve hours after the potassium-salt addition. The conversion dropped rapidly from over 80% to 55%, while the reactor temperature on the upper portion of the slurry reactor was 5°C

lower than that at the lower portion of the reactor. The high conversion was recovered after a higher gas velocity operation for three days. It was suspected that the catalyst had settled during the low-velocity operation. The run was shut down due to repeated occurances of this upset.

The Schulz-Flory distribution of F-T products always attracts large attention. A plot of such a distribution based on Run CT-256-3 data at 11.5 days on-stream-time is given in Slide #10. With hydrocarbons of carbon numbers larger than 20, the distributions fall below the Schulz-Flurry straight line when the reactor-wax is excluded from the total balance while they fall very much above the line when the reactor-wax is included. A similar plot with the distribution bent at the same carbon number was observed in Run CT-256-1. The phenomena may be explained by the fact that in a slurry system large molecules can re-adsorb themselves onto active catalyst sites, allowing for further chain growth.

Reactor-wax samples were analyzed for carbon-number distributions as shown in Slide #11. Two distributions at two different operating pressures are given here. The distribution for the high pressure case is shifted slightly toward higher carbon-numbers than that of the low pressure case. The difference is also reflected in the higher peak and average carbon number.

After the goal of a long-term stability operation for the slurry reactor was established, a number of process variables studies were carried out. In the next three slides, some of these results will be reported. Slide #12 shows the exit H_2/CO molar ratio versus H_2 + CO conversion at the two feed H_2/CO ratios (0.7 and 0.6). Dramatic differences between the two feed H_2/CO ratios are clearly shown. At 0.6 feed H_2/CO ratio, the exit ratio was practically constant at about 0.6. This indicates that the H_2/CO usage ratio in this case was very close to 0.6. In the case of the 0.7 feed H_2/CO ratio, excess H_2 in the feed was strongly reflected in the higher and increasing H_2/CO ratio of the reactor exit. The other important effect of the H_2/CO ratio on the F-T reactor performance is the decreased methane + ethane yield with lower H_2/CO feed-gas. This was confirmed in an earlier run (Run CT-256-1) where the methane + ethane yield was decreased from 11 to 9 wt% when the H_2/CO ratio was changing from 0.7 to 0.6

The next slide (Slide #13) shows the effect on the slurry reactor performance due to variations in the superficial feed-gas velocity. The most significant effect is on the H_2 + CO conversion. As expected, a decrease in the gas velocity reflects a corresponding decrease in the space velocity and therefore an increase in H_2 + CO conversion. Slide #14 shows the effect of operating pressure on the slurry F-T reactor performance. To maintain an approximately constant residence time for the

reactant gas, the same superficial feed-gas velocity (2.6 cm/s) was maintained by simultaneously adjusting the feed throughput and the pressure. The major effects are shown here. The first was that the methane yield was reduced from 10.8 wt% to 8.7 wt% when the pressure was raised from 1.48 (200 psig) to 2.51 (350 psig). This demonstrates another means of reducing the methane + ethane yield. The other effect is a slight decrease in H_2 + CO conversion. The drop is relatively small considering the large increase in the feed-gas throughput.

The next three slides will show the performance of the second-stage ZSM-5 reactor. Slide #15 shows the catalyst temperatures versus catalyst days on-stream during Run CT-256-3. Two regenerations were carried out during this run. The dotted points on the slide are the catalyst bed inlet temperature. A policy of rasing the reactor inlet temperature was used to compensate for the catalyst aging so that a target operational severity could be maintained. After the first regeneration, it took a few days to search for the inlet temperature needed to reach a pre-determined operational severity measured by a severity index (molar butane/(propylene + butenes) ratio). After the second regeneration, this initial temperature was quickly established. For the second and the third cycles, the inlet temperature was raised 4.5-5°C/Day. The data given in "cross" on the slide are the temperature rises across the catalyst bed. The temperature rises were 40-45°C, about what was expected for the

adiabetic temperature rise.

Slide #16 gives the product yields from the second-stage reactor, plotted against the severity index. In making this plot, the product yields are normalized after excluding the components that are either nonreactive to or bypassing the ZSM-5 catalyst, such as C_4^- paraffins and the reactor-wax. The products include C_5-C_{11}, alkylate, C_{12}^+, and C_4^-. The alkylate was estimated from alkylating first the butene and then propylene with i-butanes. When the severity indeces were less than 1.0, there was excess propylene and butenes. In this plot, the excess olefins were converted to "Cat-Poly" gasoline. The small amount of C_{12}^+ can be separated out using conventional refinery separation processes and marketed as a distillate blending stock. All other components are gasoline stocks except for C_3^- and some butanes. If one excludes the Cat-Poly gasoline, the maximum gasoline yield occurred at severity indeces beteen 0.8 to 1.0. At lower severities, the alkylate yields were low because of the low yield of i-butanes. At higher severities, the alkylate yields were also low because of low yield of light olefins. In addition, high severity resulted in the formation of more aromatics, and propane and butanes which further lowered the gasoline yields as shown in Slides #16 and 17. Slide #17 also shows the octane number of the raw liquid hydrocarbon collected in the cold and chilled condensers of the two-stage pilot plant. The research octane

without tetraethyl lead reached above 90 when the severity indeces exceeded 0.4. The octane number increased only slowly with increasing severity.

Since methane and ethane are lower-valued products, means for producing low methane + ethane yields were investigated. In the next few slides, detailed results from Runs CT-256-4 and -5 will be discussed. Slide #18 summarizes the performance from these two runs. Run CT-256-4 used the same F-T catalyst as that used in Run CT-256-3. The catalyst was also activated in the same way. But it was operated at a higher pressure, 2.51 MPa (350 psig), and slightly lower temperature (257°C) practically all the time. This resulted in low methane + ethane yields (less than 5.0 wt%). Run CT-256-5 demonstrated an even lower methane + ethane yield using a different F-T catalyst and low temperature (240-250°C). However, the corresponding reactor-wax yields were increased substantially when the methane + ethane yields became low. These reactor-wax and methane yields data together with similar data from Run CT-256-3, are summarized in Slide #19. Data from several other references [Benson et. al., (1954), Dry (1981), Farley and Ray (1964), Kunugi et. al., (1968), Sakai and Kunugi (1974), and Schlesinger et. al., (1951)] are also included. Data scattering is expected in this case since this relationship of reactor-wax versus methane depends on many variables, including catalysts, bubble-column designs, and operating conditions. However, the

relationship is well-established.

Another interesting result obtained during these three runs is the difference in the oxygenate yields, as shown in Slide #20. In Run CT-256-3, data from 2.51 MPa (350 psig) operation show substantially higher oxygenate yields and acid numbers than those from 1.48 MPa (200 psig) operation. Similar trends were observed in the 2.51 MPa operation of Run CT-256-4 except that the acid numbers were much higher than those of Run CT-256-3 at a similar pressure. We intend to analyze samples from Run CT-256-3 to re-confirm this finding. This trend of higher oxygenate yield at a higher operating pressure is consistent with observation by others (Hall, et al., 1952). In Run CT-256-5, the low methane + ethane F-T catalyst also gave higher oxygenates in the reactor-wax and higher acid numbers although the oxygenate content of the reactor-wax was not as high as that of Run CT-256-4.

One of the major objectives of Run CT-256-4 was to evaluate methods for separating reactor-wax from F-T catalyst slurry. The most successful method was to use an on-line catalyst settling vessel as shown in Slide #21. A quantity of catalyst slurry was introduced into the settling vessel and was allowed to settle for a specified length of time. The decanted reactor-wax was then removed from the vessel through the dip-tube. The remaining highly concentrated slurry was finally pressured back into the reactor. A "solvent pot" was installed

above the settling vessel for introducing a solvent when needed. A series of settling studies were carried out and results are summarized in the next slide (Slide #22). Good reactor-wax separation was successfully demonstrated. We also found that the use of a magnet, dilution of slurry with dodecane, higher dip-tube position and higher temperature all contributed to an improvement of the separation.

IV. Conceptual Process Design and Scoping Cost Estimate

The last task of the contract was to perform a conceptual process design and scoping economic evaluation based on the data obtained so far. Slide #23 shows the objectives, basis, and results from this scoping economic study. The major objectives are twofold. The first is to see how all the process units and equipment fit together. The other is to provide guidance for future research and development. The capacity of the plant is 27,000 BPSD at a Wyoming location. The plant is a battery limits plant using a clean synthesis gas from a BGC/Lurgi slagger processing a Wyoming coal. The process diagram and designs of major equipment were completed. A simplified process flow diagram will be shown in the next slide (Slide #24). The investment cost using a mid-1983 instantanteous basis is estimated at $700 million. The clean synthesis gas is heated up to a specified temperature and bubbled through the F-T bubble-column reactor. Since the feed H_2/CO ratio is lower than the required ratio, a small quantity of steam is fed in with the

gas so that the water-gas shift reaction taking place in the F-T reactor will provide a proper H_2/CO ratio. This concept has been mentioned by Koelbel and Ralek previously (Koelbel and Ralek, 1980). A reactor-wax separation device is used to obtain a low solid-content reactor-wax stream. The concentrated slurry is sent back to the slurry reactor. The rest of the scheme after the fixed-bed ZSM-5 reactor contains usual refinery processing units and is self-explanatory.

V. Future Work

The last slide (Slide #25) shows the tasks under the current contract. The title of the contract is "Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels." The objective is to develop the two-stage process for converting low H_2/CO ratio synthesis gas to a high yield of gasoline and distillate. The emphasis is to establish low methane + ethane mode operation. Those are the five tasks as listed here. The first task is to establish a low methane + ethane mode two-stage operation. As we have explained before, this mode is expected to yield large amount of reactor-wax. The second task is to explore the means of upgrading the reactor-wax. The third task is to study the hydrodynamics of slurry F-T reactors for a better understanding of their operation. The fourth task is to evaluate various liquid hydrocarbon products. The last task is to update the conceptual process design and scoping economics.

VI. References

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SLIDE # 1

CONTRACT TITLE

Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline (DE-AC22-80PC30022)

Contract Period: October 1, 1980 — April 30, 1983

OVERALL OBJECTIVE

To develop a Two-Stage Slurry Fischer-Tropsch/ZSM-5 Process for Direct Conversion of Syngas to High Octane Gasoline

STATUS OF PROJECT

- Three slurry F-T catalysts (containing $Fe/Cu/K_2CO_3$) were evaluated. One catalyst demonstrated high activity and long-term stability and produced 815 gHC/gFe in eighty-six days.
- A second-stage ZSM-5 catalyst accumulated eighty-seven days on-stream time with two regenerations. It satisfactorily converted the F-T products into high octane gasoline. The gasoline showed satisfactory oxidation stability.
- Effects of feed H_2/CO ratio, pressure, and feed-gas velocity for the slurry F-T reactor were studied. Addition of a potassium-salt to reduce the methane + ethane yield was also demonstrated.
- Slurry reactor hydrodynamic studies were performed with hot and cold glass bubble-columns and the BSU slurry reactor.

SLIDE # 3

STATUS OF PROJECT (cont'd.)

- A complex analytical scheme for defining F-T products was developed.
- A conceptual design and scoping cost estimate of a battery limit 27,000 BPSD plant from clean synthesis gas was completed.
- Methane + ethane selectivities as low as 2-5 wt % for the F-T synthesis were demonstrated by using either higher pressure and/or lower temperature or a new catalyst. However, reactor-wax yields as high as 85 wt % were also obtained.
- An on-line settling method was demonstrated to effectively separate a low solid-content reactor-wax from the F-T catalyst slurry

SLIDE # 4

MAJOR HIGHLIGHTS OF PILOT PLANT RUNS

Run CT-256-3

- Smooth long-term operation
- Process variable studies of the slurry F-T reactor
- Addition of a potassium-salt
- Establishment of a temperature policy to monitor the second-stage operation at constant severity
- Activity was greatly reduced and the methane + ethane yield increased after a F-T catalyst was exposed to air

SLIDE # 5

MAJOR HIGHLIGHTS OF PILOT PLANT RUNS (cont'd.)

Run CT-256-4

- Achieved low methane + ethane yield (3-5 wt %) by using the F-T catalyst used in Run CT-256-3 at higher pressure and/or lower temperature
- Demonstrated on-line settling method to separate a low solid-content reactor-wax from the catalyst slurry
- Demonstrated high reactor-wax yield (>50 wt %)
- The F-T hydrocarbon liquid and aqueous phase had higher acid numbers

SLIDE # 6

MAJOR HIGHLIGHTS OF PILOT PLANT RUNS (cont'd.)

Run CT-256-5

- Evaluated a new F-T catalyst which resulted in methane + ethane yields less than 4 wt %. Reactor-wax yields as high as 85 wt % were obtained.
- Demonstrated that a F-T catalyst could be activated without using a separate pretreatment step
- The F-T hydrocarbon liquid and aqueous phase had higher acid numbers

SLIDE # 7

RUN CT-256-3

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN

Catalyst: I-B, $Fe/Cu/K_2CO_3$

Pretreatment:

Temperature, °C	282
Pressure, MPa	1.14
H_2/CO Molar Ratio	0.7
Space Velocity, NL/gFe-Hr	2.4
Total Time-on-Stream, Hrs.	9.5

Synthesis

Temperature, °C	259-267
Pressure, MPa	1.14-2.51
H_2/CO Molar Ratio	0.6-1.0
Space Velocity, NL/gFe-Hr	1.3-3.4
Total Time-on-Stream, Days	86
H_2 + CO Conversion, Mol %	54-93
Methane + Ethane Yield, Wt %	6-18
Reactor-Wax Yield, Wt %	3-13

SLIDE # 8

RUN CT-256-3 (Cont'd.)

FIXED-BED ZSM-5 REACTOR

Catalyst: II-B, ZSM-5

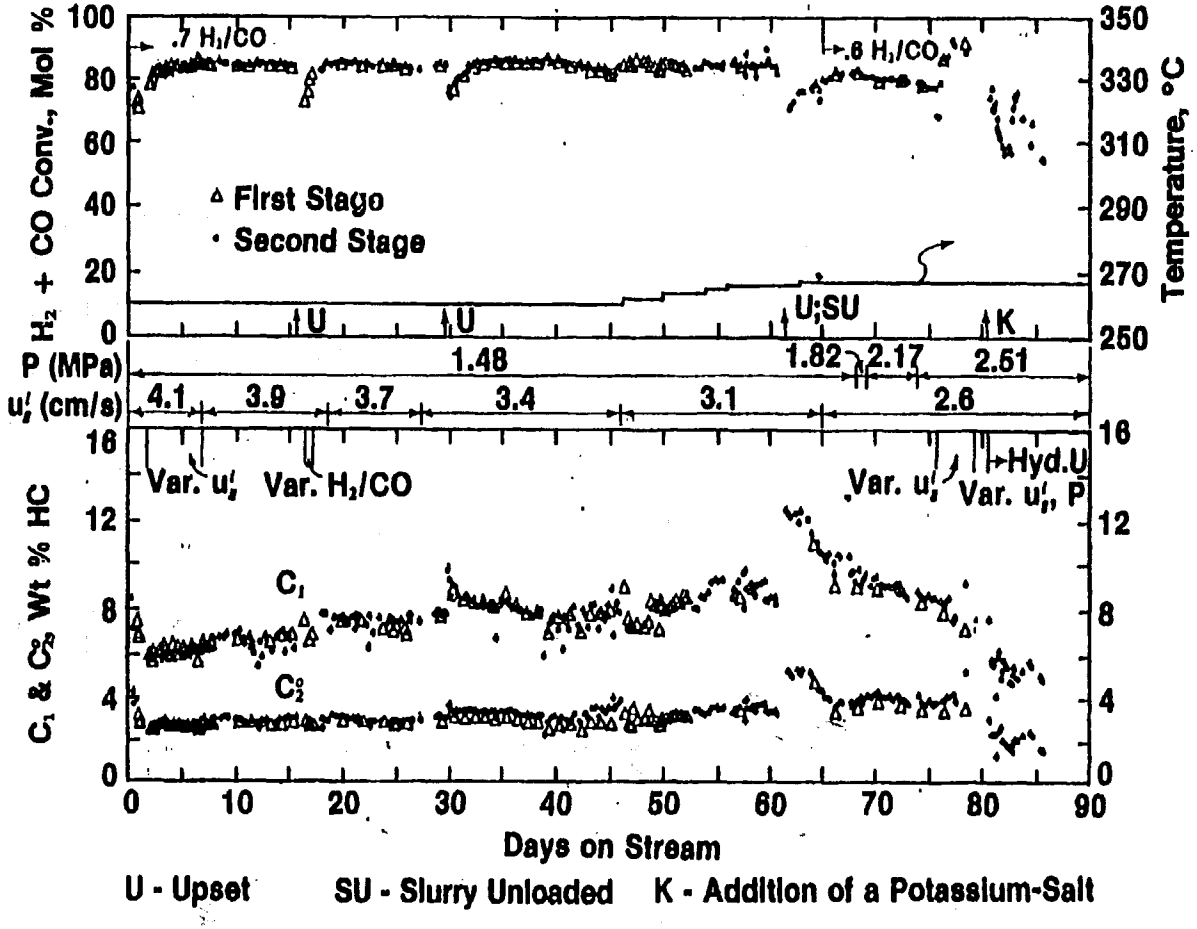
Reaction:

Inlet Temperature, °C	288-466
Outlet Temperature, °C	353-396
Pressure	Cascaded
GHSV (STP), 1/Hr	1350-4580
Total Time-on-Stream, Days	67

SLIDE #9

SYNTHESIS GAS CONVERSION AND METHANE & ETHANE YIELD

(RUN CT-256-3, 1ST-STAGE CATALYST I-B:PPTD Fe/Cu/K_2CO_3; 2ND-STAGE CATALYST II-B:ZSM-5)

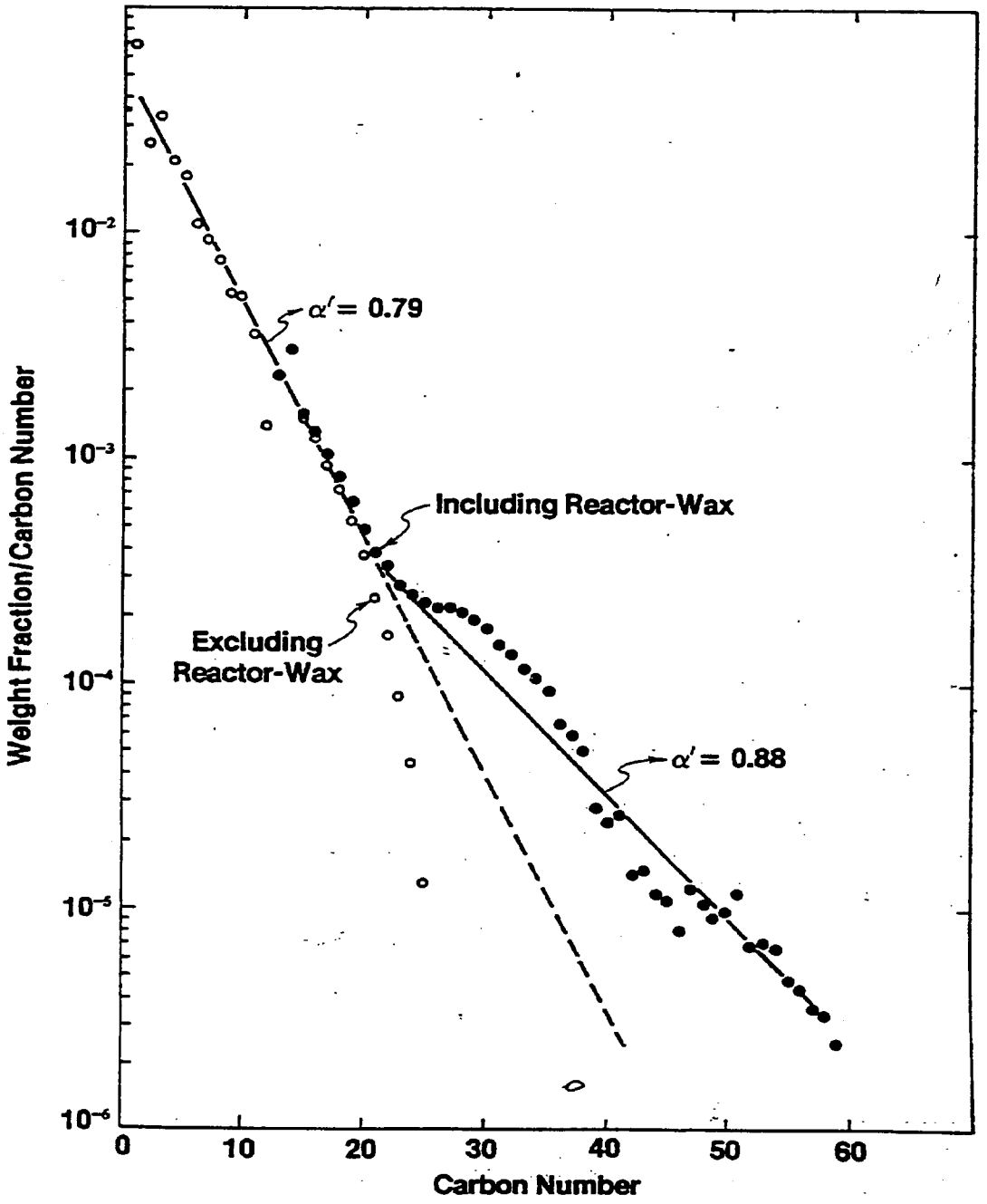


U - Upset SU - Slurry Unloaded K - Addition of a Potassium-Salt

SLIDE # 10

SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE FISCHER-TROPSCH PRODUCTS

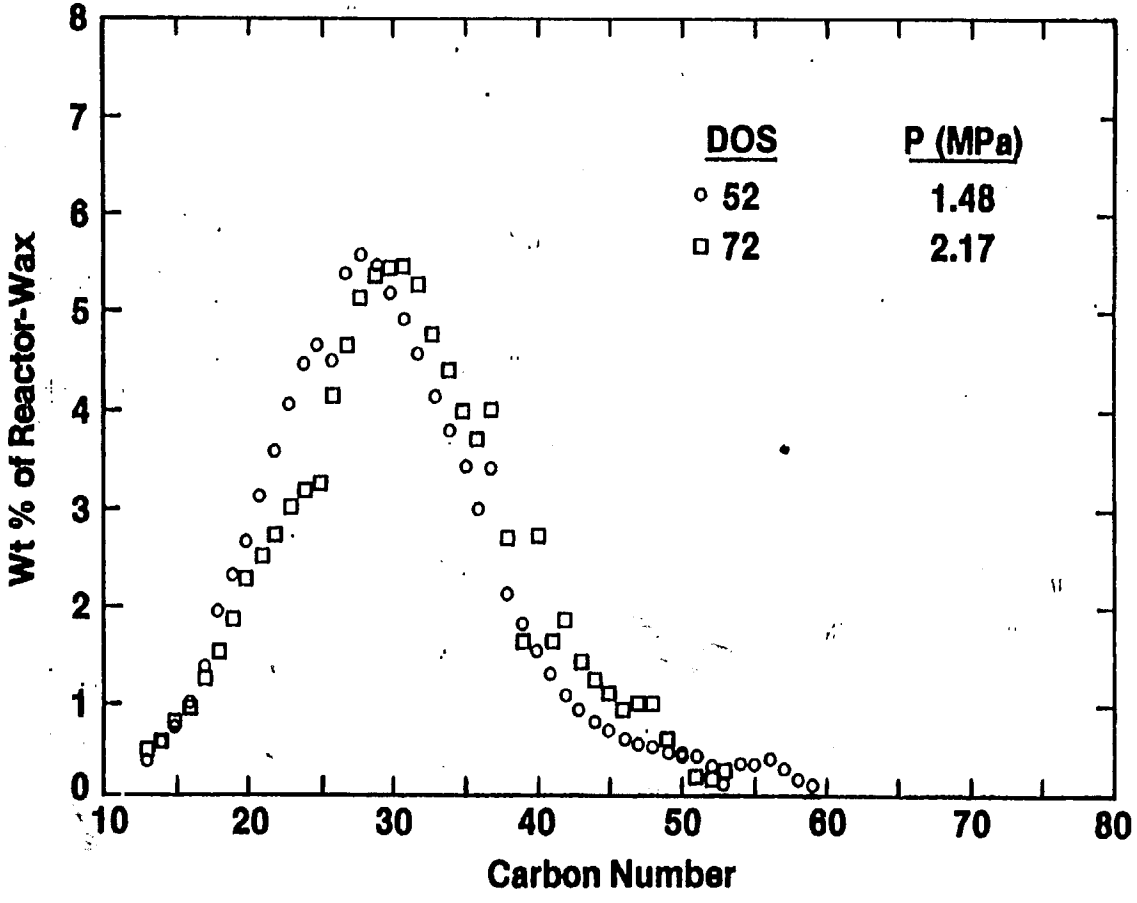
(Run CT-256-3, 11.5 DOS Reactor-Wax Yield — 9.5 wt %)



SLIDE # 11

EFFECT OF REACTOR PRESSURE ON REACTOR-WAX CARBON-NUMBER DISTRIBUTION

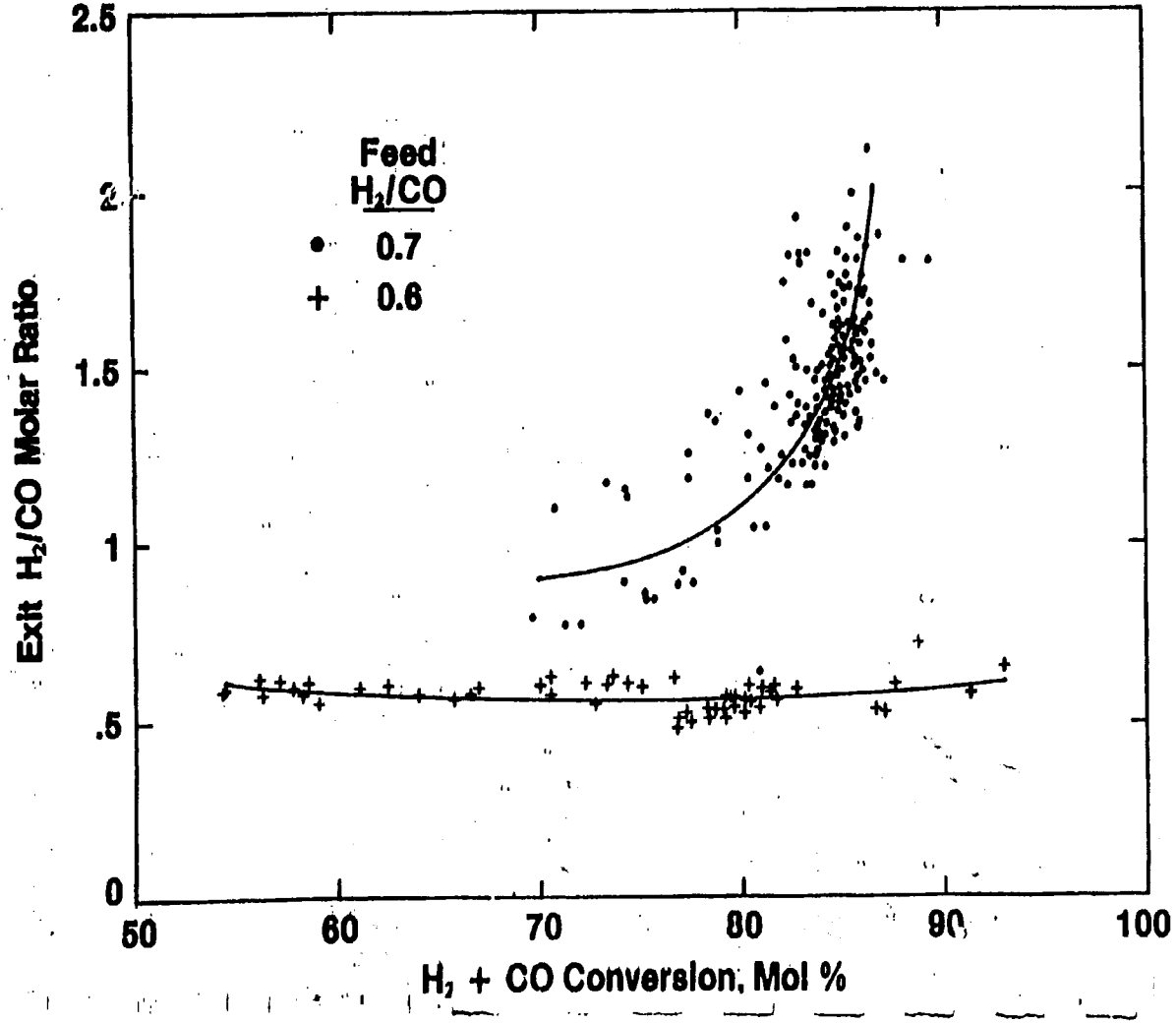
(Run CT-256-3)



SLIDE # 12

EXIT H_2/CO RATIO OF FIRST-STAGE SLURRY FISCHER-TROPSCH REACTOR

(Run CT-256-3)



SLIDE # 13

EFFECT OF SUPERFICIAL FEED-GAS VELOCITY ON SLURRY FISCHER-TROPSCH REACTOR PERFORMANCE[1] (Run CT-256-3)

DOS	75.4	76.5	77.4
Gas Superficial Velocity, cm/s	2.5	2.1	1.6
SV, NL/gFe-hr	3.12	2.53	1.95
H_2 + CO Conv., Mol %	77.1	87.2	93.1
Methane, Wt % HC	8.8	8.5	7.8
Methane + Ethane, Wt % HC	12.7	12.6	12.2

[1]0.6 H_2/CO, 267°C, 2.51 MPa

SLIDE # _1

EFFECT OF PRESSURE ON SLURRY FISCHER-TROPSCH REACTOR PERFORMANCE[1] (Run CT-256-3)

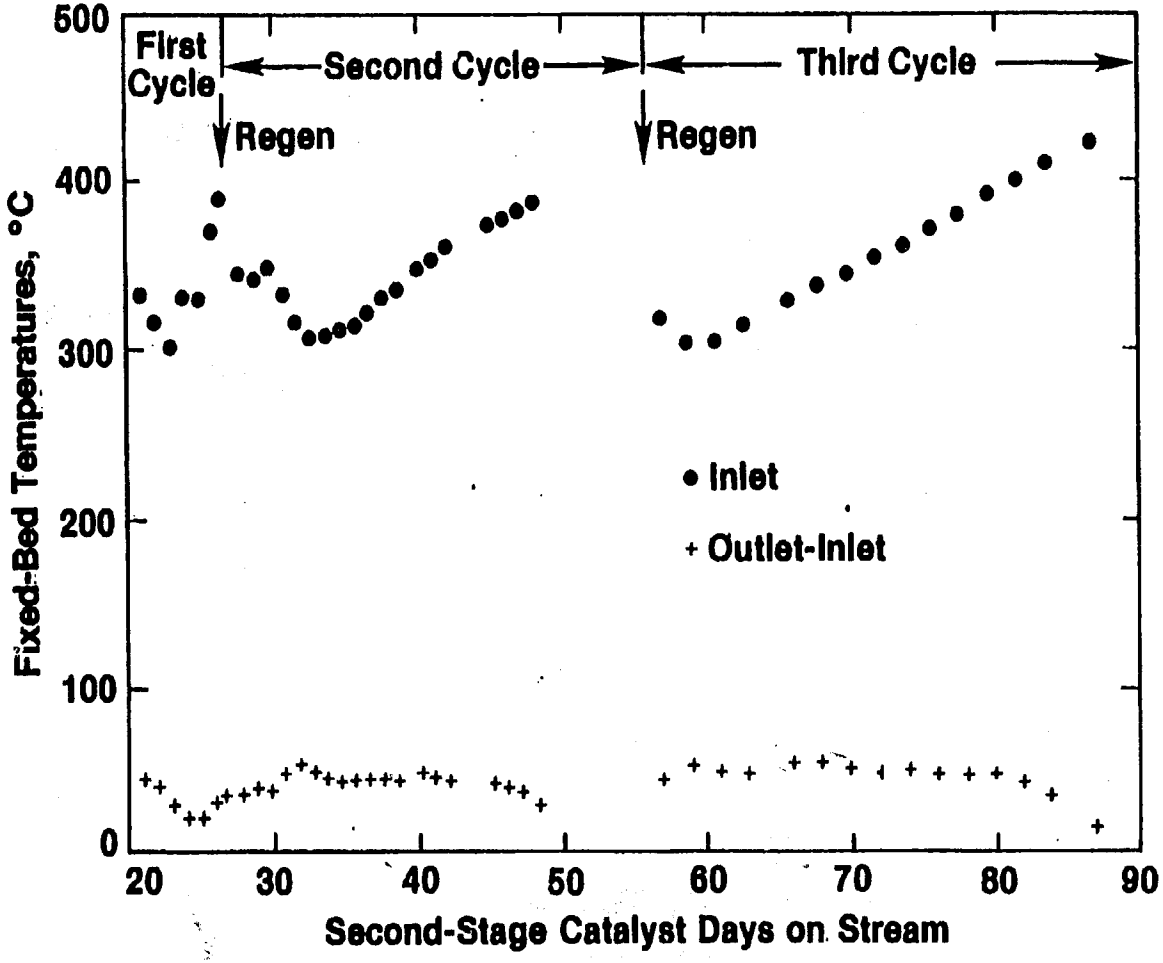
DOS	66.8	68.8	72.4	74.8
Pressure, MPa	1.48	1.82	2.17	2.51
SV, NL/gFe-Hr	1.95	2.32	2.77	3.12
H_2 + CO Conv., Mol %	81.2	81.7	79.5	77.5
Methane, Wt % HC	10.8	10.1	9.4	8.7
Methane + Ethane, Wt % HC	14.8	14.4	13.6	12.6

[1]0.6 H_2/CO, 267°C, 2.6 cm/s superficial feed-gas velocity

SLIDE # 15

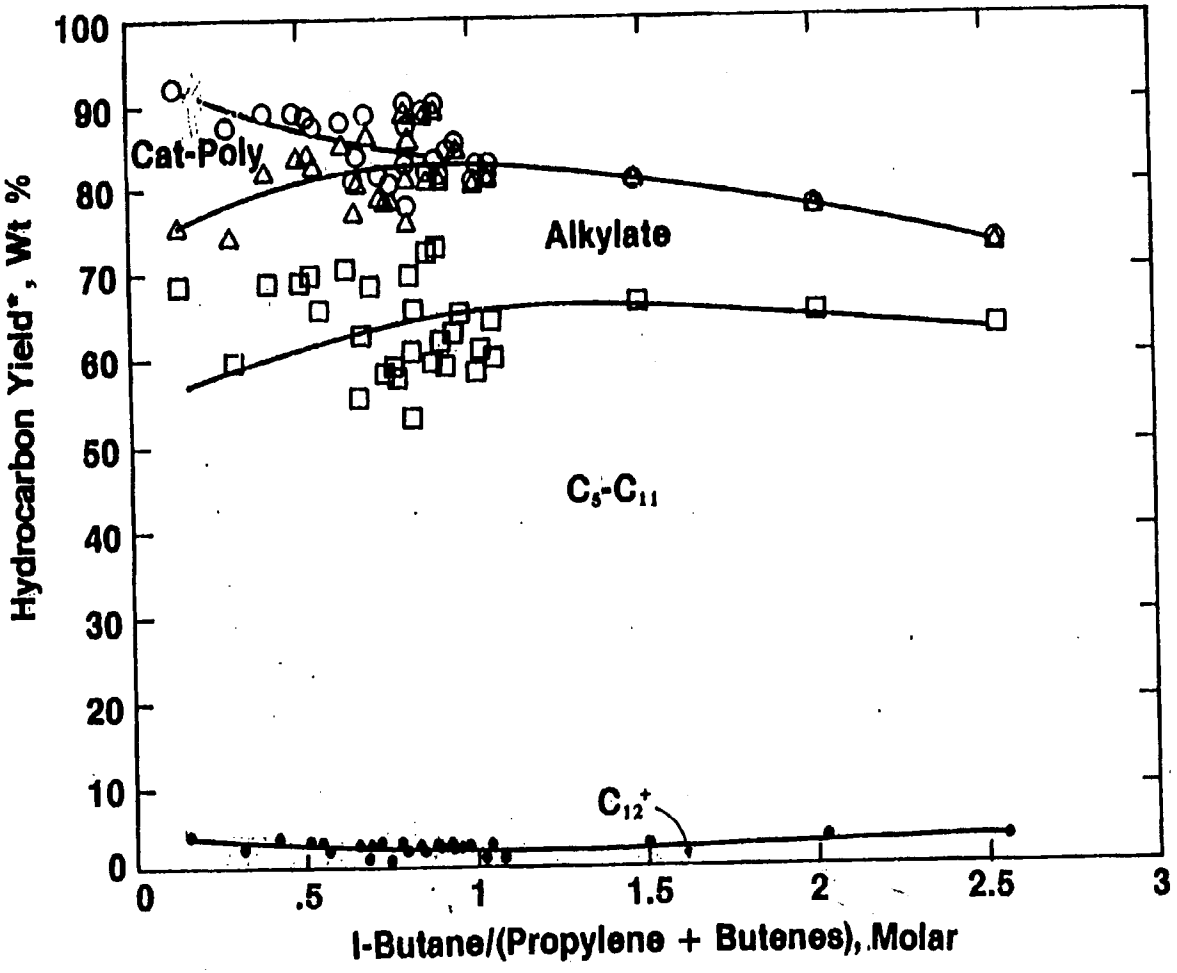
SECOND-STAGE FIXED-BED ZSM-5 REACTOR INLET AND OUTLET TEMPERATURES

(Run CT-256-3)



PRODUCT YIELDS VERSUS SECOND-STAGE OPERATING SEVERITY

(Run CT-256-3)

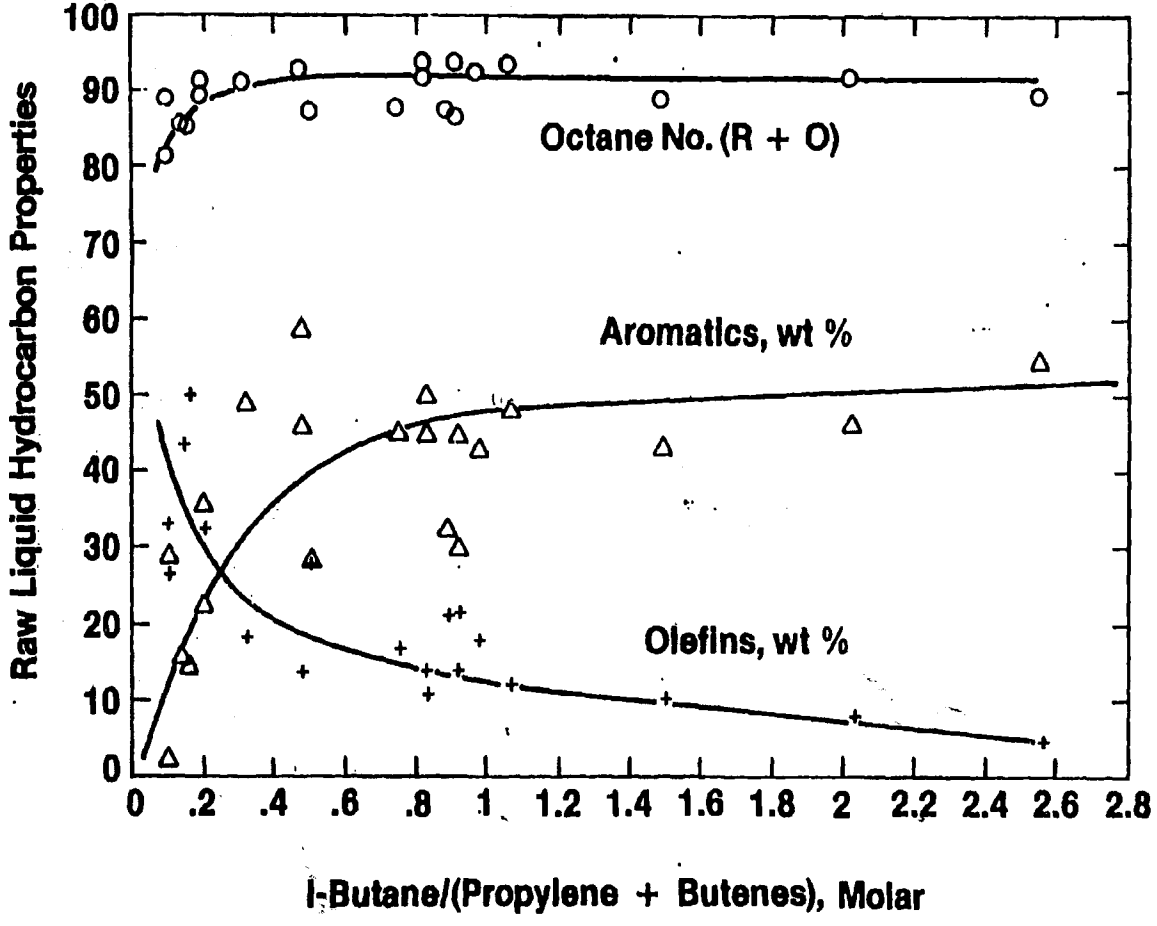


*Excluding C_4^- paraffins in feed and reactor-wax

SLIDE # 17

SECOND-STAGE
RAW LIQUID HYDROCARBON PROPERTIES

(Run CT-256-3)

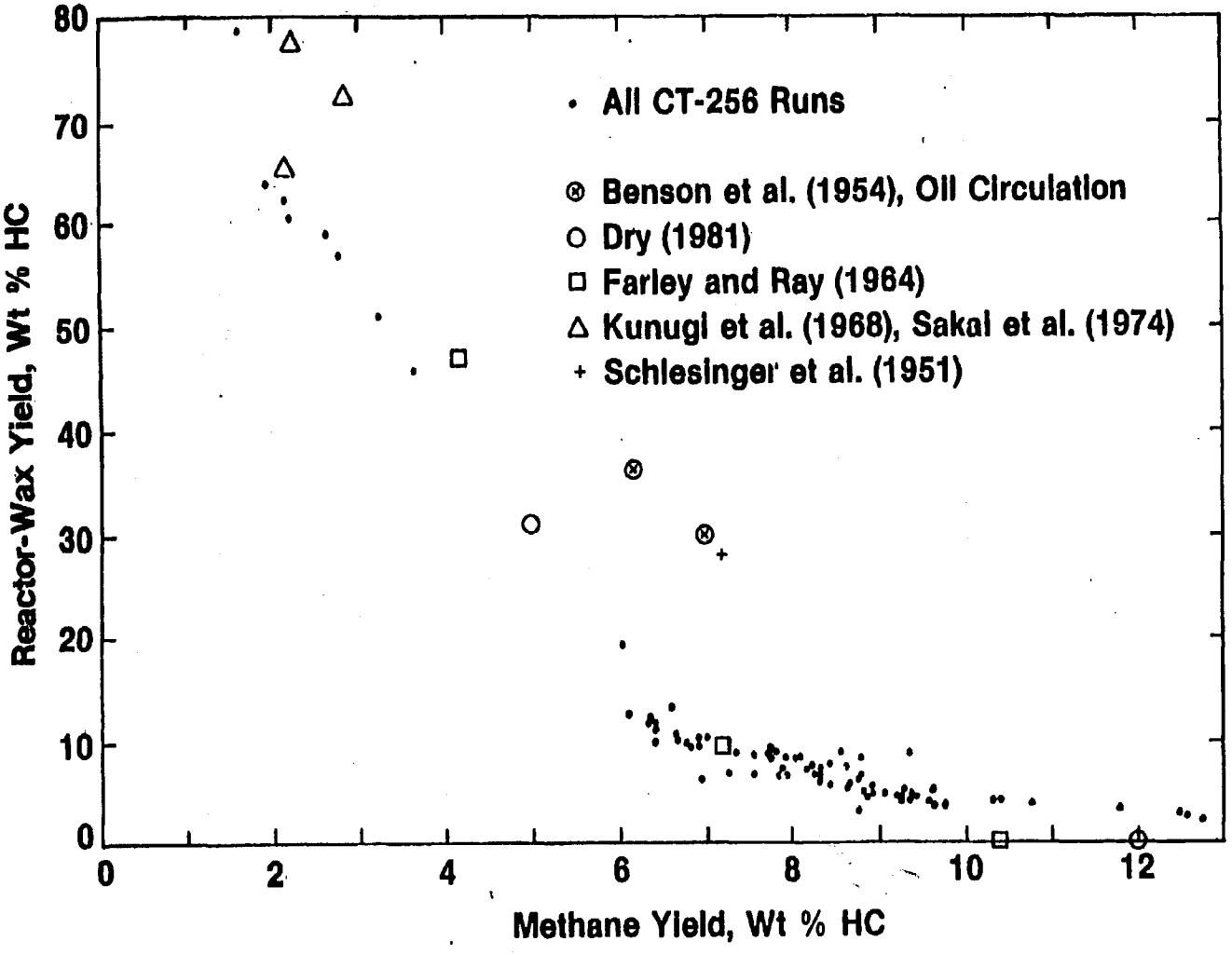


SLIDE # 18

SLURRY FISCHER-TROPSCH REACTOR PERFORMANCE (Runs CT-256-3, -4, and -5)

	Runs		
	CT-256-3	CT-256-4	CT-256-5
Catalysts ($Fe/Cu/K_2CO_3$)	I-B	I-B	I-C
Pretreatment:			
Temperature, °C	282	280	—
Pressure, MPa	1.14	1.14	—
H_2/CO Molar Ratio	0.7	0.7	—
Space Velocity, NL/gFe-Hr	2.4	1.56	—
Total Time-on-Stream, Hrs	9.5	9.5	—
Synthesis			
Temperature, °C	259-267	257-280	240-250
Pressure, MPa	1.14-2.51	1.14-2.51	1.48
H_2/CO Molar Ratio	0.6-1.0	0.7	0.7
Space Velocity, NL/gFe-Hr	1.3-3.4	1.2-6.5	2.1-2.7
Total Time-on-Stream, Days	86	37	13
H_2 + CO Conversion, Mol %	54-93	17-75	50-70
Methane + Ethane Yield, Wt %	6-18	3.5-5.0	1.6-3.5
Reactor-Wax Yield, Wt %	3-13	46-51	57-85

REACTOR-WAX YIELD VERSUS METHANE YIELD



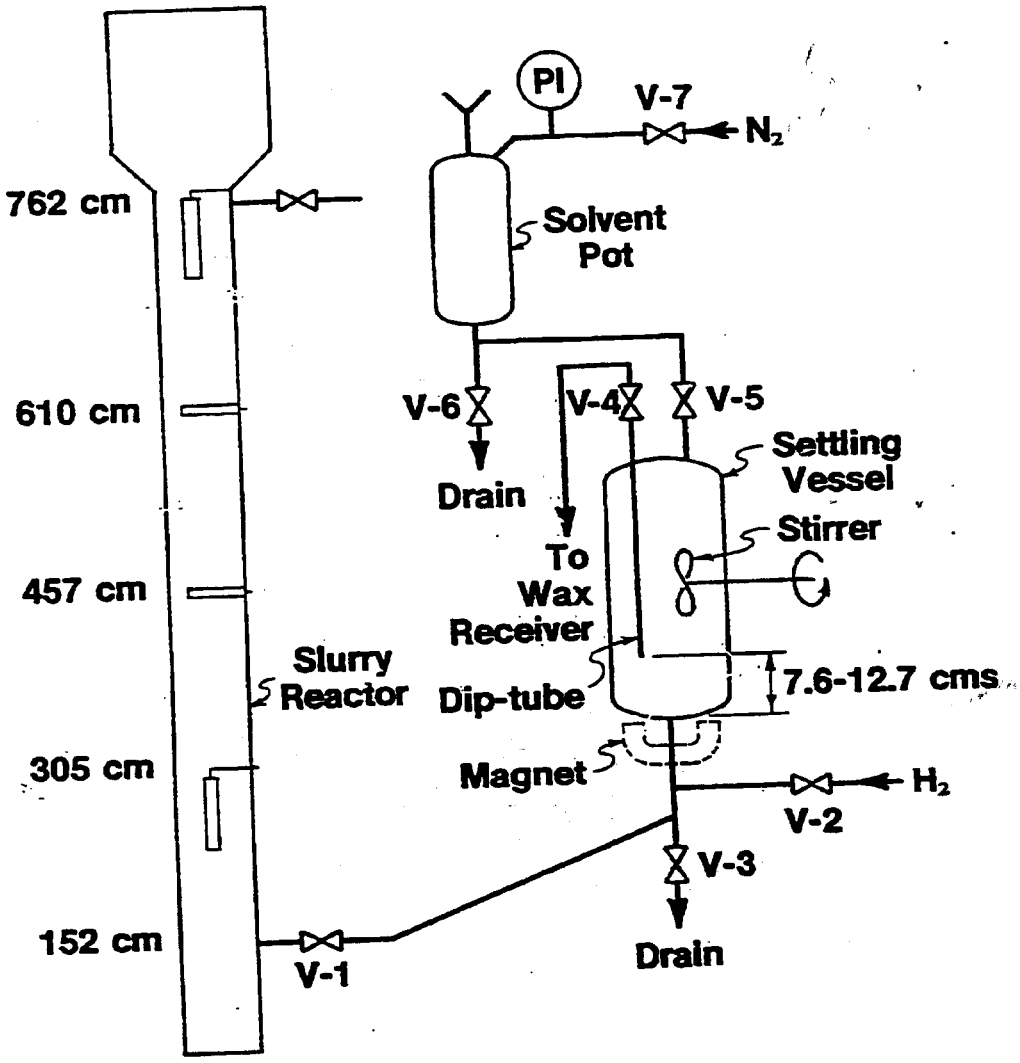
SLIDE # 20

OXYGENATES IN FISCHER-TROPSCH PRODUCTS

Run No.	CT-256-3		CT-256-4	CT-256-5
Catalysts ($Fe/Cu/K_2CO_3$)	I-B		I-B	I-C
Pressure, MPa	1.48	2.51	2.51	1.48
Wt % Oxygenates				
HC Liquids	12-17	27	—	—
Reactor-Wax	4	13	13	7
Aqueous Phase	23-41	—	—	—
Total HC	7-10	14	—	—
Acid Number (mg KOH/g)				
HC Liquids	1-2	2-3	13-32	27
Aqueous Phase	1-2	3	35-109	92

SLIDE # 21

SCHEMATIC OF A CATALYST SETTLING VESSEL FOR FISCHER-TROPSCH REACTOR-WAX REMOVAL



SLIDE # 22

RESULTS FROM F-T SLURRY SETTLING STUDIES

- A reactor-wax stream containing less than 0.2 wt % of catalyst could be obtained after one hour at 177-204°C
- Use of magnet was beneficial
- A continuous H_2 purge at 1 mL/s was detrimental
- The dilution of slurry with an equal amount of dodecane significantly reduced settling time
- Higher dip-tube position and temperature improved the separation

SLIDE #23

PROCESS ECONOMIC EVALUATION

Objectives

- To study the layout of process units and equipment
- To provide guidance for future research and development

Basis

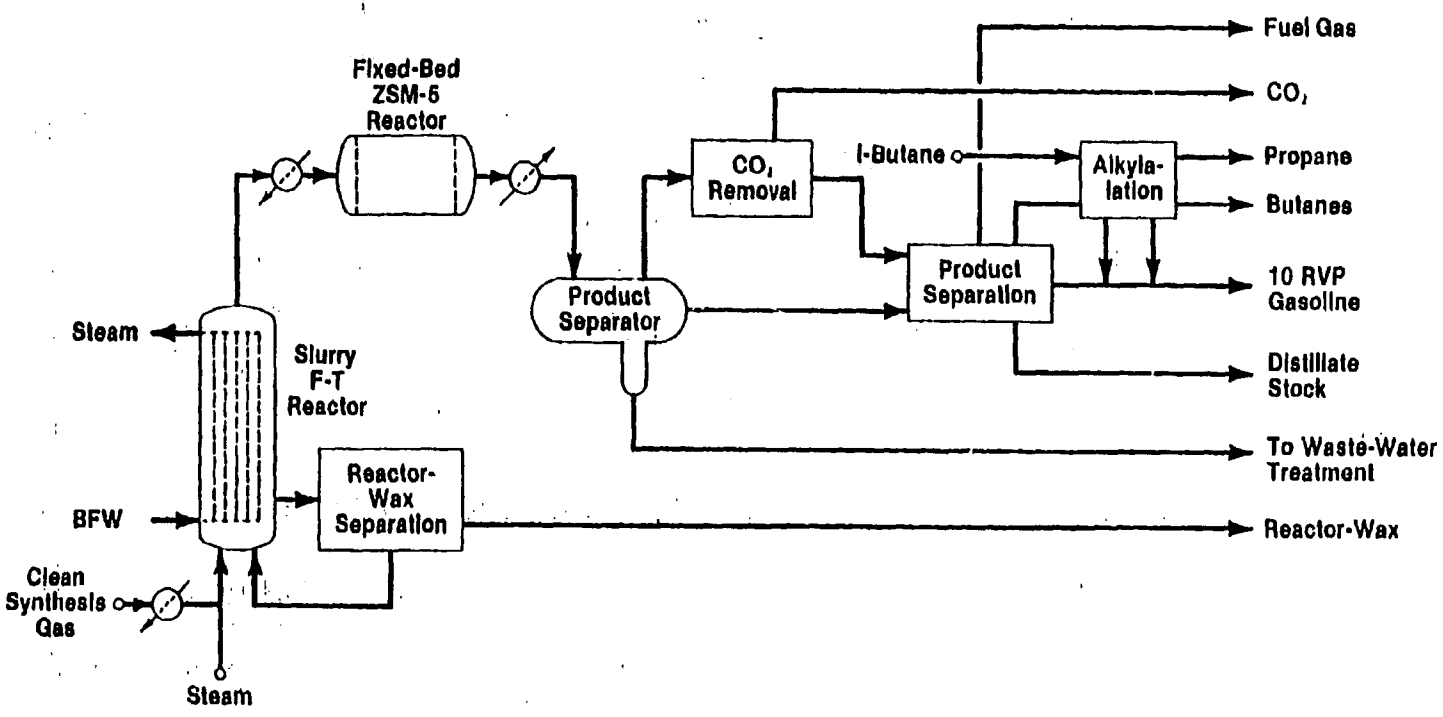
- 27,000 BPSD of 10 RVP gasoline at a Wyoming location
- Battery limited plant fed with a clean synthesis gas from a BGC/Lurgi slagger processing a Wyoming coal

Results

- Process diagram and designs of major equipment were completed
- Investment cost is estimated at $700 million using mid-1983 instantaneous basis

SLIDE #24

CONCEPTUAL PROCESS SCHEME FOR A TWO-STAGE SLURRY F-T/ZSM-5 PROCESS



SLIDE # 25

FUTURE PLAN

CONTRACT TITLE

Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels (DE-AC22-83PC60019)

Contract Period: June 8, 1983 to March 7, 1985

- Evaluate two F-T catalysts and to perform a long-term stability test and process variable study using a selected catalyst
- Explore means of upgrading the reactor-wax
- Study hydrodynamics of slurry F-T reactors
- Evaluate F-T, gasoline, and distillate products
- Study conceptual process design and scoping economics