# TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS. QUARTERLY REPORT, 1 OCTOBER-31 DECEMBER 1984 

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THO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS

QUARTERLY REPORT FOR THE PERIOD<br>1 OCTOBER - 31 DECEMBER, 198A

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## I. Abstract

This Quarterly Report describes the conclusion of the seventh run of the Two-Stage Fischer-Tropsch/ZSM-5 pilot plant, as well as the startup and early operation of the eighth run. The Iatter run uses Catalyst I-C at moderate pressures and temperatures to produce low methane + ethane yields. Also in this report are results of hydrodynamic studies performed in our 5.1 cm ID hot-flow bubble-column, using a 2 mm single orifice feed-gas distributor. Finally, we discuss some of the results of mathematical model studies of using staged CSTRs as alternatives to bubble-column reactors.

## II. Objective and Scope of Work

The general objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low $\mathrm{H}_{2} / \mathrm{CO}$ 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 will be directed toward production of hydrocarbons containing less than $8 \mathrm{wt} \%$ 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. Dne of these catalysts may be provided by DOE's alternate catalyst development projects.

Task 2 - Scoping Studies of Fischer-Tropsch
Reactor-Wax Upgrading
The methods for upgrading the reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated.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 reacto-wax upgrading processes shall be evaluated. Gasoline octane and distillate cetane quality, as well as pour points should also be determined.

Task 4 - Slurxy 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 BSU 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.

## III. Summary of Progress to Date

The seventh run of the two-stage Fischer-Tropsch pilot plant, which had accumulated 86 days on stream by the end of the last quarter, was concluded after a total of 98 DOS. The final two weeks of this run were spent unsuccessfully trying to increase $\mathrm{H}_{2}+\mathrm{CD}$ conversion. Following routine maintenance, Run CT-256-8 was started using Catalyst I-C at moderate temperatures and pressures to obtain low methane + ethane selectivities. After 25 days on stream, four major observations can be made:

- The single-orifice feed-gas distributor has little or no effect on reactor performance.
- Activated Catalyst I-C has the ability to retain a large portion of its activity when removed from the reactor and then reloaded.
- Fresh Catalyst I-C did not activate when added to the reactor during the run.
- Methane + ethane selectivities have remained low throughout the run (2.1-2.5 wt \%).

Bubble-column hydrodynamic studies continued this quarter with a 2 mm single orifice distributor being evaluated in the 5.1 cm ID tall hot flow column. This distributor gave substantially larger bubbles and lower holdups than other orifice-type distributors we have studied.

This report also outlines a new mathematical model used to explore the potential advantages of a series of mechanically agitated slurry Fischer-Tropsch reactors (CSTRs) over bubble-column (BC) reactors. Specifically, the model predicts that tolerance to higher catalyst loading in a series of three commercial-size CSTRs leads to higher throughputs than in a commercial-size bubble-column having the same total volume. For instance, a $40 \%$ increase in catalyst loading ( $25 \mathrm{wt} \%$ in the BC vs $35 \mathrm{wt} \%$ in the CSTRs) results in a 40-100\% increase in throughput for a target $\mathrm{H}_{2}+\mathrm{CD}$ conversion of $88 \%$. This predicted increase in throughput depends strongly on the mass transfer limitations of the base case bubble-column.

Finally, the Restrictive Distribution Appendix of this report describes the results of scoping hydrocracking studies of Fischer-Tropsch reactor-wax.
A. Task 1 - Process Studies in Two-Stage Bench-Scale Unit

1. Run CT-256-7 - Conclusion

Run CT-256-7 of the two-stage Fischer-Tropsch/ZSM-5 pilot plant was voluntarily ended on October 11, 1984, after 98 days on-stream. The main objective of the run was to evaluate catalyst I-B for low methane + ethane mode operation. A detailed description of the first 86 days of the run appears in the July-September Quarterly Report. The last twelve days of the run were used to try and increase the $\mathrm{H}_{2}+\mathrm{CO}$ conversion while maintaining the low methane + ethane selectivities ( $<6.0 \mathrm{wt} \%$ ) we had observed throughout the run. This short period was therefore characterized by changing conditions and wide swings in $\mathrm{H}_{2}+\mathrm{CO}$ conversion. One flow interruption also occurred, making any conclusions on performance difficult. A brief description of these final twelve days follows.

The material balance data for this run are given in Appendix A. Tables A-1 and A-3 summarizes the operating conditions and results for the first-stage operation. Tables A-2 and A-A give the corresponding hydrocarbon product compositions. Similarly, Tables A-5 and A-6 report the operating conditions and.results and hydrocarbon product compositions for second-stage operation. Only those balances, which had balance recoveries between $90-110 \mathrm{wt} \%$, are reported. Also, the recovery of hydrocarbons produced is within $\pm 20 \%$ of the expected hydrocarbons production (i.e. $204 \mathrm{gHC} / \mathrm{Nm}{ }^{3}$ $\mathrm{H}_{2}+\mathrm{CO}$ converted). Since not all the $\mathrm{F}-\mathrm{T}$ hydrocarbon liquid streams (light and heavy hydrocarbons and reactor-wax) were analyzed for detailed composition, a $\mathrm{CH}_{2} .06$ composition was assumed for 211 these streams for estimation of the hydrocarbon production per $\mathrm{Nm}^{3} \mathrm{H}_{2}+\mathrm{CD}$. The second-stage gasoline on the other hand was assumed to be $\mathrm{CH}_{1} .7$, whenever the detailed composition was not available.

## a. First-Stage Fischer-Tropsch Reactor Operation

As described in the last Quarterly Report ( QR ) the $\mathrm{H}_{2}+\mathrm{CO}$ conversion had been holding at $40 \mathrm{~mol} \%$ (at $277^{\circ} \mathrm{C}, 2.51 \mathrm{MPa}$ ) since the shutdown at 76 DOS. Figure 1 is an extension of the run plot which appeared in the last GR, showing the conversion, and metharie and ethane selectivities for the entire run. The list of major events appears in Table 1, also a continuation from the last gR.

The last major event described in the last GR was the decreasing of the temperature to $280^{\circ} \mathrm{C}$. Several hours after this, a valve in the feed-gas system malfunctioned, causing the reactor to be under nitrogen for 15 hours. When the synthesis conditions were resumed, the $\mathrm{H}_{2}+\mathrm{CO}$ conversion had fallen to $30 \mathrm{~mol} \%$, and the methare + ethane yield was up to over $9.0 \mathrm{wt} \%$.

Feeling the high pressure operation may have been inhibiting the catalyst activity, as was observed in Run CT-256-6 with Catalyst I-D, the pressure was lowered to 2.17 , then 1.48 MPa . This had only a small effect, however, raising the $\mathrm{H}_{2}+\mathrm{CO}$ conversion to $35 \mathrm{~mol} \%$ with little change in the methane + ethane selectivity.

Next, the temperature was raised back to $277^{\circ} \mathrm{C}$, and the conversion reached 60 mol \%. Increasing the temperature should also have increased the methane + ethane yield, but the opposite occurred; the methane + ethane yield dropped rapidly down to 6.7 wt $\%$. While this was happening, the $\mathrm{H}_{2}+\mathrm{CO}$ conversion was also falling, reaching $53 \mathrm{~mol} \%$ in only 36 hours.

The pressure was then increased for the last time, to 2.51 MPa at 92 DOS. The methane + ethane selectivity decreased as expected, to $4.9 \mathrm{wt} \%$, but the conversion continued to decline at a high rate, falling to 30 mol $\%$ by the end of the run. This type of behavior had not been observed previously under identical conditions (67-84 DOS), so it was logical to assume that the catalyst had somehow been damaged when the flow was interrupted at 85 DOS. This makes any conclusions on the end-of-run performance risky. Still, a great deal had been learned to that point, as described in the last QR.
2. Run CT-256-8 - Startup

The eighth run of the two-stage pilot plant was started on November 20, 1984. The main objective of the run is to evaluate Catalyst I-C for low methane + ethane mode operation. An important incentive for evaluating Catalyst I-C is that it can be activated without a separate pretreatment step, as was demonstrated in Run CT-256-5 (Kuo, 1983).

Also, this run marked the first conclusive test of a 1 mm single-orifice feed-gas distributor in the first-stage bubble-column reactor. The same distributor was used in Run CT-256-7, but leakage around its edges prevented definitive conclusions on its performance (see July-September 1984 Quarterly Report).

By the end of this quarter, 25.5 days on-stream had been accumulated. The unit was shut down after four days on-stream for repairs to the wax withdrawal system, and is also currently shut down for the Christmas Holiday. Because of catalyst losses early in the run, $\mathrm{H}_{2}+\mathrm{CO}$ conversions have ranged from 37 to 73 mol \%, while the methane + ethane yield has been a low 2.3-2.9 wt \% of hydrocarbons produced.

Three major highlights can be reported at this point:

- The catalyst activated in an identical fashion to Run CT-256-5, indicating no adverse influence of the orifice distributor.

Catalyst which was accidently removed from the reactor regained a significiant amount of its activity when it was reloaded, the first time we have observed this ability.

- Additions of fresh Catalyst I-C did Iittle to improve converison or methane + ethane selectivity. Attempt's at activating the catalyst in-situ with high $\mathrm{H}_{2} / \mathrm{CO}$ ratio gas were also unsuccessful.

A detailed account of this run will be presented upon its completion.

## a. Fischer-Tropsch Slurry Catalyst Loading and Pretreatment, and Testing of a Single-Orifice Feed-Gas Distributor

Run CT-256-8 was initially loaded with 2300 g of Catalyst I-C: The wax medium at the start consisted of Run CT-255-5 reactor-wax. The following synthesis conditions were then established:

| Temperature, ${ }^{\circ}{ }^{\circ} \mathrm{C}$ | 250 |  |
| :--- | :--- | :--- |
| Pressure, MPa |  | 1.48 |
| $\mathrm{H}_{2} / \mathrm{CO}$ Feed Ratio, Molar | 0.67 |  |
| Superficial Feed-Gas Velocity, $\mathrm{cm} / \mathrm{s}$ | $\cdots$ | 4.42 |
| Space Velocity, NL/EFe-hr |  | $\therefore 2.0$ |

These conditions are identical to those used in Run CT-256-5, except that the space velocity there was $2.7 \mathrm{NL} / \mathrm{gFe} \mathrm{ehr}$ : A plot of the volume contraction versus time is shown in Figure 2. Also shown is the corresponding curve from Run CT-256-5. The similarity of these two catalyst activations shows that the orifice distributor was not a hindrance to the reactor performance.
b. Brief Description of Fischer-Tropsch Reactor Operation

After 22 hours, the $\mathrm{H}_{2}+\mathrm{CO}$ conversion leveled off at -70 mol \%. This level of activity is equivalent to other F-T catalyst we have used. At the same time, the methane + ethare selectivity was falling to 2.1 wt \% of hydrocarbons. By the end of the quarter, it had risen to only $2.5 \mathrm{mt} \%$.

Reactor-wax withdrawal operations were started after two days on-stream, using our continuous catalyst/wax separation and withdrawal device which had worked very well during Run CT-256-7 (see July-September Quarterly Report). This time, however, it malfunctioned, causing roughly one-third of the catalyst inventory to be removed in the wax drains. While trying to correct this, the feed-gas line to the unit.plugged at 4.3 DOS, causing further catalyst loss and forcing a cold shutdown of the reactor, with the remaining slurry still inside.

With the unit down, modifications were made to the wax withdrawal and feed-gas systems. On November 30, the run was restarted. Upon re-establishing conditions, the conversion had dropped to 37 mol \% due to catalyst losses and possible damage to the catalyst from the shutdown. Then, between six and eight DOS, most of the catalyst which had been removed in the wax drains was reloaded into the reactor. This, combined with a $20 \%$ lower feed-gas rate, raised the conversion to about 65 mol \%. The methane + ethane yield was unaffected.

Subsequently, fresh Catalyst I-C was loaded into the
reactor, but this had little or no effect on conversion or methane + ethane selectivity. Attempts were made to activate it in-situ using a high $\mathrm{H}_{2} / \mathrm{CO}$ ratio feed gas for 18 hours, but this was unsuccessful as well.

After 17 days, conversion was raised by increasing the temperature to $255^{\circ} \mathrm{C}$ and the pressure to 2.17 MPa while maintaining the same gas throughput. Five days later the pressure was dropped to 1.83 MPa because the conversion had dropped from 67 down to 60 mol \%. This did not change matters, however, because the decline continued, with the conversion dropping to 57 mol \% over the next 3.5 days. The methane + ethane yield by this time (the end of the quarter) had risen to only 2.9 wt $\%$ of hydrocarbons produced, and the wax make, which was being easily handled by the repaired wax withdrawal system, was ranging from 55-65 wt \%.

## 3. Future Work

- Continue Run CT-256-8; determine if catalyst aging rate can be reduced by changing operating conditions. Also, we will try to increase $\mathrm{H}_{2}+\mathrm{CO}$ conversion by adding catalyst which has been pretreated in a smaller bubble-column reactor.
B. Task 2-Scoping Studies of

Fischer-Tropsch Reactor-Wax Upgrading

1. $\frac{\text { Hydrocracking of Fischer-Tropsch }}{\text { Reactor-Wax }}$

Preliminary results from proprietary hydrocracking studies to upgrade F-T reactor-wax are described in the Appendix-Restrictive Distribution.
C. Task 3-Product Evaluation

1. Field-Ionization-Mass-Spectrometry (FIMS) Analysis

As discussed in the "Future Work" of the last Quarterly Report, we have sent two reactor-wax samples for FIMS analyses. The
samples were obtained from a CT-256-4 reactor-wax sample analyzed previously. The sample was separated into an oxygenates fraction and a remaining hydrocarbons fraction. By separating these two fractions we can study the fragmentation, if any, of these two classes of hydrocarbons. This will help us in interpreting the FIMS spectrum of the combined (i.e. "as is" reactor-wax) sample.

## 2. Product Analyses

The necessary product analyses to support other tasks were carried out.

## 3. Future Work

- Continue evaluation of Field-Ionization-Mass-Spectrometry (FIMS) technique.
- Continue providing product analyses to support other tasks.
D. Task 4-Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

1. Hydrodynamic Studies Using a Tall Hot-Flow Bubble-Column

We have previously reported the hydrodynamic studies in the 5.1 cim ID 9.1 m tall hot-flow bubble-column using three different distributors. The studies have revealed that the two orifice-type distributors ( 1 mm single-orifice and a 0.5 mm 3 -hole distributor) behave very similarly; but both gave lower gas holdup than a 20 micron sintered-metal plate (SMP). Even the low gas holdups produced by a 1 mm single-orifice distributor appear to be satisfactory in the slurry bubble-column reactor of the two-stage BSU as described in a previous subsection. However, the pressure drop across a 1 mm orifice distributor is expected to be high at superficial gas velocities normally encountered in a commercial-size bubble-column reactor. Hence, a larger diameter orifice distributor with a lower pressure-drop would be favored in a commercial-size reactor. We have, therefore, evaluated a 2 mm single-orifice distributor. As in the previous studies, the liquid medium used was a F-T derived paraffinic wax, FT-200. The results are compared to those obtained with the other two orifice-type distributors.

Figure 3 compares the gas holdups obtained with the three orifice-type gas distributors. The gas holdups shown for the 1 mm single-orifice and 0.5 m 3 -hole distributor were obtained from the correlation given in the last Quarterly Report. As shown in the figure, the 2 mm orifice gave substantially lower gas holdups (by $50-70 \%$ ) than those given by the other orifice-type distributors.

The bubble-size was relatively larger. Furthermore, the bubble size did not appear to change along the length of the column as observed with the other two orifice distributors. Also, large bubbles were seen to rise near the center of the column at gas superficial velocities as low as $1.1 \mathrm{~cm} / \mathrm{s}$. These large bubbles form slug-type bubble as they rise upward. These large bubbles are called slug-type because they are quite large; but unlike slugs, they do not occupy the whole column-diameter.

At superficial gas velocities greater than $1.1 \mathrm{~cm} / \mathrm{s}$, the slugging at constant frequency was observed. The frequency of slugs was, however, substantially higher (three times that for other orifice distributors). Also, the small bubbles surrounding the large slugs were relatively larger. The existence of more slugs and larger bubbles is consistent with the observed lower holdup.

## a. Effect of Static Liquid Height

Unlike the SMP distributor and the other two orifice-type distributors, the 2 mm single orifice gave the same gas holdup when the static liquid height was lowered from 7.1 m to 75 cm . In the case of the $20 \mu \mathrm{~m}$ SMP distributor, the existence of a high holdup zone of constant length at the top results in a higher gas holdup when the static liquid height is lowered. In contrast to the SMP distributor, the gas holdup in the case of the two orifice distributors ( 1 mm single orifice and $0.5 \mathrm{~mm}-3$ hole distributor) decreased when the static liquid height was lowered. This was mainly due to presence of large bubbles in the lower holdup bottom zone. In the case of the 2 mm orifice, however, the bubble size distribution and consequently gas holdup did not vary significantly along the column height. Hence, the gas holdup did not change when the static height was lowered from 7.1 m to 75 cm .

## b. Effect of Pressure

As in the case of the other three distributors, no significant differences in the hydrodynamic behavior were observed for pressure variations of 138 to 221 KPa .

## c. Other Work

Bubble flow patterns were photographed for bubble size analysis. Dynamic gas disengagement studies were also carried out to obtain the bubble size distribution. The results will be reported in the next Quarterly Report.

## 2. CSTRs as Alternative to Fischer-Tropsch Bubble-Columns: Mathematical Model Applications

In the previous Quarterly Report (July-September 1984) we described the potential advantages in using CSTRs instead of
bubble-column reactors for F-T reactions. The main features of a new mathematical model intended to explore the potential advantage of higher catalyst loading in the CSTR were also given. Here we describe in detail the new mathematical model, and present predicted results from a comparison of a comercial scale $F-T$ bubble-column reactor and a series of three commercial scale CSTRs.

The new model includes hydrodynamic correlations applicable to both bubble-columns and CSTRs. As a result, a new bubble-column model compatible with the new CSTR model was also developed. This bubble-column model is represented by a series of CSTRs, the number of stages being correlated with the asial dispersion in the liquid. The predicted bubble-column performance using this new model is quite different from that using the previous model. The major differences are a larger bubble size (7.6 versus 0.7 mm ) and a lower bubble density obtained from the kydrodynamic correlations used in the current model. This resulted in a three-fold increase in the gas-liquid mass transfer resistance (equivalent to a two-third decrease in $\mathrm{k}_{\mathrm{L}} \mathrm{a}$ ). Unfortunately; there is no information on hydrodynamics of a commercial size slurry F-T bubble-column to verify these correlations.

The major results from calculations with $25 \mathrm{wt} \mathrm{\%}$ catalyst in the bubble-column reactor and $35 \mathrm{wt} \mathrm{\%}$ catalyst loading in the CSTRs are:

- $40-100 \%$ higher gas throughput in the CSTRs at the same $\mathrm{H}_{2}+$ CO conversion ( $88 \mathrm{~mol} \%$ ) and for the same total reactor volume as that of the bubble-column. The mechanical power required to achieve the highest throughput was very small ( 1.5 watts per liter, W/L, of the reactor volume).
- The increase in throughput depends strongly on the mass transfer resistances present in the base case (bubble-column reactor).
- Based on hydrodynamic correlations used in the new bubble-column model, the mass transfer resistance is large in the bubble-column. Hence, up to $100 \%$ increase in throughput can be achieved in the CSTRs due partly to reduced mass transfer resistance by mechanical agitation.
- For the other extreme of no mass transfer limitaitions in the bubble-column, the increase in throughput is limited by the increase in catalyst loading. Hence, orly a $40 \%$ increase is expected.


## a. Assumptions

The major assumptions are:

- Mass transfer resistances only at the liquid side of the gas-liquid interface ( $\mathrm{H}_{2}, \mathrm{CO}, \mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}$ )
- Two consecutive reactions:

Fischer-Tropsch

$$
\begin{align*}
& \mathrm{CO}+(1+\mathrm{m} / 2) \mathrm{H}_{2}=\mathrm{CB}_{\mathrm{m}}+\mathrm{H}_{2} 0  \tag{1}\\
& \mathrm{r}_{1}=\mathrm{k}_{1}\left[\mathrm{H}_{2}\right][\mathrm{CO}] /\left([\mathrm{CO}]+\mathrm{k}_{1}^{\prime}\left[\mathrm{CO}_{2}\right]+\mathrm{k}_{1}{ }^{\mathrm{n}}\left[\mathrm{H}_{2} \mathrm{O}\right]\right) \tag{2}
\end{align*}
$$

Water-Gas Shift

$$
\begin{align*}
\mathrm{CO}+ & \mathrm{H}_{2} \mathrm{O}=\mathrm{H}_{2}+\mathrm{CO}_{2}  \tag{3}\\
\mathrm{I}_{2}= & \mathrm{k}_{2}\left([\mathrm{CO}]\left[\mathrm{H}_{2} \mathrm{O}\right]-\left[\mathrm{H}_{2}\right]\left[\mathrm{CO}_{2}\right] / \mathrm{k}_{2}^{\prime}\right) / \\
& \left([\mathrm{CO}]+\mathrm{k}_{1}^{\prime}{ }^{\prime}\left[\mathrm{CO}_{2}\right]+\mathrm{k}_{1}^{\prime \prime}\left[\mathrm{H}_{2} \mathrm{O}\right]\right)^{2} \tag{4}
\end{align*}
$$

- Molar contraction due to synthesis reaction is linear function of synthesis gas conversion
- Gas holdup, bubble-size and mass transfer coefficients vary with power input, and the first two vary with superficial gas velocity
- Steady-state isothermal and isobaric operation
- Perfectly mixed gas and liquid phases

The $\mathrm{F}-\mathrm{T}$ reaction rate expression includes $\mathrm{CO}_{2}$ inhibition in addition to $\mathrm{H}_{2} \mathrm{O}$ inhibition used in our previous bubble-column model. Deckwer (1984) showed that this term is essential when there is substantial $\mathrm{CD}_{2}$ present. The denominator is consistent with an Elly-Rideal mechanism, obtained when an enolic polymerization mechanism is assumed for the F-T reactions. The water-gas shift reaction rate expression has a denominator consistent with a Langmuir-Hinshelwood mechanism, and was recommended by Podolski (1974).

The gas holdup, bubble size and mass transfer coefficients are obtained from literature correlations which include the effect of mechanical agitation (for CSTR) and gas sparging (for bubble-column). The major assumption in these correlations is that hydrodynamics are a function of the total power input per unit volume. The total power input is a linear combination of the mechanical power input and the power input by gas sparging. These correlations are sumarized in Appendix B.

The liquid phase can be assumed to be well mixed in a CSTR. The mixing in the gas phase, however, can range from perfect mixing (one equivalent gas CSTR) to the equivalent of two gas CSTRs (Chapman et al., 1983). For simplicity, we assumed that the gas phase is well mixed as well. This assumption is valid for high mechanical power input.

## b. Material Balances

The CSTR configuration used in all subsequent calculations is the "standard" configuration (Holland and Chapman, 1966), and it is described in Figure 4. The stirrer is a six-blade turbine, and the vessel is equipped with four baffles. The size and geometry of the stirrer assembly is expected to give good mixing performance.

Material balances on stage $j$ of a series of M CSTRs (Figure 5) yields:

Gas Phase:


Liquid Phase:

$$
\begin{equation*}
\left(1-\epsilon_{g} j\right)\left(1-v_{C}\right) C_{F e^{I}} S_{i n} S_{n}{ }^{j}-k_{L i} j a_{g} j\left(C_{L i} j-C_{g i} j / K_{i}\right)=0, i=1, \ldots 4 \tag{6}
\end{equation*}
$$

The arial contraction due to the F-T reaction is represented by the dependence of the gas superficial velocity on $\mathrm{H}_{2}+\mathrm{CO}$ conversion (the same dependence was used in our previous bubble-column model, Kuo, 1983):
$u_{g}{ }^{j}=u_{g}^{o}\left(1+a f_{S G}{ }^{O} X_{H_{2}}+C_{0}^{j}\right)$

Using the same dimensionless variables as in our previous model (Kuo, 1983), Equations (6)-(7) can be expressed as:

Gas Phase:
$\bar{C}_{g i}{ }^{j-1}-\bar{u}_{g} j \bar{C}_{g i}{ }^{j-S t_{d i}}{ }^{j}\left(\bar{C}_{g i}{ }^{j}-\bar{C}_{L i}{ }^{j}\right)=0, i=1, \ldots 4$

Liquid Phase:
$S_{t_{d i}}{ }^{j}\left(\bar{C}_{g i}{ }^{j}-\bar{C}_{L i}{ }^{j}\right)+\sum_{n} S_{i n} S t_{k n}{ }^{j} \bar{r}_{n} j=0, i=1, \ldots 4$
Axial contraction:
$u_{g}{ }^{j}=\left(1+\alpha f_{S G}{ }^{j-1}\right)\left(1+f j^{j-1}\right) /\left(1+f{ }^{j-1}+\alpha f{ }^{j-1} f_{f_{G}}{ }^{j-1}\left(\bar{C}_{g 1}+\bar{C}_{g}\right)\right)$

The set of nonlinear Equations (8)-(10), combined with the hydrodynamic correlations given in Appendix B is solved by using the following scheme:

1. Assume initial guess for $\overline{\mathrm{C}}_{\mathrm{gi}}{ }^{1}, \overline{\mathrm{C}}_{\mathrm{Li}}{ }^{1}$.
2. Calculate $\bar{u}_{g}$ for stage 1 .
3. Calculate hydrodynamic parameters for stage 1.
4. Use a Newton-Raphson routine to solve Equations (8)-(10).
5. Repeat 4, this time itterating on the hydrodynamic parameters as well.
6. Use output of stage 1 as both input and initial guess for stage 2.
7. Repeat 2-6 above for all subsequent stages.
c. Bubble-Column Model

The case of a bubble-column with axial dispersion can be also simulated by the series of CSTRs model above, if the number of CSTRs is related to the axial dispersion coefficient. Such a correlation is obtained by assuming identical standard deviations of the residence time distribution functions for a series of homogeneous CSTRs and a homogeneous axially mixed column (Levenspiel, 1979):
$H B C=0.5 P e_{L} /\left(1-\left(1-\exp \left(-\mathrm{Pe}_{\mathrm{L}}\right)\right) / \mathrm{Pe}_{\mathrm{L}}\right)$
where Pel is obtained from literature correlations (Appendix B).
The other assumptions are similar to those used in our previous bubble-column mathematical model. (Kuo, 1983).

## d. Estimation of Kinetic Parameters and Base Case Bubble-Column Calculations

Koelbel's Rheinpreussen data (Koelbel, 1980) was used to estimate the intrinsic kinetic parameters. The Rheinpreussen plant Was the largest $F-T$ bubble-column reactor ever tested (1.5m ID $x$ 8II L) and operated succesfully with precipitated Fe/Cu/K catalysts. The conditions and parameters used and the results of the estimate are summarized in Table 2. The hydrodynamic parameters are estimated from correlations in Appendix B. Other parameters; such as diffusivities, solubilities, and reactor-way physical properties are the same as in the previous model calculations (Kuo, 1983), and for convenience are summarized in Appendix C.

The numerical scheme used to estimate the intrinsic kinetic parameters $k_{1}, k_{1}, k_{1} "$, and $k_{2}$ was the method of parametric regression, minimizing the following target function:
$F=\left(1-\left(X_{Z_{2}}+C 0\right)_{c a l c} /\left(X_{\mathrm{H}_{2}}+C 0\right)_{\text {exp }}\right)^{2}+\left(1-U_{c a l c} / U_{\text {exp }}\right)^{2}$
The kinetic parameters estimated are quite different from those estimated using the earlier model (Kuo, 1983). Improved kinetic expressions containing $\mathrm{CO}_{2}$ inhibition terms (Equations (2) and (4)) are used. However, the major difference arises from use of new hydrodynamic correlations for estimation of the bubble-size and gas holdup (Calderbank, 1958). These correlations gave a muck larger bubble-size than that. used in the previous estimation ( 5.8 mm versus 0.7 mm ). This resulted, in a three-fold increase in the gas-liquid interphase mass transfer resistance, and therefore, 4-5 time increase in the estimated intrinsic kinetic rate. The hydrodynamic corrrelations contained complete information for both bubble-column and CSTR calculations. They were developed mainly from aqueous (with or without alcohols) systems. Unfortunately, there is no information on hydrodynamics of a commercial-size siurry F-T bubble-column to verify these correlations.

We feel that the gas-liquid interphase mass-transfer resistance estimated from these correlation probably provides the upper-bound of the mass-transfer resistance, in a slurry F-T bubble-column. Currently, work is being carried out to estimate the F-T kinetic parameters using data from a stirred-tank reactor of a
similar catalyst. We will then estimate the gas-liquid interphase mass-transfer resistance from the Rheinpreusssen demonstration plant data. Since the Rheinpreussen plant's bubble-column had a hydraulic diameter (i.e., equivalent diameter of a circle that gives the same flow cross sectional area to wetted perimeter ratio) similar to that of a commercial-size reactor, the gas-liquid interphase mass-transfer resistance thus estimated would be comparable to that of a commercial-size bubble-column. The potential benefits of a CSTR system can then be estimated.

It is interesting to note that according to Equation (11), seven CSTRs in series are required to simulate the Rheinpreussen bubble-column (assuming that the hydraulic diameter is the characteristic diameter used in the axial dispersion correlation of Appendix B).

The parameters used in the base case bubble-column are summarized in Table 3 . Hydrodynamic and other parameters are estimated from Appendix B and C. The size of the bubble-column ( 3.5 m ID $\times 10.5 \mathrm{~m} \mathrm{~L}$ ) is similar to that in our conceptual design (Kuo, 1983). The maximum catalyst loading in the bubble-column was chosen as $25 \mathrm{wt} \mathrm{\%}$, which is the highest we have ever tried in our bench-scale unit. Also, nine CSTRs in series were required to simulate the bubble-column base case.

## e. Model Predictions - Series of three CSTRs

The objective of our study was to compare on the same basis the performance of a commercial size F-T bubble-column reactor with that of a series of three CSTRs having the same total volume, producing the same syngas conversion, but having higher catalyst loading. To achieve the same syngas conversion with the CSTRs, the syngas throughput was increased at a given stirring speed (i.e., given power input) and for a fixed catalyst loading. This procedure was repeated for the range of power inputs of commercial interest ( 0.2 to 5 watts per liter, $W / \mathrm{L}$, Hughmark, 1980), and the results were expressed as increased throughput versus power required. These terms may be converted into economic terms, i.e., reduced capital costs (higher throughput ---> lower total reactor volume) versus increased capital and operating costs due to power requirments.

For the CSTRs, the range of stirring speeds was limited on one side by the speed required to suspend the catalyst ( $\mathrm{N}_{\mathrm{CS}}$ ), and on the other side by the maximum power input employed in commercial operation ( $5 \mathrm{~W} / \mathrm{L}$ ). A parametric study was performed first to test the behaviour of the hydrodynamic correlations. The parameters used in these calculations are summarized in Table 4. The stirring speed required for complete catalyst suspension was insensitive to the gas throughput for the particle size of $30 \mu \mathrm{~m}$ assumed in these calculations.

Figures 6-7 show the bubble-size and gas holdup versus gas superficial velocity and stirring speed. The gas holdup is less sensitive to stirring speed and it increases with the gas velocity (Figure 6). The bubble-size, however, is a strong function of the stirring speed, and is less dependent on the gas velocity (Figure 7).

Figure 8 shows the $k_{L} a_{g}$ for $H_{2}$ versus the gas superficial velocity and stirring speed $N$. The $k L a g$ increases strongly with $N$ and moderately with the superficial gas velocity. The behavior of the $\mathrm{kI}_{\mathrm{L}} \mathrm{g}^{\prime}$ 's for the other components $\left(\mathrm{CO}, \mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}\right)$ is similar, the actual values being proportional to some power of the diffusivities (the power depends on the bubble size - see Appendix B).

Figure 9 shows the predicted syngas conversion versus space velocity, with the stirring speed as parameter, for a CSTR catalyst loading of $35 \mathrm{wt} \mathrm{\%}$. In Figure 10, these results are replotted as increased space velocity in the CSTR versus power requirment, for a target syngas conversion of 88 mol\%. Figure 10 indicates that at $1.5 \mathrm{~W} / \mathrm{L}$, the throughput in a series of three CSTRs can be double that in the bubble-column reactor. Furthermore, there is no real incentive for increased power input above ${ }^{-2} \mathrm{~W} / \mathrm{L}$. The improved performance is the result of increased catalyst loading, and also of lower mass transfer resistance due to stiring. The percent of mass-transfer resistance as the total resistance (defined as $R_{d i} /\left(R_{d i}+R_{k i}\right)$; see Leib and Kuo, 1984) versus the stirring speed is plotted for $\mathrm{H}_{2}$ and CO in Figure 11 . The mass transfer and kinetic resistances are defined as:

$$
\begin{align*}
& R_{d i}=K_{i} / k_{I i} a_{g}, \quad i=1, \ldots, 4  \tag{13}\\
& R_{k i}=K_{1} C_{L i} /\left(k_{I I} C_{1} C_{F e}\left(1-v_{c}\right)\left(1-\epsilon_{g}\right)\right), i=1, \ldots, 4 \tag{14}
\end{align*}
$$

The percent of mass-transfer resistance for CO, for instance, decreases from $70 \%$ to $35 \%$ as the stirring speed increases from $I$ to 2 rps.

Note also, that there is no large detrimental effect due to backmixing in the CSTRs, since there is some backmixing already present in the commercial size bubble-column. Thus, assuming that the hydraulic diameter is the characteristic diameter, the base case bubble-column was found to be equivalent to a series of nine CSTRs.

In previous CSTR calculations (Quarterly Report, Dctober-December 1983) we showed that there is no advantage in raduced mass transfer resistances in the CSTR, since the mass transfer resistances were already small in the base bubble-column case. In those calculations, we used a 0.7 mm bubble-size and large gas holdup given by Deckwer's correlation, which resulted in small mass transfer resistances. In our subsequent hydrodynamic studies, we found that orifice distributors can produce bubbles substantially
larger than 0.7 mm , and the gas holdups can also be smaller with certain F-T waxes than those predicted by Deckwer's correlation. However, even though the hydrodynamic correlations used in the current calculations were developed for the turbulent regime prevailing in commercial size reactors, there is no proof that these are applicable to F-T mediums. Hence, in the limiting case of no mass transfer resistance in the bubble-column, the increase in CSTR throughput is reduced to $40 \%$; the increase in catalyst loading.

## 3. Future Work

- Evaluate a 2 mm single orifice in the 10.2 cm ID $\times 9.1 \mathrm{~m}$ tall hot flow bubble-column.
- Continue model applications to explore potential advantage of CSTRs.


## V. Nomenclature

| $\mathrm{ag}_{\mathrm{g}}$ | Gas bubble interfacial area, $6 \epsilon \mathrm{~g} / \mathrm{dB}$, ( $\mathrm{cm}{ }^{2}$ gas-liquid area/cm ${ }^{3}$ expanded slurry) |
| :---: | :---: |
| C | Concentration, (mol/cmin liquid or gas) |
| C * | Concentration at gas-1iquid. interface, (mol/cm ${ }^{3}$ ) |
| CD | Drag Coefficient |
| $\mathrm{CFe}^{\text {c }}$ | Iron loading, (gFe/cm ${ }^{3}$ Iiquid) |
| $\bar{C}_{E}$ | $\mathrm{C}_{g} / \mathrm{C}_{g 1}{ }^{\text {i }}$ |
| $\bar{C}_{\underline{L}}$ | $\mathrm{C}_{\underline{1}} \mathrm{~K}_{\text {/ }} \mathrm{Cl}_{\text {I }}{ }^{\text {i }}$ |
| $\mathrm{C}_{1}$ | An empirical variable obtained by solving Equations (B1), (B2), and (B12) simultaneously |
| $\mathrm{D}_{\text {I }}$ | Impeller diameter, (cm) |
| d | Pitch of Distributor Holes, (cm) |
| dB | Bubble diameter, (cm) |
| $\mathrm{d}_{c}$ | Catalyst particle diameter, (cm) |
| $\mathrm{d}_{\mathrm{R}}$ | Reactor diameter, (cm) |
| E | Axial dispersion coefficient, (cm²/s) |
| $\pm$ | Molar $\mathrm{H}_{2} / \mathrm{CO}$ ratio at the inlet of each stage |
| fre | Weight fraction of Fe in catalyst |
| $\ddagger_{\text {fG }}$ | Molar fraction of $\mathrm{H}_{2}+\mathrm{CO}$ at the inlet of each stage |
| 5 | Gravitational constant, ( $\mathrm{cm} / \mathrm{s}^{2}$ ) |
| H | Hej̇ght, (cmi) |
| $\mathrm{H}_{\mathrm{I}}$ | Impeller location from the tank bottom, (cm) |
| K | Solubility coefficient $G_{g} * / C_{L} *,\left(\mathrm{~cm}^{3}\right.$ iiquid/c. ${ }^{3}$ gas) |


| $\mathrm{k}_{1}, \mathrm{k}_{2}$ | Intrinsic kinetic rate constants for $F-T$ and water-gas shift reactions, respectively, $\left(\mathrm{cm}^{3}\right.$ liquid/s-gFe and mol/s-gFe, respectively) |
| :---: | :---: |
| $k_{1}{ }^{\prime}, k_{1}{ }^{\prime \prime}, k_{2}{ }^{\prime}$ | Constants used in the rate expressions (2) and (4) |
| $\overline{\mathrm{k}}_{1}$ | $\mathrm{k}_{1}$ |
| $\overline{\mathrm{k}}_{2}$ | $\mathrm{k}_{2} \mathrm{~K}_{1} \mathrm{~K}_{2} / \mathrm{K}_{4} \mathrm{Cg}_{1}$ |
| $\overline{\mathrm{k}}_{1}$, | $\mathrm{k}_{1}{ }^{\prime} \mathrm{K}_{2} / \mathrm{K}_{3}$ |
| $\overline{\mathbf{k}}_{1}{ }^{\prime \prime}$ | $\mathrm{k}_{1}{ }^{\prime \prime} \mathrm{K}_{2} / \mathrm{K}_{4}$ |
| $\bar{k}_{2}$, | $\mathrm{K}_{2} \mathrm{~K}_{4} / \mathrm{k}_{2}{ }^{\prime} \mathrm{K}_{1} \mathrm{~K}_{3}$ |
| $\mathrm{k}_{\mathrm{L}}$ | Liquid side mass transfer coefficient, (cm ${ }^{3}$ liquid/s-(cm ${ }^{2}$ gas-liquid area)) |
| L | Reactor height, (cm) |
| M | Number of CSTRS |
| m | Average $\mathrm{H} / \mathrm{C}$ atomic ratio of $\mathrm{F}-\mathrm{T}$ products |
| N | Stirrer speed, (1/s) |
| $\mathrm{N}_{0}$ | Number of distributor holes |
| $\mathrm{N}_{0}{ }^{\prime}$ | Corrected number of distributor holes |
| P | Pressure, (Pa) |
| $\mathrm{Pe}_{\mathrm{e}}$ | Total power input, (W) |
| $\mathrm{P}_{\mathrm{g}}$ | Power input by gas sparging, (W) |
| $\mathrm{P}_{\mathrm{m}}$ | Power input by mechanical agitation (W) |
| $\mathrm{P}_{\text {mo }}$ | Power input by mechanical agitation in absence of gas (W) |
| $Q$ | Volumetric flow rate, ( $\mathrm{cm}^{3} / \mathrm{s}$ ) |
| R | Universal gas constant, (atm-1iter/mol- ${ }^{\circ} \mathrm{K}$ ) |
| $\mathrm{R}_{\mathrm{di}}$ | Transport resistance from gas-lqiuid interphase to bulk liquid, Equation (13), ( $s-\mathrm{cm}^{3}$ expanded slurry/ $\mathrm{cm}^{3}$ gas) |


| $\mathrm{R}_{\text {ki }}$ | Kinetic resistance, Equation: (14), : (s-cm ${ }^{3}$ expanded slurry/cmiceas) |
| :---: | :---: |
| 11 | Kinetic rate of $F-T$ reaction, given as Equation (2), (molls-gFe) |
| I2 | Kinetic rate of water-gas shift reaction, given as Equation (4), (mol/s-EFe) |
| $\overline{1}$ | $\overline{\mathrm{C}}_{\mathrm{L} 1} \overline{\mathrm{C}}_{\mathrm{L} 2} /\left(\overline{\mathrm{C}}_{\mathrm{L} 2}+\overline{\mathrm{k}}_{1}, \overline{\mathrm{C}}_{\mathrm{L} 3}+\overline{\mathrm{k}}^{\prime \prime} \mathrm{C}_{\mathrm{L} 4}\right)$ |
| $\mathrm{I}_{2}$ | $\left(\bar{C}_{L 2} \overline{\mathrm{C}}_{\mathrm{L} 4} \overline{\mathrm{C}}_{\mathrm{L} 1} \overline{\mathrm{C}}_{\mathrm{L} 3} / \mathrm{k} \overline{2}^{\prime}\right)\left(\overline{\mathrm{C}}_{\mathrm{L} 2}+\overline{\mathrm{k}}_{1}{ }^{\prime} \overline{\mathrm{C}}_{\mathrm{L} 3}+\overline{\mathrm{k}}_{1}{ }^{\prime \prime} \overline{\mathrm{C}}_{\mathrm{L} 4}\right)$ |
| $s_{\text {in }}$ | ```Elements of stoichiometric matrix i"=1,\ldots.,4; and n=1,2``` |
| T | Temperature, ( ${ }^{\circ} \mathrm{C}$ ) |
| U | Molar $\mathrm{H}_{2} / \mathrm{CO}$ usage ratio |
| $u$ | Superficial velocity; (cm/s) |
| $u_{t}$ | Bubble rise velocity, (cm/s) |
| V | Volume, ( $\mathrm{cm}^{3}$ ) |
| $\mathrm{v}_{\mathrm{c}}$ | Volumetric fraction of catalysts in slurry, $\rho_{L^{w}} /\left(\rho_{S^{+}}\right.$ $\mathrm{w}_{\mathrm{C}}\left(\rho_{\mathrm{L}}-\rho_{\mathrm{S}}\right)$ ), (cmil catalyst/cm3 slurry) |
| w | Width, (cm) |
| $\mathrm{w}_{\mathrm{c}}$ | Weight fraction of catalyst in slurry, (gCat/g slurry) |
| ${ }^{W} \mathrm{Fe}$ | Weight fraction of Fe in slurry, (gFe/g slurry) |
|  | Greek Letters |
| $a$ | Molar contraction per mole of $\mathrm{H}_{2}+\mathrm{CO}$ converted excluding the inierts |
| $\epsilon_{\text {g }}$ | Gas holdup, ( $\mathrm{cm}^{3} \mathrm{gas} / \mathrm{cm}^{3}$ expanded siurry) |
| $\rho$ | Density, ( $\mathrm{g} / \mathrm{cm}{ }^{3}$ ) |
| $\rho_{\text {c }}$ | Catalyst particle density, (gCat/cm ${ }^{3}$ catalyst particle) |
| $\rho_{s}$ | Catalyst solid density, (gCat/cm ${ }^{3}$ catalyst solid) |
| $\sigma$ | Interfacial tension, (dyne/cm) |


| $\mu$ | Viscosity, (g/s-cm) |
| :---: | :---: |
| $\eta$ | Fraction of jet kinetic energy imparted to bulk liquid |
|  | Dimensionless Numbers |
| PeL | Axial Peclet number (liquid), $u_{g}{ }^{\circ} / E_{L}\left(1-\epsilon_{g}\right)\left(1-v_{c}\right)$ |
| ReI | Impeller Reynolds Number, $\rho_{\text {SL }} \mathrm{ND}^{2} / \mu_{\text {SL }}$ |
| Stdi | $\begin{aligned} & \text { Stanton number (diffusion resistance), } \\ & L / u_{\mathrm{g}}{ }^{i} R_{\mathrm{di}} \end{aligned}$ |
| Stikij | Stanton number (kinetic resistance), $\mathrm{Lk}_{\mathrm{j}} \mathrm{C}_{\mathrm{Fe}}(1-\epsilon)\left(1-\mathrm{v}_{\mathrm{C}}\right) / \mathrm{u}_{\mathrm{g}} \mathrm{OK}_{1}$ |
|  | Superscripts |
| $\bigcirc$ | At reactor inlet |
| j | Stage j |
|  | Subscripts |
| b | Baffle |
| c | Catalyst |
| cs | At complete suspension |
| $g$ | Gas |
| I | Impeller |
| i | Components, $i=1,2,3,4$ for $\mathrm{H}_{2}, \mathrm{CO}, \mathrm{CO}_{2}$, and $\mathrm{H}_{2} \mathrm{O}$, respectively |
| L | Liquid, at height $L$ |
| $\bigcirc$ | At orifice |
| SL | Slurry |
|  | Acronyms |
| $\begin{aligned} & \text { CSTR } \\ & \text { DOE } \end{aligned}$ | Continuous Stirred-Tank Reactor Department of Engergy |


| DOS | Days on Stream <br> FIMS <br> F-T$\quad \therefore \quad$ Field-Ionization-Mass-Spectrometry |
| :--- | :--- |
| G | Fischer-Tropsch |
| ID | Gallon Diameter |
| RPS | Inside Dial |
| SMP | Revolutions Per Second |

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Table 1

Major Events in Run CT-256-7 (85-98 DOS)

| DOS | MAJOR EVENTS |
| :---: | :---: |
| 85 | Flow Interruption; $\mathrm{N}_{2}$ in for 17 hrs |
| 85.7 | Re-established flow at $2.52 \mathrm{MPa}, 260^{\circ} \mathrm{C}$ |
| 88.4 | $2.52-\cdots>2.17 \mathrm{MPa}$ |
| 88.9 | $2.17---->1.48 \mathrm{MPa}$ |
| 80.4 | $260----->27{ }^{\circ} \mathrm{C}$ |
| 82.3 | $1.48-\cdots{ }^{\text {a }}$ 2.52 MPa |

## Table 2

## Estimation of Kinetic Parameters

## Parameters Used

| L, cm | 770 | $\epsilon_{\mathrm{g}}, \%$ | 23 |
| :---: | :---: | :---: | :---: |
| $\mathrm{d} \mathrm{R}, \mathrm{cm}$ | 129 | $\mathrm{d}_{\mathrm{B}}, \mathrm{cm}$ | 0.58 |
| $\mathrm{d}_{\mathrm{E}}, \mathrm{cm}$ | 25 | $\mathrm{dBo}^{\text {a cm }}$ | $0.75{ }^{\circ}$ |
| M | 7 | dBE, cm | 0.44 |
| T, ${ }^{\circ} \mathrm{C}$ | 268 | PeL | 13.0 |
| $\mathrm{P}, \mathrm{MPa}$ | 1.21 | $\mathrm{X}_{\mathrm{H}}^{2}$, $\%$ | 86 |
| $\mathrm{ug}^{\circ} \mathrm{C}$ cm/s | 9.5 | $\mathrm{X}_{\mathrm{CO}}, \%$ | 91 |
| Wcat, \% | 22 | $a$ | -0.62 |
| f | 0.67 | m | 2.24 |

## Estimated Kinetic Parameters

$k_{1}, \operatorname{cm}^{3}$ Iiquid/gFe-s $\quad 16.19$
$\mathrm{k}_{2}$, gmol/gFe-s
$k_{1}{ }^{\prime}$
$k_{1}{ }^{\prime \prime}$
$13.0 \times 10^{-3}$
0.28
3.70

Table 3

## Summary of Bubble-Column Base Case Calculations

## Paramters Used

| L, cm | 1050 | $\epsilon_{g}, \%$ | 0.22 |
| :---: | :---: | :---: | :---: |
| $\mathrm{d}_{\mathrm{R}}, \mathrm{cm}$ | 350 | $\mathrm{dB}, \mathrm{cm}$ | 0.76 |
| dE, cm | 25 | dBo, cm | 1.30 |
| M | 9 | $\mathrm{dB}^{\mathrm{E}}, \mathrm{cm}$ | 0.45 |
| T, ${ }^{\circ} \mathrm{C}$ | 260 | PeL | 13.0 |
| $\mathrm{P}, \mathrm{MPa}$ | 1.48 | $f$ | 0.7 |
| $\mathrm{ug}^{\circ}{ }^{\circ} \mathrm{cm} / \mathrm{s}$ | 9.5 | $\boldsymbol{\alpha}$ | -0.62 |
| weat, \% | 25 | II | 2.24 |
| $\mathrm{k}_{1}$, $\mathrm{cm}^{3}$ liquid/gFe-s | 11.9 |  |  |
| $\mathrm{k}_{2}$, gmol/gFe-s | $7.8 \times 10^{-3}$ |  |  |
| $\mathrm{k}_{1}{ }^{\prime}$ | 0.28 |  |  |
| $\mathrm{k}_{1}{ }^{\prime \prime}$ | 3.70 |  |  |
| $\mathrm{k}_{\mathrm{L}}\left(\mathrm{H}_{2} / \mathrm{CO} / \mathrm{CO}_{2} / \mathrm{H}_{2} \mathrm{O}\right)$, | /s | .10,.04,.04,.05 |  |

Calculated Conversions
$\mathrm{X}_{\mathrm{H}_{2}+\mathrm{CO}}, \% \quad 88$
$\mathrm{X}_{\mathrm{H}_{2}}, \% \quad 85$
$\mathrm{X}_{\mathrm{CO}}, \% \quad 89$

## Parameters for CSTR Calculations

| L, CIII |  | 1050 |
| :---: | :---: | :---: |
| - d R, Cm |  | 350 |
| M |  | 3 |
| T, ${ }^{\circ} \mathrm{C}$ | $\because \because$ | 260 |
| P, atm | $\because$ | 14.6 |
| ${ }^{W}$ cat $\%$ \% | $\because$ | 35 |
| f | ;- | 0.7 |
| a | : | -0.62 |
| m | * | 2.24 |
| $\mathrm{k}_{1}$, cmin liquid/gFe-s |  | 11.9 |
| $\mathrm{k}_{2}$, gmol/gFe-s |  | $7.8 \times 10^{-3}$ |
| $\mathbf{k}_{1}{ }^{\prime}$ |  | 0.28 |
| $\mathbf{k}_{1}{ }^{\prime \prime}$ |  | 3.70 |

Figure 1





Figure 5
A SERIES OF M CSTR




COMPARISON OF BUBBLE-COLUMN AND THREE CSTRS IN SERIES

TH


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\% 'induønoryi sseox]


## APPENDIX A

SUMMARY OF DATA FROM RUN CT-257-7

Tacluding Dxyeerintes
(3) In Gug lhage Unly
(8) Gollected in Ghillod and Ambient Gondensera
(4) Gollected in Mot Condonuer

Including Dxygenater
(a) Collected in Chilled and A


Firat Stage Fizcher-Tropach Slurry Reactor Operating Conditione and Material B
(Second-Stage Not Operative) (Run CT-250-7)

| (Nitrogen-Pree Barie) <br> M.B. No. <br> Dage On-wtremm | $\begin{array}{r} 7-55 \\ 84.4 \end{array}$ | $\begin{array}{r} 7-50 \\ 65.6 \end{array}$ | $\begin{array}{r} 7-57 \\ 68.4 \end{array}$ | $\begin{array}{r} 7-58 \\ 67.4 \end{array}$ | $\begin{array}{r} 7-59 \\ 68.4 \end{array}$ | $\begin{array}{r} 7-68 \\ 80.4 \end{array}$ | $\begin{array}{r} 7-01 \\ 70.4 \end{array}$ | $\begin{array}{r} 7-62 \\ 71.4 \end{array}$ | $\begin{array}{r} 7-68 \\ .72 .4 \end{array}$ | $\begin{array}{r} 7-64 \\ 78.4 \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pirat-Stage Conditions: |  |  |  |  |  |  |  |  |  |  |
| Charge M2/G0 (Molar) | 0.684 | 0.887 | 0.085 | - 0.677 | C. 878 | 0.878 | 0.678 | 0.674 | 4.875 | 4.678 |
| Temperature, oC | 255 | 257 | 257 | 268 | 275 | 275 | 276 | 275 | 274 | 278 |
| Preasure, LPa | 2.615 | 2.515 | 2.621 | 2.521 | 2.615 | 2.615 | 2.518 | 2.621 | 2.521 | 2.521 |
| Feed Sup. Vel., cm/a | 4.048 | 4.888 | 4.461 | 4.448 | 4.108 | 4.167 | 4.184 | 4.180 | 4.189 | 4.109 |
| Space Vel., NL/gPe-br | 4.0832 | 4.1188 | 4.188 | 4.171 | 4.228 | 4.278 | 4.385 | 4.423 | 4.578 | 4.682 |
| N2 in Feed, Mol \% | 1.2 | 1.1 | 1.1 | 1.2 | 1. ${ }^{\text {b }}$ | 1.6 | 1.1 | 1.1 | 1.4 | 1.5 |
| Conversione, Mol \% |  |  |  |  |  |  |  |  |  |  |
| 12 | 80.18 | 48.28 | 44.88 | 80.47 | 68.88 | 6. 6.57 | 64.47 | 57.06 | 69.77 | 58.27 |
| CO | 88.85 | 81.74 | 28.28 | 810.98 | 06.30 | 68.77 | 58.78 | 60.17 | 63.48 | 68.56 |
| $\mathrm{H2+CO}$ | 85.08 | 86.42 | 84.98 | 88.17 | 09.51 | 02.48 | 61.48 | 68.82 | 61.04* | 60.68 |
| Yielde, Et \% of Producte: Hydrocarbode (1) | 0.29 | 9.77 | 0.61 | 9.10 | 16.58 | 18.18 | 10.85 | 16.82 | 17.80 | 17.04 |
| C02 | 24.27 | 22.92 | 22.14 | 22.75 | 44.4 | 48.51 | 48.55 | 48.61 | 44.04 | 42.88 |
| H20 (1) | 0.84 | 1.14 | 1.19 | 1.82 | B.88 | e.87 | 0.89 | 6. 8 | 1.87 | 6.8\% |
| $\mathrm{H2}$ | 2.84 | 2.62 | 2.47 | 2.88 | 1.81 | 1.84 | 1.50 | 1.81 | 1.85 | 1.89 |
| CO | 62.75 | 88.56 | 06.18 | 84.16 | 87.44 | 84.85 | 87.88 | 35.46 | 84.55 | 88.78 |
| Total | 180 | 185 | 186 | 100 | 180 | 10든 | 1040 | 18. | 18 | 186 |
| Bel Recorery, \#t \% of Charge: | 18.48 | 182.28 | 104.89 | 102.86 | 101. 18 | 09.85 | 104.86 | 100.76 | 10\%.05 | 102.27 |
| (CO2) (H2) / (C0) (H20) : | 7.45 | 4.72 | 4.88 | 5.88 | 14.21 | 16.89 | 11.76 | 10.81 | 16.88 | 18.54 |
| gHC/Nms (H2+C0) conr. | 201 | 212 | 289 | 221 | 2011 | 281 | 218 | 225 | 226 | 248 |
| (H/C) Atomic Ratio in HC: | 2.16 | 2.14 | 2.14 | 2.14 | 2.15 | 2.18 | 2.14 | 2.18 | 2.15 | 2.14 |
| Selectivities, Wt \% of RC : Methane | 8.86 | 8.18 | 8.16 | 8.20 | 8.88 | 8.95 | 8.88 | 4.18 | 3.51 | 8.82 |
| Ethene | 2.28 | 2.86 | 2.88 | 2.11 | 2.47 | 2.57 | 2.80 | 2.81 | 2.41 | 2.28 |
| Bthane | . 0.54 | \%. 48 | 8. 48 | 8.48 | -. 66 | 8.62 | 0.64 | 0.80 | 0.81 | 0.58 |
| Propene | 2.84 | 3.16 | 2.74 | 2.78 | 8.28 | 8.40 | 8. 86 | 8.67 | 8.16 | 8.02 |
| Propane | 0.99 | - 08 | 0.70 | 6.84 | ¢. 89 | 6.94 | \%.85 | 1.68 | E.90 | 0.87 |
| Butenem | 2.08 | 2.58 | 2.24 | 2.28 | 2.65 | 2.80 | 2.68 | 2.98 | 2.61 | 2.40 |
| i-Butane | . 0.88 | - 60 | 8.8 | \#.08 | 0.68 | 0.108 | 0.68 | . 1.87 | 0.8 | - . $0^{1}$ |
| n-Butane | 1.18 5.95 | 8.97 | 6.98 | 6. 0.14 | 1.88 | 1.18 18.28 | 1.09 | 1.17 6.88 | 1.84 | 1.81 0.89 |
| Light Hiddrocarbons (8) | 20.38 | 24.48 | 24.40 | 24.92 | 25.98 | 38.88 | 28.82 | 25.76 | 28.48 | 10.80 |
| Heary Irydrocarbong (4) | 18.20 | 18.81 | 17.04 | 18.65 | 28.61 | 28.88 | 20.61 | 28.82 | 22.12 | 28.86 |
| Slurry Re. - Tex | 85.8 | 30.54 | 88.0 | 88.72 | 29.57 | 28.89 | 27.18 | 27.47 | 86. | 86.04 |
| Totel | 180. | $1{ }^{10}$ | 103 | 100 | 18\% | 108 |  | 110 | 1W ${ }^{\text {W }}$ | 1580 |Daye On-wtremPirst-Stage Condition

Charge i2/00
Preseure, MPa
Feed Sup: Vel. cm/e
N2 in Peed, Mol $\%$
H2
,


| $\begin{array}{r} 7-48 \\ 61.4 \end{array}$ | $\begin{gathered} 7-46 \\ 53.4 \end{gathered}$ | $\begin{gathered} 7-47 \\ 68.4 \end{gathered}$ | $\begin{gathered} 7-48 \\ 54.4 \end{gathered}$ | $7-40$ | $\begin{gathered} 7-60 \\ 67.4 \end{gathered}$ | $\begin{gathered} 7-61 \\ 60.4 \end{gathered}$ | $\begin{gathered} 7-62 \\ 00.4 \end{gathered}$ | $\begin{gathered} 7-68 \\ 82.3 \end{gathered}$ | $\begin{gathered} 7-\quad 54 \\ \hline \text { 日as. } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0．077 | ต．ans | ต．สอข | －6． 681 | 0.881 | 0．078 | ©．670 | 0.675 | 0.671 | 0.677 |
| 356 | 357 | 358 | 260 | 368 | 356 | 367 | 357 | 967 | 356 |
| 3.631 | 3.521 | 3.621 | 3.631 | 3.621 | 3.631 | 3.531 | a． 631 | 3.521 | 3.515 |
| 3.009 | 4.535 | 4．e9x | 4．697 | 4.017 | 4.15180 | 4.018 | 4.618 | 4．646 | 4.015 |
| 3.873 | 8.413 | 3.445 | 18． 886 | 8.641 | 3.618 | 8.707 | 3.743 | 3．814 | 8.008 |
| 0.7 | ต．\％ | a． 5 | ©． 5 | ๓． 7 | 3.7 | 6． 7 | 0.7 | 1.3 | 1.2 |
| ．03 | ． 07 | 48.8 | 42.07 | 14.10 | 41．36 | 43.40 | 40.12 | 410 | 18 |
| 85.34 | 43.38 | 41.61 | 48.31 | 43．al | 38.1 | 46.19 | 36.43 | 38.08 | 39.37 |
| 41.07 | 42.60 | 42.38 | 41.58 | 43.85 | 30.11 | 41.180 | 41.38 | 88 | 40 |
| 10.75 | ．89 | ． 57 | 13.38 | 11.38 | 16.33 | 11.06 | 19.08 | 16.81 | 42 |
| 28.10 | 20．80 | ad． | 38.4 | 39.98 | 37.33 | 37.08 | 26.72 | 35.07 | 33.43 |
| $0.0 \%$ | （3．01］ | 9． 06 | 9．0\％ | 9.00 | 9．07 | 0.30 | 9.85 | ต． 01 | 9．73 |
| 3.18 | \％．6日 |  | 3.84 | 3. | 3.73 | 3.88 | 3.36 | 2.88 | 3.89 |
| 56.05 | 54.75 | 54.80 | 51． | 54.08 | ．a | 6.64 | 50.45 | 60.55 | 86.31 |
| 100 | 160 | 1¢9\％ | 1168 | 1 10\％ | 1018 | 109 | 168 | 1 108 | 1048 |
| 1 106．8® | 103.34 | 101．61 | 1m1．64 | 00．00 | 1\％1\％．63 | 1 10．87 | 101.01 | 0.81 | 1101．35 |
| 8.41 | 0.63 | 6.32 | 7.78 | 0.34 | 7.48 | 3.41 | 0.05 | 55 | 6.70 |
| 312 | 335 | $34_{4}$ | 334 | 361 | $3{ }^{314}$ | 338 | 308 | 215 | 178 |
| 2.18 | 2.18 | 3.18 | 2.18 | 3.14 | 3.15 | 3.14 | 3.14 | 3.14 | 3.16 |
| ． 85 | 3.80 | 3.73 | 3.88 | 2．35 | 3.14 | 3.185 | 3.31 | A．a1 | 8.03 |
| 1.978 | 11.68 | 1.78 | 1.83 | 9，3a | 3.017 | 1.81 | 1.04 | 2.61 | 3.46 |
| （1．30 | 0.43 | （6．48 | 9．47 | 13．57 | 6． 58 | 0.45 | 6.40 | 6.40 | 0.53 |
| 1.81 | 1.01 | 4．18 | 3.34 | 3.80 | 8.67 | 4.30 | 2.87 | 2.43 | 3.83 |
| \％．71 | 9．75 | （18．89 | ©． 34 | 6．00 | 6.87 | \％．82 | 0.84 | （09 | a．oa |
| （1）．6\％ | 1.68 | 11.73 | 1.88 | 2.14 | 3.97 | 1.78 | 1.06 | 1.02 | ． 17 |
| ©．04 | ๓．๗5 | 0.08 | 6． $0^{64}$ | 3． 63 | 0．68 | （1）．6） | 6．698 | 6．68 |  |
| 0.03 | 6.01 | 6．04 | 6.07 | 1.13 | 1.18 | 0.07 | 0.07 | 1.63 | 08 |
| 8．09 | 4.08 | 4.01 | 6.47 | 『． 73 | （11） | 4.02 | 5.41 | 5.43 | 5.75 |
| 34． 60 | 13.38 | 31.0 \％ | 21.74 | 28．54 | 15.78 | 35.48 | 34.64 | 24．38 | 35.08 |
| 14．818 | 16．＇2 | 16.65 | 17.19 | 10.05 | 10.38 | 37.05 | 17.80 | 17.18 | 19．62 |
| 43.78 | A5．37 | 45．00 | A4．13 | 38.57 | 35．${ }^{\text {am }}$ | ． 18 | ． 64 | ${ }^{30} 0$ | 1 |
| 1\％ | 10 | 1 | 10 |  | 1 190\％ | 10 CH | 11 ¢19 | 180 | 1 198 |

[^0](Mitrogen-Free Bania)

| (Mitrogen-Free Banie) M.B. No. <br> Daye Oa-mitren | $\begin{array}{r} 7-85 \\ 74.4 \end{array}$ | $\begin{array}{r} 7-80 \\ 75.4 \end{array}$ | $\begin{array}{r} 7-71 \\ 80.6 \end{array}$ | $\begin{gathered} 7-78 \\ 88.8 \end{gathered}$ | $\begin{array}{r} 7-82 \\ 02.8 \end{array}$ | $\begin{array}{r} 7-88 \\ 98.8 \end{array}$ | $7-84$ $04.8$ | $\begin{array}{r} 7-85 \\ 05.8 \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pirgt-Stage Condition*: |  |  |  |  |  |  | E.871 | 0.671 |
| Charge Ez/C0 (Molar) | 6.677 | 0.678 | 0.678 | 8.887 | 0.870 | .078 270 | .681 279 | .871 278 |
| Temperature, oc | 274 2.591 | 278 2.521 | 276 2.515 | 282 2.184 | 279 2.615 | 2.8708 | 2.608 | 2.688 |
| Preseura, MPa | 2.521 4.177 | 2.521 4.217 | 2.515 4.176 | 2.184 4.645 | 2.615 4.204 | 2.508 4.245 | 2.608 4.207 | 2.688 |
| Spmee Vel., Mi/sFe-hr | 4.84 | 4.958 | 6.587 | 6.77 | 0.094 | 6.081 | 6. 988 | 7.0 |
| 1 N in Peed, Mol \% | 1.4 | . 1.7 | 1.0 | 1.2 | 1.2 | 1.2 | 1.2 | 1.8 |
| Conversions, Mol \% : |  |  |  |  |  |  |  |  |
| E2 | 58.88 | 58.28 | 89.70 | 24.80 | 41.87 | 86.88 | 8.418 | 24.94 |
| CO | 61.02 | 6 6. 67 | 89.58 | 88.98 | 51.80 | 47.10 | 41.09 | 84.57 |
| $\mathrm{H2}+\mathrm{CO}$ | 08.15 | 50.88 | 89.88 | 30.20 | 47.52 | 48.88 | 88.8 8 | 8.71 |
| Yielde, Wt $n$ of Producta 1 Iydrocerbone (1) | 17.72 | 17.72 | 11.87 | 8.98 | 18.09 | 18.12 | 11.89 | 9.89 |
| con | 44.10 | 42.47 | 26.57 | 21.42 | 88.75 | 20.84 | 25.48 | 21.81 |
| \%20 (1) | ¢. 88 | 0.03 | 0.01 | 0.88 | 1.13 | 1.04 | 1.18 | 1.48 |
| 32 | 1.82 | 1.98 | 2.86 | 8.87 | 2.87 | 8.88 | 8.85 | 3.59 |
| co | 86.80 | 80.97 | 58.70 | 86.08 | 418.8 | 62.81 | 68.67 | 04.83 |
| Totinl | 186 | 188 | $1{ }^{18}$ | 18 | 180 | 180 | 188 | 106 |
| Dal lecovery, wt \% of Chmrget | 104.98 | 181.86 | 98.81 | 08.72 | 05.16 | 05.10 | 95.71 | 08.50 |
| (C02) (E2)/(C0) (120) : | 14.77 | 18.84 | 7.77 | -.8n | 10.87 | 9.55 | 7.16 | 0.24 |
|  | 241 | 288 | 278 | 22\% | 217 | 228 | 231 | 281 |
| (H/C) Atamie matio in HC : | 2.15 | 2.15 | 2.16 | 2.18 | 2.18 | 2.16 | 2.15 | 2.16 |
| Selectivities, Wt \% of HC : Methme | 8.78 | 8.57 | 8.80 | 4.46 | 8.92 | 8.50 | 8.48 | 8.16 |
| Ethene | 2.58 | 2.68 | 2.64 | 1.88 | 2.74 | 2.46 | 2.42 | 2.89 |
| Ethane | 6. 0.67 | 0.67 | 6. 68 | - 6.60 | -. 84 | - . 68 | 0.67 | E. 57 |
| Propene | 8.46 | 8.44 | 8.35 | 2.418 | 8.64 | 8.18 | 8.10 | 8.607 |
| Propane | 6.97 | 0.08 | 6. 95 | 6.78 | 0.04 | 0.88 | 0.88 | . 8.87 |
| Butenes | 2.82 | 2.82 | 2.82 | 1.95 | 2.84 | 2.68 | 2.51 | 2.40 |
| i-Butene | 4.07 | 0.08 | *.78 | B.E4 | 0.98 | 5.67 | 1.46 | 0.06 |
| n-Butmae | 1.80 | 1.68 | 1.83 | ¢ . 88 | 1.04 | \%. 98 | 0.98 | 0.09 |
| C6-C11 (2) | 12.46 | 10.44 | 0. 20 | 12.67 | 6.88 | 8.11 | 8.68 | 9.38 |
| Light Eydrocarbona (8) | 15.80 | 18.46 | 18.62 | 16.88 | 15.78 | 18.87 | 16.10 | 16.11 |
| Henty Bydrocmrbona (4) | 20.34 | 21.72 | 24.18 | 21.38 | 26.28 | 24.56 | 24.55 | 24.86 |
| Slurry Re. -Wax | 85.48 | 85.8 | 35.88 | 85.00 | 86.000 | 85.06 | 85.6 | 85.08 |
| Totel | 166 | $1{ }^{\text {dem }}$ | 180 | $10 \pm$ | 1 10. | 1.0 | 100 | 10 |

(1) Including Oxygenaten (1) Including Oxygenaten
(2) In Gan Phame Only (2) Io Gae Phawe Only
(8) Collected in Chilled and Ambient Condenser:
(4) Collected in Hot Condenzer

| 1.1. No. | 7-38 | 7-37 | 7-88 | 7-30 | 7-40 | 7-41 | 7-42 | 7-43 | 7-44 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Daym On-ntream | 41.4 | 42.4 | 43.4 | 44.4 | 45.4 | 40.4 | 47.4 | 40.4 | 50.4 |
| LIPTIANAL | 8.38 | 8.88 | 8.4 | 8.38 | 3.63 | a. 48 | 8.88 | 8.38 | 3.12 |
| ETITENE | 2.618 | 2.32 | 2.11 | 2.12 | 2.31 | 2.23 | 2.10 | 2.41 | 1.61 |
| ETIIANT | c. 53 | 6. 09 | 6. 64 | 0.64 | 6.50 | 67.54 | 0.62 | 0.61 | 0.48 |
| Propinit | 2.80 | 2.78 | 2.51 | 2.52 | 2.74 | 2.70 | 2.68 | 2.88 | 1.84 |
| phopant | ©.02 | 1.188 | 0.04 | 0.05 | 1.61 | 0.08 | 67.08 | 1.04 | 0.70 |
| I- Inutans | 1.80 | 10.78 | 0.62 | \%. 88 | 6.077 | 0.07 | 0.67 | 0.080 | 8.60 |
| 1-BUTILNE + - LITETIYLPPROPENB | 1.02 | 2.23 | 2.676 | 2.61 | 2.18 | 2.18 | 2.14 | 2.26 | 1.63 |
| N-BUTANS | 1.077 | 1.38 | 1.60 | 1.08 | 1.15 | 1.10 | 1.18 | 1.15 | 0.08 |
| CIS-2-DUTENL | \%. 60 | - . 10 | 6. 615 | 4.18 | 0.15 | 0.16 | 0.18 | 6. 10 | 6. 6 \% |
| 8-HITIITL-1-BUTENIS | 0.12 | 0.14 | 6.13 | 0.08 | 4.68 | 9.074 | \%. 077 | 6.18 | 0.680 |
| I-pientamil | 6.48 | 0.61 | 6.51 | 1.68 | 1.64 | 1.67 | 1.63 | 8.60 | 6.30 |
| 1-PENTHENS | 1.44 | 1.60 | 1.59 | 9.08 | 0.638 | 9.08 | 0.00 | 1.62 | 1.37 |
| 2-LICMIL-1-DUTENE | \%. 15 | 4.848 | 0.68 | - . 0 | 6. 610 H | 6.64 | \% \% 68 | 0.07 | 0.808 |
| N-PCNTANL | 6.87 | 1. ¢ $_{\text {¢ }}^{6}$ | \%.80 | \%.80 | 6.03 | 0.01 | 0.008 | 0.01 | 6.88 |
| cYClOPRNTANE | 7.19 | 6.11 | 6.10] | 0. 0.11 | 6.06t | \% 4 , 18 | 6. 988 |  | 9.608 |
| Imidenis + ISO-midentes | 1.08 | 1.75 | 1.60 | 0.11 | 0.12 | 0.13 | 0.11 | 0.13 | 6.68 |
| 3, 3-dimetivlditanim | \%.010 | 64, 018 | 1. 1 (15) | 0.17 | ta. 17 | 0.17 | 6. 38 | 6. 8.8 | 6. 615 |
| 3-LIETITVIPENTANE | 6. 14 | $\$ .10$ | 6.15 | 0.10 | 6. 110 | 60.60 | 0.18 | 6.17 | 13.10 |
| 8-LIETIMLPENTANTS | 6.08 | 0.10 | ต. 9 \% | \%.60\% | 0.818 | 94. 6 $_{\text {H }}$ | ©. 16 | 0.00 | ©. 07 |
| 1-mmxenit | \%. 6 |  |  | 1.12 | 1.10 | 1.38 | 1.18 | 1.17 | 0.05 |
| S-IIIPXANT | 0.84 | 6.78 | 6.86 | 9.00 | 0.70 | 6.73 | 0.78 | 0.68 | 0.63 |
| MEPTIENILS + ISO-ITEPTANES | 0.000 | 0.608 | \$.08 | 6.67 | 0.60 | 0.68 | 1.80 | 8.00 | 6.08 |
| 1-MIEPTENL | 6.ayd | 0.010 | 6. 60 | *. 60 | 0.63 | 9.05 | \%i. 61 | 6.34 | 0.608 |
| 3-hbtifylimexanic | 6.96 | 0.10 | 8 808 | 6. 6 \% | 6. 818 | 67.00 | 6.850 | 0.08 | 8.68 |
| 1-TLANS-3-DIAETITVL-N5 | 6.63 | \%.7\% | 6. 58 | 6.015 | 0.0.837 | (13.098 | 6. | 0.68 | 5.005 |
| N -mpptant | 6.34 | 0.45 | (3.85 | 0.87 | 0.38 | 9.944 | 0.61 | 6.88 | 0.34 |
| 1-0CTENIL | 6. 68 | 67.680 | 6. 0 (1) | 6. 10 | 6.33 | 0.31 | 65.315 | 0.31 | 6.10 |
| N-DCTANTS | 68.6818 | 6.613 | 6. 34 | 8.11 | 0.18 | 0.12 | 0.11 | 6.13 | 0.11 |
| TOLUTATE | 6.26 | 6.87 | \%.80 | 4.710 | 6, \#18 | \%. 0 | 6. 618 | \$. \% $^{\text {\% }}$ | 0.080 |
| ACETONR | 6 6. 815 | 6. 6 | 6. 18.4 | 50.62 | 0.65 | 0.67 | 0.65 | 0.63 | 8. 16 |
| I-PMOPANOL, | 6. $0^{\text {cos }}$ |  | 6, 6 Cat | 0.48 | \$4. 48 | 0.68 | W. 45 | 6.46 | 6.17 |
| UNRNOTN LITE TTYDRO-GADB LIQ (1) | 35.74 | 89.68 | 14.08 | 35.42 | 95.06 | 27.01 | 25.73 | 26.65 | 24.109 |
| UNHMOMN IVY ITDDE-CARB LIC (2) | 30.44 | 13.10 | 29.38 | 910.914 | 81.67 | 21.86 | 33.68 | 17.13 | 10.65 |
| slundy blaction-wat | 85. |  | 85. 6 $^{\text {d }}$ | 84.68 | 31.10 | 20.36 | 38.21 | 34.03 | 80.85 |





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1


(1) Collected in Ambient and Chilled
(2) Collected in Hot Condenaer

| $\begin{array}{r} 7-45 \\ 51.4 \end{array}$ | $\begin{array}{r} 7-46 \\ 52.4 \end{array}$ | $\begin{array}{r} 7-47 \\ 52.4 \end{array}$ | $7-48$ | $\begin{gathered} 7-40 \\ 65.4 \end{gathered}$ | $\begin{gathered} 7-60 \\ 67.4 \end{gathered}$ | $\begin{gathered} 7-51 \\ 50.4 \end{gathered}$ | $\begin{gathered} 7-62 \\ 60.4 \end{gathered}$ | $\begin{gathered} 7-58 \\ 82.8 \end{gathered}$ | $\begin{array}{r} 7-54 \\ 63.5 \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.85 | 2.69 | 2.78 | 2.68 | 8.25 | 8.44 | 8.65 | 8.21 | 8.81 | 3.08 |
| 1.47 | 1.58 | 1.77 | 1.88 | 2.22 | 2.07 | 1.81 | 1.94 | 2.01 | 2.46 |
| 4.80 | c. 42 | -. 40 | 6.47 | 6.57 | 0. 52 | \%. 46 | 8.46 | 0.40 | 9.62 |
| 1.81 | 1.01 | 2.18 | 2.24 | 2.60 | 2.67 | 2.28 | 2.87 | 2.42 | 2.80 |
| 6.71 | 9.75 | 6.86 | . 6.8 | 0.80 | 0.07 | . 82 | . 84 | 6. 88 | . 80 |
| ¢. 64 | 9.05 | 0.00 | 0.07 | . 68 | . 68 | 0.07 | . 06 | 6.08 | 0.69 |
| 0.6 | 1.56 | 1.72 | 1.70 | 2.14 | 2.07 | 1.78 | 1.88 | 1.92 | 2.67 |
| 6. 02 | 0.91 | 0.94 | 6.97 | 1.18 | 1.18 | 6.97 | 0.07 | 1.68 | . 10 |
| ¢. 6 | 6.60 | 6.11 | E. 12 | 0.14 | c.15 | . 12 | . 14 | ${ }^{6} 18$ | . 18 |
| 1.68 | 6. 6 | 6. 68 | 6.87 | 6. 10 | 8. | .07 | . 1.18 |  | 1.61 |
| 1.25 | 1.22 | 1.27 | 1.82 | 1.65 | 1.61 | 1.27 | 1.30 | 1.87 |  |
| . 0.6 | 0.64 | -. 85 | 8.65 | 6. 68 | ${ }^{\text {c.es }}$ | . 78 | 6.78 | \%.82 | 0.75 |
| 0.79 | 6.75 | 6.76 | 6.78 | . 8.8 | 0.01 | . 78 | .11 |  |  |
| 0.60 | 0.67 | 0.08 | 8.80 | 6.11 | . 11 | . 68 | . 17 | 6.18 | 0.24 |
| 9.15 | E.14 | 0.18 | 8.14 | 8.15 | \%.198 | 8. 86 | -.17 | 6. 67 | \%.68 |
| ¢. 61 | 6. 67 | 6.54 | 6. 67 | 0.02 | 0.66 | -. 65 | 0.57 | 0.60 | E. 56 |
| 0.87 | ¢. $\cdot 8$ | -. ${ }^{\text {c }}$ | . 88 | 0.87 | 0.11 | c. 8 | 0.60 | 0.69 | 6. 12 |
| 0.46 | 0.45 | 0.42 | 6. 51 | 6.18 | 6.67 | 6.80 | 6. 48 | 0.45 | 9. 62 |
| 0.31 | 0.20 | 6. 27 | 0.88 | 0.86 | . 88 | 6. 28 | 6.86 | 6. 36 | . 32 |
| 6. 15 | . 6.15 | 0.18 | 0.18 | 0.14 | . 15 | 0.12 | 0.15 | 0.15 | . 19 |
| 6.60 | -. 60 | 0.67 | 6. ${ }^{88}$ | 5.68 | 8. 80 | -. 08 | 8.69 | 0.60 | .6.E |
| 5.6 | -... | -.60 | 6.68 | . 16 | . 6 | -. 0.0 | . 52 | 0.68 | 6.61 |
| 6.58 | 0.61 | 9.48 | 8.50 | . 6.56 | . 8.61 | 6.89 | 0.62 | 0.42 | 0.45 |
| (6.88 | $\begin{array}{r}82.87 \\ \hline 288\end{array}$ | 21.88 | 21.72 | 20.54 | 25.76 | 25.63 | 24.64 | 24.28 | 25.98 |
| 18.68 | 16.72 | 16.65 | 17.16 | 10.05 | 19.28 | 22.06 | 17.89 | 17.28 | 18.52 |
| 43.78 | 45.27 | 46.69 | 44.18 | 38.67 | 85.6 | 36.60 | 30.64 | 38.85 | 36.68 |



®"


[^1]















[^2]


[^3]
## M.B. No.

Table A-3
First Stage Fischer-Tropsch Slurry Reactor Operating Conditions and Material Balances (Based on Inter-Reeactor Sample)
(Run CT-256-7)

| (Nitrogen-Free Basis) |  |  |  |
| :---: | :---: | :---: | :---: |
| M.B. No. | 7- 9 | 7-10 | 7-16 |
| Days On-stream | 12.4 | 13.4 | 20.4 |
| First-Stage Conditions: |  |  |  |
| Charge H2/C0 (Molar) | 0.659 | 0.655 | 0.674 |
| Temperature, oC | 258 | 256 | 258 |
| Pressure, MPa | 2.521 | 2.521 | 1.970 |
| Feed Sup. Vel ${ }^{\text {, }, ~ c m / s ~}$ | 3.412 | 3.418 | 2.720 |
| Space Vel., NL/EFe-hr | 3.272 | 3.324 | 2.690 |
| N2 in Feed, Mol \% | 4.6 | 4.8 | 0.7 |
| Conversions, Mol \% : |  |  |  |
| H2 | 78.26 | 76.31 | 74.27 |
| CO | 84.52 | 82.33 | 83.16 |
| $\mathrm{H} 2+\mathrm{CO}$ | 82.03 | 79.92 | 79.58 |
| Yields, Ht \% of Products : |  |  |  |
| Hydrocarbons (1) | 18.21 | 17.79 | 18.32 |
| $\mathrm{CO2}$ | 64.70 | 63.48 | 62.40 |
| H 2 O (1) | 0.91 | 0.94 | 1.31 |
| H2 | 1.01 | 1.07 | 1.24 |
| CO | 15.16 | 16.71 | 16.73 |
| Total | 100 | 100 | 100 |
| Bal Recovery, Ht \% of Charge: | 87.42 | 100.85 | 95.97 |
| (CO2) (H2)/(CO) (H2O) : | 28.96 | 24.82 | 20.18 |
| gHC/Nm3 ( $\mathrm{H} 2+\mathrm{CO}$ ) conv.: | 170 | 176 | 172 |
| (H/C) Atomic Ratio in HC : | 2.14 | 2.14 | 2.14 |
| Selectivities; Wt \% of HC : |  |  |  |
| Methane | 3.32 | 3.42 | 3.60 |
| Ethene | 1.83 | 1.88 | 1.83 |
| Ethane | 0.68 | 0.67 | 0.71 |
| Propene | 2.80 | 2.83 | 2.92 |
| Propane | 0.75 | 0.78 | 0.76 |
| Butenes | 2.46 | 2.49 | 2.59 |
| i-Butane | 0.05 | 0.05 | 0.05 |
| n-Butane | 0.87 | 0.92 | 0.92 |
| C5-C11 (2) | 12.91 | 13.15 | 8.35 |
| Light Hydrocarbons (3) | 2.89 | 7.75 | 11.17 |
| Heavy Hydrocarbons (4) | 10.65 | 7.67 | 15.62 |
| Slursy Rx.-Hax | 59.68 | 57.21 | 50.53 |
| Total | 100 | 100 | 100 |
| (1) Including Oxygenates |  |  |  |
| (2) In Gas Phase Only |  |  |  |
| (3) Collected in Chilled and | ent Cos | denser |  |
| (4) Collected in Hot Condense |  |  |  |

Table A-4
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor (Based on Inter-Reactor Sample)
(Run CT-256-6)

| M.B. No. | 7-9 | 7-10 | 7-16 |
| :---: | :---: | :---: | :---: |
| Days On-stream | 12.4 | 13.4 | 20.4 |
| yethane | 3.32 | 3.42 | 3.60 |
| ETHENE | 1.83 | 1.88 | 1.83 |
| ETHANE | 0.68 | 0.67 | 0.71 |
| PROPENE | 2.80 | 2.83 | 2.92 |
| PROPANE | 0.75 | 0.78 | 0.76 |
| I-BUTANE | 0.05 | 0.05 | 0.05 |
| 1-BUTENE+2-METHYPPROPENE | 2.43 | 2.46 | 2.53 |
| N-BUTANE | 0.87 | 0.82 | 0.82 |
| TRANS-2-BUTENE | 0.00 | 0.00 | 0.02 |
| CIS-2-BUTENE | 0.04 | 0.04 | 0.04 |
| 3-METHYL-1-BUTENE | 0.12 | 0.12 | 0.12 |
| I-PENTANE | 0.36 | 0.36 | 0.15 |
| 1-PENTENE | 2.01 | 2.04 | 2.11 |
| 2-METHYL-1-BUTENE | 0.08 | 0.07 | 0.07 |
| N-PENTANE | 0.73 | 0.76 | 0.74 |
| TRANS-2-PENTENE | 0.45 | 0.48 | 0.00 |
| CIS-2-PENTENE | 0.02 | 0.03 | 0.02 |
| 2-METHYL-2-BUTENE | 0.03 | 0.03 | 0.00 |
| HEXENES + ISO-HEXANES | 0.15 | 0.16 | 0.55 |
| 1-hEXENE | 1.75 | 1.79 | 1.80 |
| N-HEXANE | 0.68 | 0.70 | 0.65 |
| HEPTENES + ISO-HEPTANES | 0.56 | 0.56 | 0.28 |
| 1-HEPTENE | 1.44 | 1.46 | 1.34 |
| 1-TRANS-3-DIMETHYL-N5 | 0.18 | 0.21 | 0.00 |
| N-HEPTANE | 0.58 | 0.60 | 0.50 |
| C8-OLEFINS + ISO-PARAFFINS | 0.43 | 0.40 | 0.00 |
| 1-0CTENE | 1.20 | 1.16 | 0.00 |
| N-DCTANE | 0.49 | 0.48 | 0.00 |
| C9-OLEFINS + ISO-PARAFFINS | 0.19 | 0.24 | 0.00 |
| 1-NONENE | 0.82 | 0.78 | 0.00 |
| N-NONANE | 0.34 | 0.33 | 0.00 |
| N-DECANE | 0.31 | 0.38 | 0.00 |
| ACETONE | 0.09 | 0.08 | 0.07 |
| I-PROPANOL | 1.02 | 1.08 | 0.89 |
| UNKNOWN LITE HYDRO-CARB LIQ (1) | 2.89 | 7.75 | 11.17 |
| UNKNOWN GVY HYDRD-CARB LIC (2) | 10.65 | 7.67 | 15.62 |
| SLURRY REACTOR-WAX | 59.68 | 57.21 | 50.53 |

(1) Collected in Ambient and Chilled Condensers
(2) Collected in Hot Condenser

Table A-5
Second-Stage Fized-Eed ZSM-E Reactor Operating Conditions mad Material Bulances


| ```(Mjtroged-Free Basis) H.B. Ho.``` | $\begin{array}{r} 7-\quad 5 \\ 8.4 \end{array}$ | 7- 6 | 7-7 | 7-8 | $\begin{array}{r} 7.9 \\ 12.4 \end{array}$ | $\begin{array}{r} 7-11 \\ 38.4 \end{array}$ | $\begin{aligned} & 7-11 \\ & 15.4 \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Days On-streara |  | 0.4 | 10.4 | 13.4 |  |  |  |
| First-Stage Conditions: 12.10 .1 |  |  |  |  |  |  |  |
|  | 0.671 | 6.688 | 0.689 | 0.653 | 0.659 | 0.es5 | 0.837 |
| Temperature, $0 \subset$ | 257 | 258 | 256 | 258 | 288 | 288 | 285 |
| Pressure, WPa | 2.494 | 2.528 | 2.523 | 2.581 | 2.621 | 2.681 | 2.881 |
| Feed Sup. Vel., cm/s | 3.888 | 8.884 | 2.876 | 8.375 | 3.499 | 8.417 | 2. ${ }^{\text {d }} 81$ |
| Space Vel., NL/EFe-hs | 2.989 | 3.074 | 3.145 | 3.288 | 3.272 | 3.834 | - 3.495 |
| N2 in Feed, Hol ${ }^{\text {r }}$ | 2.4 | 3.7 | 8.4 | 8.7 | 4.8 | 4.7 | 4.8) |
| Second-Stage Conditions: |  |  |  |  |  |  |  |
| Tenp.: Inlet, oc | 289 | 293 | 298 | 294 | 838 | 293 | 344 |
| Outlet, oc | 812 | 813 | 313 | 814 | 812 | 318 | 388 |
| Pressure, HPa | 2.487 | 2.616 | 2.615 | 2.615 | 2.516 | 2.615 | 2.535 |
| GESV, I/hr | 4238 | 4241 | 4839 | 4327 | $4{ }_{4} 12$ | 4479 | 471 |
| Days On-stresm | 1.5 | 2.5 | $3 . E$ | 4.5 | $8 . E$ | B. 5 | B. 5 |
|  |  |  |  |  |  |  |  |
| H2 | 78.67 | 73.84 | 79.69 | 79.88 | 73.70 | 73.85 | 71.35 |
| CO | 85.92 | 89.28 | 88.85 | 85.25 | 84.75 | 85.63 | 74.81 |
| E2+C0 | 82.97 | 85.29 | 83.64 | 88.02 | 82.24 | B2.7』 | 72.93 |
|  |  |  |  |  |  |  |  |
| Hgdrocarbons | 19.69 | 21.84 | 21.29 | 29.89 | 23.32 | 10.52 | $2 \geqslant 3.85$ |
| C02 | 64.42 | 68.25 | 83.15 | 62.97 | 82.37 | 84.87 | 48.78 |
| E20 | 1.53 | 1.42 | 1.61 | 1.44 | 1.53 | 3.15 | 1.73 |
| E2 | 1.99 | 0.98 | 6.53 | ©.94 | 0.99 | ©. 97 | 2.44 |
| 0 | 18.47 | 18.65 | 12.93 | 14.28 | 14.84 | 12.80 | 27.28 |
| Totel | 1985 | 189 | 189 | 18 | 185 | 193 | 139 |
| Bal Recovery, Ft \% of Charge: | 99.62 | 393.93 | 399. ${ }^{81}$ | 03.62 | 97.42 | 1893.85 | .9․ |
| (C02) (E2)/(CD) (\#20) : | 17.78 | 24.83 | 17.31 | 18.48 | 34.88 | 13.6 | 8.89 |
| E\#C/hims ( $\mathrm{Hz}+\mathrm{CO}$ ) conv.: | 134 | 209 | 288 | 159 | 189 | 187 | 293 |
| (\#\#/C) Atomic Eatio in EC: | 2.11 | 2.8 | 2.62 | 2.03 | 2.63 | 2.64 | 2.63 |
| Selectivities, Wt of EC : |  |  |  |  |  |  |  |
| Hethane | 2.99 | 8.97 | 2.83 | 2.83 | 2.89 | 8.32 | 2.18 |
| Ethene | c. 63 | 0.62 | E.73 | 0.95 | 1.58 | 1.49 | E.E3 |
| Ethane | 0.81 | 0.67 | ¢. 59 | 9.89 | 0.89 | 0.68 | 0.141 |
| Propene | $1 . \mathrm{Es}$ | 1.67 | 1.18 | 1.19 | 1.20 | 3.67 | 1.42 |
| Propane | 3.35 | 1.38 | 1.14 | 3.68 | \%.94 | 3.13 | 1.98 |
| Butenes | 8.88 | 2.68 | 8.11 | 2.23 | 8.69 | 4.18 | 8.89 |
| i-Eutane | 1.61 | 1.52 | 1.14 | 6.98 | 0.67 | 0.92 | 3.54 |
| n-Butane | 1.75 | 1.49 | 1.24 | 3.18 | 1.ça | 1.2 23 | 1.45 |
| Cs-CII | 22.44 | 85.11 | 35.75 | 83.28 | 82.98 | 33.08 | 81.27 |
|  | 8.85 | E. 15 | 0.48 | ©. 82 | 9.97 | 0.45 | 6.28 |
| Slury Rax.-Faz | 54.25 | E2.88 | 51.89 | 54.13 | 53.48 | 52.14 | 55.85 |
| Totel | $1 \times 9$ | 1島 | 1485 | 1¢ | 3es | 1493 | 13983 |
| i-CA/(CS $=+\mathrm{Cd}=$ ) Holar | ¢. 35 | 6.88 | 0.23 | 9.19 | ¢. 18 | 9.14 | c. 27 |
| (C3/C3 $)$ Holar Satio | 1.21 | 1.21 | 8.93 | 0.88 | ¢. 89 | 8.85 | 0.78 |
|  | 2.15 | 2.83 | 2.28 | 1.92 | 1.38 | 1.81 | 3.53 |
| Cat-Poly, ${ }^{\text {P }} \mathrm{F}$ of EC C5 - Cil Pora, Vt $\quad$ : | 2.68 | 2.28 | 3.23 | 8.63 | 4.48 | 4.83 | 3.82 |
| Farafifins | 42.85 | -- | -- | -- | -- | -- | 23.83 |
| Olefins | 29.42 | - | -- | -- | -- | -- | 23. 71 |
| Maptthenes | 6.78 | -- | -- | -- | -- | -- | 6.24 |
| Aromatics | 21.28 | -- | - | -- | -- | -- | 21.22 |

Table A-5 (Cont'd)
Second-Stage Fixed-Bed 2SM-5 Reactor
Operating Conditions and Material Balances
(Run CT-258-7)

| (Nitrogen-Free Basis) <br> M.B. No. | 7-12 | 7-18 | 7-14 | 7-15 | 7-18 | $7-10$ | $\begin{gathered} 7-20 \\ 24.4 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Daye On-stream | 18.4 | 17.4 | 18.4 | 19.4 | 20.4 |  |  |
| First-Stage Conditions: <br> Charge $\mathrm{Hz} / \mathrm{CD}$ (Molar) | 0.676 | 0.687 | . 680 | 0.675 | 0.674 | 0.881 | 0.687 |
| Temperature, oc | 268 | 256 | 257 | 257 | 268 | 257 | 258 |
| Preasure, MPa | 2.628 | 2.628 | 2.528 | 2.528 | 1.978 | 2.521 | 2.521 |
| Feed Sup. Vel., cm/s | 8.128 | 8.127 | 3.125 | 2.608 | 2.786 | 2.877 | 2.785 |
| Space Vel., $\mathrm{KL} / \mathrm{gFe}$-hr | 8.495 | 8.522 | 3.675 | 3.687 | 2.890 | 8.976 | 4.171 |
| N2 in Peed, Mol \% | 5.5 | 5.6 | 6.8 | 1.8 | 2.3 | 0.8 | 8.1 |
| Second-Stage Conditione: <br> Temp., Inlet, oC | 885 | 848 | 847 | 848 | 846 | 866 | 865 |
| ( Outlet, oc | 883 | 878 | 372 | 879 | 883 | 409 | 467 |
| Pressure, MPa | 2.621 | 2.521 | 2.521 | 2.621 | 1.976 | 2.615 | 2.616 |
| GESV, $1 / \mathrm{hr}$ | 4029 | 4829 | 4738 | 8790 | 2652 | 3083 | 4617 |
| Daye On-stream | 9.6 | 10.5 | 11.6 | 12.5 | 13.5 | 16.5 | 17.5 |
| Conversionc, Mol |  |  |  |  |  |  |  |
| H2 | 79.62 | 78.88 | 89.82 | 75.54 | 77.47 | 71.89 | 68.68 |
| CO | 82.09 | 78.62 | 64.18 | 74.84 | 88.98 | 87.08 | 85.80 |
| H2+CO | 81.40 | 77.57 | 68.44 | 74.84 | 84.88 | 88.87 | 87.16 |
| Yields, Wt of Products : Eydrocerbon: | 25.21 | 10.88 | 16.18 | 15.68 | 19.88 | 17.85 | 17.88 |
| C02 | 60.28 | 87.24 | 45.81 | 58.20 | 86.84 | 48.49 | 44.88 |
| H20 | 1.74 | 1.48 | 1.86 | 1.98 | 1.28 | 1.62 | 1.98 |
| H2 | 1.60 | 1.06 | 1.44 | 1.14 | 1.89 | 1.82 | 1.50 |
| CO | 16.77 | 36.92 | 85.62 | 24.91 | 16.97 | 81.52 | 24.87 |
| Total | 186 | 180 | 163 | 168 | 108 | 164 | 160 |
| Bal Recovery, wt of Charge: | 96.71 | 180.15 | 98.14 | 09.29 | 96.97 | 09.64 | 94.82 |
| (CO2) (H2)/(CO) (820) : | 11.70 | 11.10 | 6.55 | 7.48 | 29.52 | 7.13 | 6.78 |
| GHC/Nm3 ( $\mathrm{H} 2+\mathrm{CO}$ ) conv.: | 188 | 105 | 182 | 183 | 178 | 104 | 191 |
| (18/C) Atomic Ratio in EC : | 2.67 | 2.89 | 2.12 | 2.14 | 2.14 | 2.18 | 2.12 |
| Selectivities, Wt \% of HC : |  |  |  |  |  | 2.02 |  |
| Methane | 2.98 | 8.18 | 8.16 | 8.76 8.56 | 8.81 8.50 | 8.81 | 8.81 |
| Bthene Bthane | 6.48 | 6.48 | 6.64 6.71 | 0.66 0.80 | 5.98 | 8.88 | E.87 |
| Brhane | 6.71 | 1.52 | 2.87 | 1.88 | 1.74 | 1.67 | 1.98 |
| Propane | 2.81 | 8.80 | 8.87 | 4.11 | 4.85 | 5.64 | 5.17 |
| Butenes | 2.81 | 2.22 | 3.44 | 2.58 | 2.15 | 1.77 | 2.80 |
| i-Butane | 8.20 | 4.86 | 4.64 | 5.83 | 8.12 | 5.46 | 5.79 |
| n-Butane | 2.10 | 2.67 | 8.63 | 8.86 | 8.83 | 8.63 | 8.02 |
| C5 - $\mathrm{Cl}_{11}$ | 88.84 | 81.70 | 88.78 | 86.29 | 29.20 | 28.86 | 27.90 |
| C12+ (Excl. Mx.-Tax) | 6.25 | 6.18 | 6.23 | 6.33 | 0.48 | 6.28 | 6.18 |
| Slurry Ex.-Tax | 58.88 | 50.08 | 44.74 | 46.24 | 46.88 | 58.95 | 48.88 |
| Total | 180 | 108 | 180 | 166 | 168 | 180 | 160 |
| i-C4/(C3) + C4F) Molar | 6.76 | 6.08 | 6. 78 | 1.18 | 1.82 | 1.82 | 1.14 |
| (C3/C8=) Molar Ratio | 1.58 | 1.93 | 1.41 | 2.41 | 2.55 | 2.87 | 2.62 |
| Alkylate, $7 t$ of EC | 6.25 | 7.98 | 8.84 | 0.11 | 8.52 | 7.69 | 9.35 |
| Cat-Pols, It $\%$ of EC : CE - C1I PONA, Wt \% : | ©.77 | ¢. 67 | 1.27 | 0.08 | 0.60 | ©.60 | 6.00 |
| Paraffing | -- | -- | 48.89 | 43.96 | -- | -- | 15.81 |
| Olefins | -- | -- | 17.08 | 12.59 | -- | -- | 6.83 |
| Naphthenes | -- | -- | 8.76 | 9.48 | -- | -- | 18.29 |
| Aromatica | -- | -- | 86.28 | 33.98 | -- | -- | 42.67 |

Table $A-\bar{t}$ (Cont'd)
Second-Staze Fizec-Eed 2SE-6 Reactor Oparating Conditions nod Material Balances
(Eun CT-253-7)

| (Mitrogen-Frae Basis) H.B. No. | 7-21 | 7-22 | 7-23 | 7-34 | 7-28 | 7-27 | 7-29 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Days On-stream | 25.4 | 28.4 | 27.4 | 28.4 | 31.4 | 32.4 | 24.4 |
| Firgt-Stage Conditions: |  |  |  |  | 0.689 | 6.671 | c. 689 |
| Charge E2/CO (Holer) | E. 687 | 0.828 | 0.688 | 0.685 | 0.689 | - 9.65 | * 257 |
| Temperatura, oc | 257 | 258 | 268 | 257 | 258 | 257 | 257 |
| Presbure, tra | 2.523 | 2.621 | 2.521 | 2.628 | 2.621 | 2.525 | 2.523 |
| Feed Sup. Vel., cm/s | 2.677 | 2.763 | 2.895 | 2.715 | 8.288 | 3.288 | 2.685 |
| Space Vel., NL/8Fe-hr | 4.487 | 4.497 | 4.728 | 4.824 | E. 123 | 6.287 | 5.188 |
| N2 in Feed, Hol \% | 8.9 | 3.6 | 6.8 | G. 8 | 9.5 | E. 5 | 0.8 |
| Second-Stage Conditions: <br> Temp., Inlet, oC | 889 | 875 | 374 | 874 4 | 876 893 | 878 898 | 378 4.98 |
| Pressure, kpa | 2.621 | 2.615 | 2.615 | 2.623 | 2.515 | 2.621 | 2.521 |
| GESY, 1/hr | 8988 | 85.53 | 4335 | 4418 | $68: 55$ | 8271 | 4994 |
| Deja On-strevm | 18.5 | 19.5 | 29.5 | 21.6 | 24.5 | 25.6 | $27 . E$ |
| Gonversions, Mol : H2 | 69.88 | 74.6 ¢ | 83.85 | 69.42 | 89.38 | 47. 49 | 52.68 |
| CO | 88.89 | 67.28 | 63.83 | 61.62 | 47.55 | 44.47 | 48.88 |
| H2-C0 | 68.98 | 79.53 | 63.54 | 61.18 | 48.68 | 45.6 \% | 48.52 |
| Tields, $\begin{gathered}\text { \#t } \\ \text { G of Products }: ~\end{gathered}$ Eydrocarbons | 17.16 | 17.37 | 14.69 | 18.47 | 11.11 | 12.52 | 12.49 |
| CO2 | 48.89 | 48.45 | 47.78 | 45.6중 | 83.82 | 32.82 | 34.20 |
| \#20 | 1.29 | 2.62 | 1.78 | 1.85 | 2.12 | 1.89 | 2.82 |
| H2 | 1.89 | 1.48 | 1.67 | 1.9 9 | 2.84 | 2.34 | 2.17 |
| C0 | 81.78 | 32.12 | 84.19 | 37.18 | E1.12 | 51.24 | 49.6 |
| Totel | 1985 | 169 | $1{ }^{169}$ | 1893 | 18 | 119 | 1 5 |
| Eal Recovery, Wt $\mathrm{F}_{\text {of }}$ Charge: | 89.49 | 88.22 | 1 192. 12 | 08.8す | 97.81 | 183.32 | 10-4.84 |
| (CO2) (표2)/(CO) (E20) : | 9.32 | 4.68 | 7.48 | 7.18 | 4.96 | 4.43 | 4.28 |
|  | 198 | 171 | 183 | 188 | 174 | 221 | 238 |
| (E/C) Atomic Batio in EC : | 2.18 | 2.11 | 2.16 | 2.15 | 2.14 | 2.13 | 2.13 |
| Selectivities, Wt of ES : Hethane | 2.81 | 2.14 | 8.93 | 4.12 | 4.10 | 3.79 | 8.48 |
| Ethens | 0.76 | 8.75 | 6.81 | 0.92 | 1.24 | 1.18 | 1.25 |
| Ethane | 1.34 | 1.07 | 1.87 | 1.11 | E.97 | ¢. 37 | 3.94 |
| Propene | 2.62 | 2.85 | 2.22 | 2.61 | 4.35 | 4.09 | 3.84 |
| Propane | 7.29 | E.57 | 6.87 | 6.67 | 4.88 | 4.23 | 4.48 |
| Euteres | 2.27 | 2.21 | 2.84 | 3.93 | 5.32 | 4.03 | 4.71 |
| i-Butare | 7.71 | 5.92 | 7.14 | 7.16 | 5.48 | 4.76 | 4.81 |
| n-Eutane | 6.21 | 8.97 | 4.82 | 3.89 | 3.87 | 8.83 | 8.84 |
| C5-C1I | 28.26 | 85.69 | 85.62 | 38.69 | 84.58 | 89.43 | 82.88 |
| C12+ (EICl. Ex.-Ta工) | c. 10 | 0.25 | E. 37 | 0.92 | 0.38 | 0.18 | 0.85 |
| SIurci Ex.-En | 41.31 | 39.67 | 34.48 | 29.82 | 35. | 42.38 | 49.99 |
| Total | 189 | 10영 | 19 | 16E] | 109 | 163 | 1598 |
| i-C4/(C3= + C4=) Holar | 1.58 | 1.17 | 1.30 | 1.08 | 0.48 | 6.44 | E. 47 |
| (C3/C3) Moler Ratio : | 8.39 | 2.65 | 2.98 | 2.18 | 1.88 | 1. 6 ㄱT | 2.11 |
| Alkflate, Wt \% Of EC | 2.45 | 0.27 | 19.64 | 12.12 | 19.78 | 0.35 | 9.48 |
| Cet-Poly, CE - CII PGid, Wt \% : | ©. $0^{3}$ | C.es | 6.69 | 6.65 | 4.86 | 4.45 | 2.81 |
| Paraffing | 41.28 | -- | -- | -- | 37.81 | 24.05 | 88.23 |
| Olefina | E.78 | -- | -- | -- | 18.83 | 27.11 | 16. 51 |
| Naphtienes | 18.28 | -- | -- | -- | 16.68 | 6.81 | 9.Es |
| Aromatics | 39.68 | -- | -- | -- | 32.75 | 22.24 | 33.67 |

Table A- $\delta$ (Cont'd)
Second-Stage Fixed-Bed 2SM-5 Reactor Operating Conditions and Yaterial Balances (Run CT-256-7)

| (Nitrogen-Free Basia) M.B. No. | 7-38 | 7-31 | 7-32 | 7-33 | 7-84 | 7-85 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Day: On-stream | 35.4 | 88.4 | 37.4 | 88.4 | 80.4 | 48.4 |
| First-Stage Conditions: <br> Charge E2/C0 (Molar) | 6. 693 | 6. 688 | 6. 886 | 6. 888 | 0.889 | 6.878 |
| Temperature, oc | 258 | 257 | 257 | 258 | 258 | 257 |
| Pressure, MPa | 2.621 | 2.542 | 2.585 | 2.635 | 2.536 | 2.621 |
| Feed Sup. Vel., em/s | 2.686 | 8.297 | 8.266 | 8.282 | 8.265 | 8.298 |
| Space Vel., ML/gFe-hr | 6.157 | 6.780 | 8.848 | 8.789 | 3.782 | 8.833 |
| N 2 in Yeed, Mol $\%$ | 0. 5 | 8.6 | 6.5 | 0.6 | 6.5 | 0.5 |
| Second-Stage Conditions: Temp., Inlet, oC | 870 | 888 | 886 | 889 | 894 | 898 |
| (emp., Outlet, oc | 460 | 484 | 488 | 481 | 485 | 401 |
| Presaure, MPa | 2.615 | 2.685 | 2.528 | 2.542 | 2.628 | 2.516 |
| GESV, 1/hr | 4684 | 6839 | 0817 | 6782 | 5842 | 5918 |
| Daya On-straam | 28.5 | 29.5 | 84.6 | 81.5 | 82.5 | 88.5 |
| $\underset{\text { H2 }}{\text { Conversions, }}$ Mol $\%$ | 58.81 | 48.78 | 49.84 | 56.47 | 51.37 | 51.49 |
| CO | 54.26 | 46.68 | 48.91 | 49.80 | 49.88 | 48.19 |
| H2+C0 | 54.08 | 43.05 | 49.28 | 52.22 | 66.18 | 49.61 |
| Yields, Vt $x$ of Products : Bydrocerboa: | 18.85 | 15.54 | 11.80 | 12.74 | 12.52 | 11.86 |
| C02 | 37.81 | 27.87 | 86.88 | 85.72 | 84.99 | 83.72 |
| 120 | 1.80 | 1.86 | 1.58 | 1.69 | 1.88 | 1.46 |
| H2 | 2.34 | 2.47 | 2.80 | 1.98 | 2.28 | 2.31 |
| CO | 44.31 | 67.77 | 48.96 | 47.97 | 49.15 | 54.97 |
| Total | 18. | 106 | 16t | 104 | 180 | 160 |
| Bal Recovery, It \% of Charge: | 98.24 | 98.16 | 09.61 | 180.82 | 08.19 | 96.91 |
| (CD2) (H2)/(CD) (H2O) : | 6.06 | 8.68 | 6.81 | 5.29 | 8.72 | 6.19 |
| cHC/Nims ( $\mathrm{Hz} 2+\mathrm{CO}$ ) conv.: | 104 | 188 | 188 | 192 | 191 | 177 |
| (B/C) Atomic Retio in EC : | 2.14 | 2.14 | 2.09 | 2.86 | 2.69 | 2.66 |
| Selectivitien, Et \% of BC : Yethane | 8.74 | 8.88 | 3.38 | 8.12 | 8.36 | 8.55 |
| Bthene | 1.25 | 1.77 | 1.58 | 1.88 | 2.82 | 2.43 |
| Bthane | 1.16 | 6.94 | 5.68 | ¢.68 | 6.67 | 6.72 |
| Propene | 3.83 | 8.78 | 4.86 | 4.92 | 5.71 | 8.41 |
| Propane | 4.74 | 5.03 | 8.18 | 2.68 | 2.62 | 2.37 |
| Buteres | 4.98 | 8.96 | 6.96 | 6.74 | 8.59 | 0.63 |
| i-Butare | 5.84 | 8.72 | 2.72 | 2.84 | 1.89 | 1.60 |
| n-Butane | 8.88 | 3.86 | 2.81 | 2.19 | 2.33 | 2.68 |
| C5 - C11 | 81.88 | 86.9 | 88.97 | 34.13 | 88.49 | 88.82 |
| C12+ (Excl. Rx.-Tax) | 6.61 | c. 68 | 0.65 | 6.17 | 0.61 | 0.11 |
| Slurry Rx.-Vax | 46.40 | 41.8 | 40.08 | 41.84 | 89.88 | 85.8 |
| Totel | 180 | 166 | $1{ }^{16}$ | 185 | 188 | 10. |
| i-C4/(C8x + C4=) Molar | 0.48 | 6. 30 | 6.24 | E. 15 | 6.11 | 6.88 |
| (C8/C3=) Moler Batio | 1.18 | 1.86 | 0.62 | 0. 58 | 6.42 | 0.85 |
| Alkylate, It X of EC | 9.91 | 2.81 | 5.85 | 4.62 | 8.71 | 2.95 |
| Cat-Poly, Wt $x$ of EC C5 - C11 POMA, It \% : | 8.95 | 7.87 | 9.12 | 0.69 | 12.48 | 13.98 |
| Parafifina | 89.01 | 85.12 | 82.75 | -- | 86.62 | -- |
| Olefins | 18.54 | 27.85 | 27.44 | -- | 88.35 |  |
| Naphthenes | 9.78 | 8.28 | 5.88 | -- | 4.37 |  |
| Aromatica | 82.87 | 29.26 | 84.81 | - | 29.28 | -- |



[^4]
(1) Cellected in Chilled aed Mbient Cosdonaere

Table A-s (Cost 'd)
Comporition of Gydrocerbos Preducts fros
Two-Siage Slurt p-3/2sy-5 Syizass Conversion
( 340 CT-250-7)

(1) Collectac in Ciniled amd Ambiont Cozdansors
Table A-s (Comt ${ }^{\text {' }}$ d)
Comporition of tydrocerbon Products fros Two-Stage Slurty f-T/254-5 Syage Coovernion
(1) C7-258-7)

(1) Coliected in chizied and Ambient Condeneers

## APPENDIX B

## HYDRODHMAMIC CORRETATIONS

 FOR SLUPRY REACTORSThe hydrodynamic correlations used in the current model calculations are summarized below:

- Bubble-size, Miller (1974)

$$
\begin{equation*}
\mathrm{d}_{\mathrm{B}}=.09+4 \cdot 15 \sigma \cdot 6_{\epsilon_{\mathrm{g}}} \cdot 5 /\left(\rho \mathrm{SL} \cdot 2\left(\mathrm{P}_{\mathrm{e}} / \mathrm{V}_{\mathrm{L}}\right) \cdot 4\right) \tag{Bi}
\end{equation*}
$$

- Gas holdup, Hiller (1974)
$\epsilon_{g}=\left(u_{g} /\left(u_{g}+u_{t}\right)\right)\left(d_{B} /\left(d_{B}-0.09\right)\right)^{2}$
- Bubble rise velocity, Mendelson (1967)
$u_{t}=\left(\left(2 \sigma / \rho_{L} \mathrm{~d}_{\mathrm{B}}\right)+\sigma \mathrm{d}_{\mathrm{B}} / 2\right) \cdot 5$
- Total power input, Hiller (1974)
$P_{e} / V_{\mathrm{L}}=\left(P_{\text {II }} / V_{L}\right)+C_{1} P_{g} / V_{L}$
- Power input by mechanical agitation, Hiller (1974)
$P_{m} / V_{L}=.230\left(P_{m o}{ }^{2 N D I}{ }^{3} / G_{G} \cdot 56\right) \cdot 45 / V_{\mathrm{L}}(B 5)$
- Power input by mechanical agitation in absence of gas; folland and Chapmen, (1966)
$P_{\text {mo }}=6.1 \rho$ SL $^{3} \mathrm{DII}^{5}$ for ReI $>104$
- Power input by gas sparging, Lehrer (1971)
$\mathrm{P}_{\mathrm{E}}=\mathrm{Q}_{\mathrm{g}} \rho_{\mathrm{E}}\left(\left(\boldsymbol{T U}_{0}^{2} / 2\right)+\operatorname{RTIn}\left(\mathrm{P}_{0} / \mathrm{P}_{\mathrm{L}}\right) / \mathrm{R}_{\mathrm{E}}\right)$
- Bubble-size at orifice, Miller (1974)
$\mathrm{dBo}_{0}=2.05\left(\mathrm{E}_{g} / \mathrm{N}_{0}^{\prime}\right) \cdot 4\left(3 \mathrm{C}_{\mathrm{D}} / 4 g\right) \cdot 2$
- Equilibrium bubble size in bubble-column,

Miller $(1974)$
$d_{B E}=.839 C_{D}-.6(d B-0.09) / \epsilon_{g} .5$

- Drag coefficient for turbulent chain bubbling,

Miller (1974)
$G_{D}=8 / 3$

- Parameter $\mathrm{N}_{0}^{\prime}$ in

$$
\begin{align*}
\mathrm{N}_{0} & =\mathrm{N}_{0} \text { for } \mathrm{dBO} .75<=\mathrm{d}  \tag{B11a}\\
& =1+.75 \mathrm{~d}\left(\mathrm{~N}_{\mathrm{O}}-1\right) / \mathrm{d}_{\mathrm{Bo}} \text { for } \mathrm{dBo} / .75>\mathrm{d}
\end{align*}
$$

- Mear bubble-size for bubble-column, Lehrer (1971)
$\mathrm{d}_{\mathrm{B}}=\left(\mathrm{d}_{\mathrm{Bo}} \mathrm{d}_{\mathrm{BE}}\right)$
- Mass transfer coefficients, Calderbank

$$
\begin{align*}
& \text { and Moo-Young, (1958) }  \tag{B13b}\\
& \mathrm{k}_{\mathrm{L}}=.42\left(\left(\rho_{\mathrm{SI}}-\rho_{\mathrm{g}}\right)^{2} \mathrm{~g}_{\mathrm{D}_{\mathrm{L}}}{ }^{3} / \rho_{\mathrm{SL}} \mathrm{HSI}^{1 / 3}\right)^{1 / 6} \mathrm{fOr} \mathrm{~dB}_{\mathrm{B}}>.25 \tag{Bi3a}
\end{align*}
$$

## APPENDTA C

## CORRELATIONS FOR PHYSICAL PARAMETERS

 OF SLURRY FISCHER-TROPSCH R彐ACTORSThe correlations used to estimate physical parameters, and catalyst physical properties are summarized in Tables $C-1$ and C-2.

Table C-1

Correlations Used In F-T Slurry Reactor
Mathematical Model Calculations

Correlations ${ }^{(1)}$
$\rho_{L}=.758-.555 \times 10^{-3}(\mathrm{~T}-373), \mathrm{g} / \mathrm{cm}^{3}$
$\mu_{\mathrm{L}}=.052 \exp (-6.905+3266 / \mathrm{T}), \mathrm{g} / \mathrm{cm}-\mathrm{s}$
$\mu_{s 1}=\mu_{\mathrm{L}}\left(1+4.5 \mathrm{v}_{\mathrm{c}}\right), \mathrm{g} / \mathrm{cm-s}$
(1) T in ${ }^{\circ} \mathrm{K}$.

## References

Deckwer, et al. (1982)
Deckwer, at al. (1982)
Deckwer, et al. (1982)
Solubility ( $\mathrm{cm}^{3}$ liquid/ $\mathrm{cm}^{3}$ gas)

| Erperimental | Hoelbel et al. (1055) Peter Weinert (1955) |
| :---: | :---: |
| n | - |
| n | - |
| " | * |
| Experimental + Correlation ${ }^{(2)}$ | Peter 械einert (1956) |
| Experimental + Correlation(3) | Zaidi et al (1979) |
| Experimental + Correlation(2) | Hayduk ${ }^{\text {a }}$ Cheng (1871) |
| Experimental + Correlation | Hayduk \% Cheng (1971) |

(2) Eatrapolation using correlation of diffusivity with liquid viscosity.
(3) Estimates of $D_{L 2}$ from correlation produced mass transfer coefficients which fitted experimental data.
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    （4）Collacted in Mot Gondenver

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    Gollacted in Ambiant and
    Gollectad in Mot Gondenoar界

[^3]:    Condenaer:

[^4]:    (1) Collected in Chilied and Ambient Condenaars

