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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS. FINAL REPORT

MOBIL RESEARCH AND DEVELOPMENT CORP.
PAULSBORO, NJ

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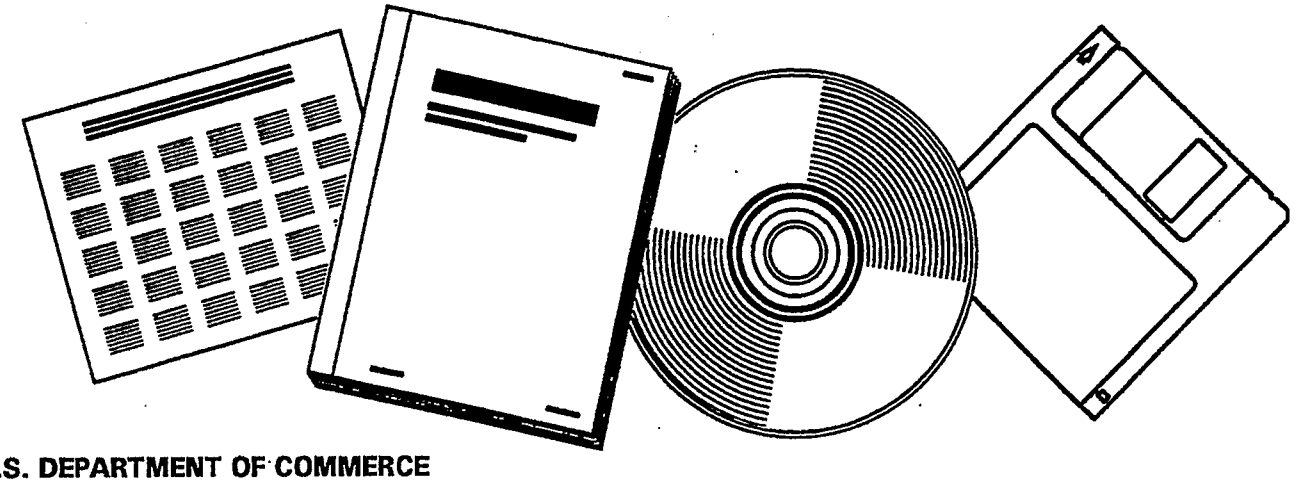

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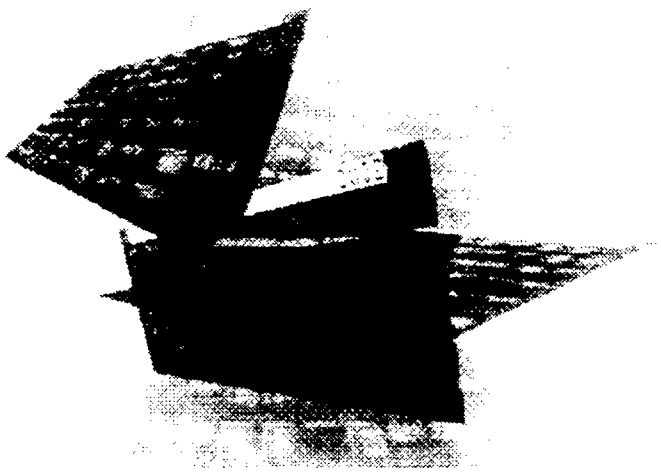

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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS

FINAL REPORT

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ABSTRACT

Scoping studies using conventional refinery technology to upgrade Fischer-Tropsch reactor-waxes were carried out. A Fischer-Tropsch reactor-wax, unlike the petroleum residues and waxes, is found very acceptable to conventional cracking processes. It was found that FCC followed by a Mobil proprietary olefins-to-(G+D) process gave the highest G+D yield and high G and D quality. Also described is a conceptual process design and scoping cost estimate for a 30,700 BPD G+D commercial plant.

I. Summary

Scoping studies of Fischer-Tropsch reactor-wax upgrading using convention refinery processes were performed starting in January 1984. The objective was to identify the processes which showed the greatest potential for commercial application and then to use it in a conceptual process design scheme.

Low pressure hydrocracking over Ketjet 742 catalyst gave high quality distillate and good G+D yields and was chosen for use in the base case wax upgrading scheme. Fluid Catalytic Cracking produced very low coke yields, moderate cetane index distillate, and highly olefinic light gas and gasoline. By applying Mobil's proprietary olefins-to-(G+D) process, excellent octane gasoline and the highest G+D yield among the processes studied was achieved. These two processes in series were therefore selected for the sensitivity case wax upgrading scheme. Hydrodewaxing gave acceptable quality distillate only at low conversions, so it was not considered further.

Unlike petroleum residues and waxes, a Fischer-Tropsch reactor-wax was found very acceptable to conventional cracking processes. This is probably resulted from its unique straight-chain hydrocarbon molecules. The wax also contains no nitrogen and heavy metal compounds that will temporarily or permanently deactivate the cracking catalyst.

The investment cost of a battery-limit commercial plant with a capacity of 30,700 BPD (G+D) was estimated at $705 million (1985 $) using the base case wax upgrading, and $735 million for the sensitivity case.

A proprietary method of using a high gradient magnetic separator was successfully used to remove the small amount of the Fischer-Tropsch catalyst in a Fischer-Tropsch reactor-wax.

II. Potentially Patentable Subject Matter

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

A.1. Low Pressure Hydrocracking of a Fischer-Tropsch Reactor-Wax

Two sets of scoping hydrocracking studies were performed in a microreactor containing 5-10 cm^3 catalyst, using Run CT-256-4 reactor-wax. The solid content of this wax was reduced from 0.13 wt % to less than 0.015 wt % using a Mobil proprietary technique described in Subsection III.A.1. A total of 3.2 kg clean wax was prepared. The first set of the studies used a Mobil proprietary hydrocracking catalyst. The conditions were 329-371°C, 4.58 MPa, 0.5-2 LHSV and 675 NL H_2/L.

The gas product was analyzed using gas chromatography. The liquid product was distilled into gasoline (to 177°C), distillate (177-344°C) and residue (344°C+). The gasoline was analyzed for PONA using liquid chromatography, and the octane numbers were obtained from a correlation based on its composition. The distillate fraction was analyzed for pour point, and the cetane index was determined from a correlation using the density and the simulated distillation midpoint. In addition, hydrogen consumption was estimated from hydrogen balance using the hydrogen contents of the hydrocarbon products and the feed reactor-wax. The results are summarized in Tables ARD-II-1 and ARD-II-2.

The major findings from high severity runs (Runs 1 to 3) are:

- 80-100 wt % conversion of 344°C+ but moderate G+D yield (47-70 wt % gasoline, 1-10 wt % distillate).
- Increased G+D (48 to 80 wt %) and decreased methane + ethane yields (1.7 to 0.2 wt %) with decreasing severity (371 to 329°C).

Table ARD-II-1

Hydrocracking of a
Fischer-Tropsch Reactor-Wax(1)
(Mobil Proprietary Catalyst,
Run CT-256-4 Reactor-Wax)

Run No.	1	2	3	4	5
DOS	1.7	2.7	3.4	5.0	5.7
Temperature, °C	371	344	329	330	329
LHSV, cm^3 per hr/cm^3-cat.	.5	.5	.5	1	2
Recovery, wt %	95.3	105.2	93.8	98.4	97.7
Conversion, wt %(2)	98.9	98.0	80.0	12.1	5.8
H_2 Consumption, NL/L Conv.	234	200	151	-	34
Selectivity, wt % ($G+D+C_4^-$)					
C_1	0.5	0.1	0.1	0	0
$C_2/C_2^=$	1.2/0	0.3/0	0.3/0	0/.4	0/0
C_3-C_4 Olefins	0.7	0.6	0.4	.8	0
C_3	7.5	3.3	4.0	7.3	4.9
iC_4	18.1	16.0	15.0	11.9	8.9
nC_4	24.2	10.9	5.0	1.4	0
C_5-177°C	46.8	66.4	65.2	53.8	37.1
177-344°C	1.0	2.4	10.0	24.4	49.1
Total	100.0	100.0	100.0	100.0	100.0

(1)5-10 cc catalyst, 4.58 MPa, 0.5 LHSV, 675 NL H_2/L.

(2)Based on 344°C$^-$ Product.

Table ARD-II-2

Products from Hydrocracking
of a Fischer-Tropsch Reactor-Wax
(Mobil Proprietary Catalyst,
Run CT-256-4 Reactor-Wax)

Run No.	1	2	3	4	5
LHSV, cm^3 per hr/cm^3-cat.	0.5	0.5	0.5	1	2
Temperature, °C	371	344	329	330	329
Distillate					
Cetane Index	34	-	65	51	59
Pour Point, °C	-52	-32	-36	-11	- 2
Raw Gasoline					
Paraffin, wt %	96.5	91.5	89.7	-	-
Olefin	.05	3.6	6.1	-	-
Naphthene	.05	3.1	4.1	-	-
Aromatic	2.4	1.8	.1	-	-
	100.0	100.0	100.0	-	-
Octane Number (R+O)	83.9	80.8	73.5	-	-

Other major findings are:

- Very low conversion (6-12 wt % of 344°C$^-$ product) and high G+D yields (78-86 wt %) at low severity (1-2 LHSV).
- Highly paraffinic, and consequently low to moderate octane number (74-84 R+0) gasoline.
- High cetane index (51-65) but high pour point (-2 to -36°C) distillate at low severity (329°C, 1-2 LHSV).
- Significant increases in G+D yield, distillate cetane index and distillate pour point, but a decrease in gasoline octane number with decreased severity (low temperature and high LHSV).

The very low conversion during low severity (1-2 LHSV) operation is inconsistent with the higher severity results. This is shown in Figure ARD-II-1, by plotting conversion versus LHSV. The dotted line is the expected theoretical curve for first order kinetics. As shown, the 1 and 2 LHSV points are well below the expected conversions. For higher order kinetics, the discrepancy is even larger. A possible explanation for this discrepancy is that the catalyst was not at the same state between these two groups of experiments, as approximately one month elapsed between them.

In the second set of experiments, a Ketjen 742 catalyst was used. Six scoping runs were performed in a microreactor containing 10 cm^3 catalyst. The conditions were 342-454°C, 4.58 MPa, 0.5 LHSV, and 675 NL H_2/L.

The gas product was analyzed using gas chromatography. The liquid product was distilled into gasoline (to 177°C), distillate (177-344°C) and residue (344°C$^+$). The results are summarized in Table ARD-II-3:

The major findings are:

- The converison ranged from 3-72 wt % of 344°C$^+$, with acceptable conversion only at high temperatures (>426°).
- The G+D yield ranged from 86-93 wt % of G+D+C_4^-, and it increased with increasing severity (temperature).
- The liquid product was predominantly in the distillate range (G/D of .03-.21), and the G/D ratio increased with severity.
- The methane + ethane yield ranged from 3.6-7.6 wt %, and it decreased with increasing severity.

Figure ARD-II-1

HYDROCRACKING OF A FISCHER-TROPSCH REACTOR-WAX

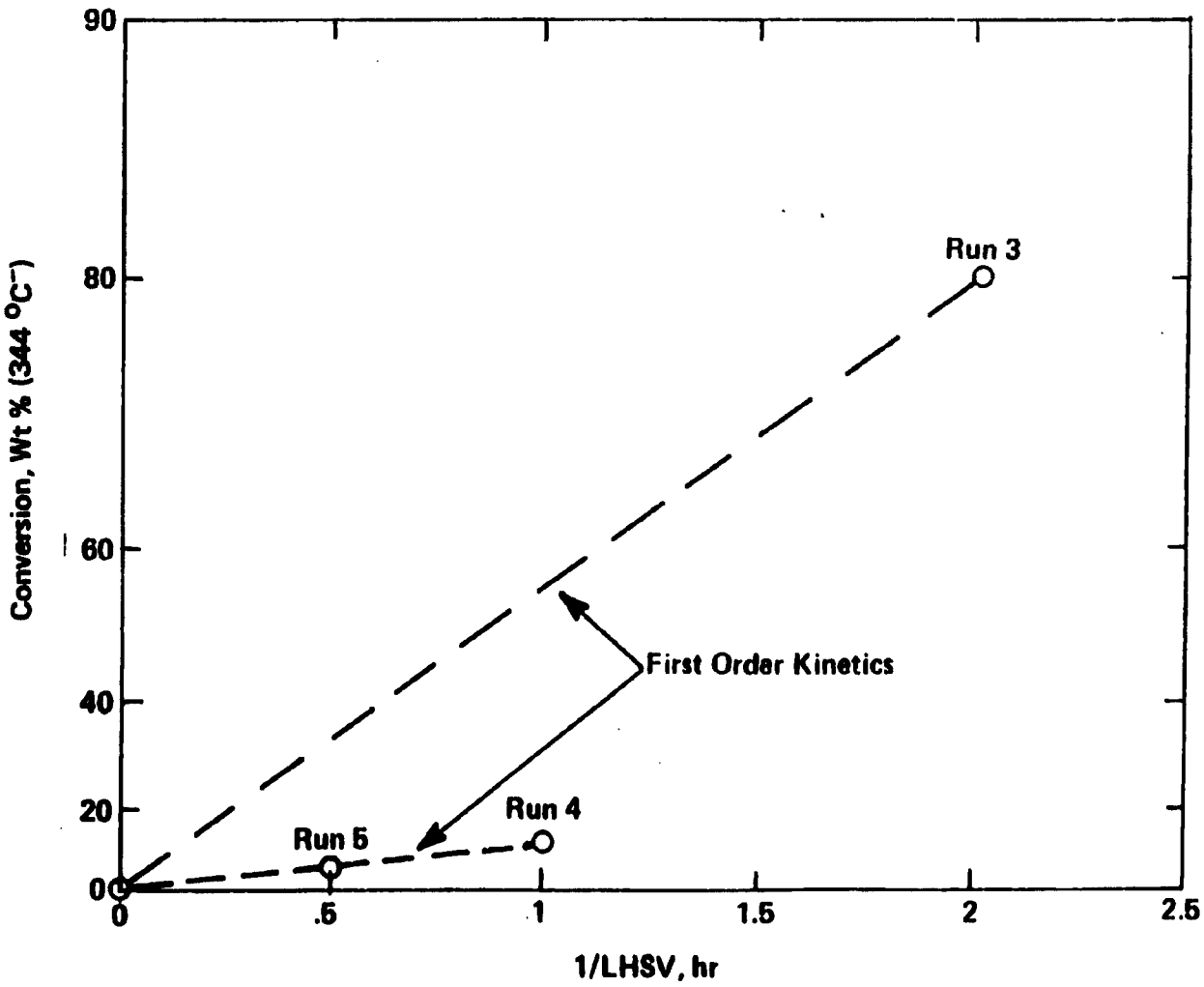


Table ARD-II-3

Hydrocracking of a
Fischer-Tropsch Reactor-Wax(1)
(Ketjen 742 Catalyst,
Run CT-256-4 Reactor-Wax)

Run No.	6	7	8	9	10	11
DOS	0.8	1.7	2.6	3.5	4.4	5.3
Temperature, °C	342	371	400	414	426	454
Recovery, wt %	98.9	101.3	99.3	99.6	99.0	98.5
Conversion, wt %(2)	3.2	4.1	6.4	11.0	18.9	71.5
Selectivity, wt % (G+D+C_4^-)						
C_1	3.2	4.7	4.5	3.7	2.6	1.9
$C_2/C_2^=$	4.4/0	1.6/4.9	3.5/0	3.5/0	1.0/0	2.2/0
C_3-C_4 Olef.	0	0.8	0.7	0.9	0	0.3
C_3	0	1.9	2.0	2.4	3.0	2.3
iC_4	1.6	0	2.5	3.1	1.9	0.2
nC_4	0	0	0	0	0	0.6
C_5-177°C	8.2	2.7	5.0	3.9	7.5	16.2
177-344°C	82.6	83.4	81.8	82.6	84.0	76.3
Total	100.0	100.0	100.0	100.0	100.0	100.0

(1)10 cm^3 catalyst, 4.58 MPa, 0.5 LHSV, 675 NL H_2/L

(2)Based on 344°C^-

The G+D yields were better than those with the Mobil hydrocracking catalyst. The best yield is slightly lower than that reported by SASOL (Dry, 1976), i.e., 93 versus 95 wt %.

The gasoline products from the two high temperature runs (Runs 10 and 11) were analyzed for PONA using liquid chromatography, and the octane numbers were estimated by using an in-house blending model. Table ARD-II-4 shows that these gasolines are highly paraffinic. Furthermore, the analysis showed that the paraffins are mostly normal (80%), thus giving very low octane number. Hence, further upgrading of this gasoline may be required.

The distillate products were analyzed for pour point and their cetane indexes were estimated from a simulated ASTM distillation, and from measured density at 16°C. The results are also shown in Table ARD-II-4. At high severity, the distillate is of good quality, having very high cetane index and acceptable pour point.

The hydrogen consumption was also estimated from analysis of the hydrogen content of the wax and liquid products, and from the hydrogen content of the hydrocarbons in the product gas. The estimate for the highest severity is given in Table ARD-II-4. The hydrogen consumption for lower severity runs could not be estimated with sufficient accuracy.

In conclusion, hydrocracking over Ketjen 742 catalyst gave good G+D yields and conversion, with mostly high quality distillate and a small yield of low octane gasoline. This process is being chosen for our conceptual design study in Task 5. The temperature used here is higher than the temperature nominally used in petroleum-based hydrocracking while the pressure is substantially lower. We believe that further catalyst exploratory may lead to a lower temperature catalyst and operation.

A.2. Fischer-Tropsch Reactor-Wax Hydrodewaxing

Scoping hydrodewaxing studies were performed in a microreactor containing 5 cm^3 catalyst, using Run CT-256-4 reactor-wax. The conditions were 316-343°C, 2.86 MPa, 1.0 LHSV and 422 NL H_2/L. The catalyst was a ZSM-5 class Mobil proprietary hydrodewaxing catalyst.

Table ARD-II-4

Products from Hydrocracking of
a Fischer-Tropsch Reactor-Wax
(Ketjen 742 Catalyst,
Run CT-256-4 Reactor-Wax)

Run No.	6	7	8	9	10	11
DOS	.8	1.7	2.6	3.5	4.4	5.3
Temperature, °C	342	371	400	413	426	454
Conversion, wt %(1)	3.2	4.1	6.4	11.0	18.9	71.5
H_2 Consumption, NL/L Conv.	-	-	-	-	-	110
Selectivity, wt % ($G+D+C_4^-$)						
C_4^-	9.2	13.9	13.2	13.5	8.5	7.5
C_5-177°C Gasoline	8.2	2.7	5.0	3.9	7.5	16.2
177-343°C Distillate	82.6	83.4	81.8	82.6	84.0	76.3
Total	100.0	100.0	100.0	100.0	100.0	100.0
Product Properties						
C_5-177°C Gasoline						
Paraffin, wt %	-	-	-	-	63.3	69.3
Olefin	-	-	-	-	14.9	3.2
Naphthene	-	-	-	-	9.7	13.1
Aromatic	-	-	-	-	12.1	14.4
Total					100.0	100.0
R+O	-	-	-	-	39	35
177-343°C Distillate						
Cetane Index	-	-	-	-	68	72
Pour Point, °C	4	3	-14	-1	-6	-16

(1)Based on 343°C⁻ Product

The gas product was analyzed using gas chromatography, the liquid product was analyzed using simulated distillation chromatography, and it was distilled into gasoline (to 177°C), distillate (177-344°C) and residue (344°C$^+$) fractions. The results of the analyses are summarized in Table ARD-II-5. The gasoline and distillate fractions were also analyzed for their properties as described in the preceding Subsection. The results are summarized in Table ARD-II-6.

The major findings are:

- 15-71 wt % conversion to 344°C$^-$ and moderate G+D yield (53-61 wt % gasoline, 11-26 wt % distillate).
- G+D yield increased only moderately (70 to 79 wt %) while conversion decreased significantly (71 to 15 wt %) with decreasing severity (343 to 316°C).
- Low hydrogen consumption (<51 NL/L converted).
- Highly paraffinic (52-61 wt %) and moderate octane number (81-86 R+O) gasoline.
- High cetane index (61-68) but also relatively high pour point (6 to -30°C) distillate from low severity operation (<330°C reactor temperature).
- Significant increase in the distillate cetane index and the gasoline octane number, but also some increase in the distillate pour point with lower reactor temperature.

It appears that acceptable distillate yields can only be obtained at very low conversions, this being probably due to the shape selectivity of the ZSM-5 class catalyst. Therefore, no further scoping studies are planned, the effort being focused on other more promising reactor-wax upgrading schemes.

A.3. Fischer-Tropsch Reactor-Wax Catalytic Cracking

Scoping studies were performed in a Fluid Catalytic Cracking (FCC) riser (Unit CT-180) using Run CT-256-4 reactor wax. The conditions were 1 s residence time, 4.2-5.5 cat/oil ratio, 478-524°C maximum temperature, 465-506°C top temperature, 0.11 MPa oil partial pressure. The catalysts were commercial equilibrium and coke zeolite (Engelhard HEZ-53) and equilibrium Si/Al cracking catalyst.

Table ARD-II-5

Hydrodewaxing of a
Fischer-Tropsch Reactor-Wax(1)
(ZSM-5 Class Catalyst,
Run CT-256-4 Reactor-Wax)

Run No.	1	2	3
DOS	1.7	2.6	3.5
Temperature, °C	343	330	316
Recovery, wt %	93.5	103.4	104.8
Conversion, wt %(2)	70.8	31.6	14.9
H_2 Consumption, NL/L Conv.	51	-	-
Selectivity, wt % ($G+D+C_4^-$)			
C_2°	1.0	0.6	0.4
C_3-C_4 Olef.	1.0	3.3	4.4
C_3	6.7	6.1	7.4
iC_4	10.6	7.2	6.5
nC_4	10.8	7.3	2.5
C_5-177°C	58.6	61.2	52.9
177-344°C	11.3	14.3	25.9
Total	100.0	100.0	100.0

(1)5 cm^3 catalyst, 2.86 MPa, 1.0 LHSV, 422 NL H_2/L

(2)Based on 344°C^- Product

Table ARD-II-6

Products from Hydrodewaxing of a Fischer-Tropsch Reactor-Wax (ZSM-5 Class Catalyst, Run CT-256-4 Reactor-Wax)

Run No.	1	2	3
Temperature, °C	343	330	316
Distillate			
Cetane Index	33	61	68
Pour Point, °C	-130	-30	6
Raw Gasoline			
Paraffin, wt %	61.1	55.9	51.8
Olefin	7.9	27.0	39.6
Naphthene	5.5	2.8	2.0
Aromatic	25.5	14.3	6.6
	100.0	100.0	100.0
Octane No. (R+O)	80.7	82.3	85.9

The gas product was analyzed using gas chromatography, the liquid product was distilled into gasoline (to 194°C), distillate (194-344°C) and residue (344°C+) fractions. The gasoline and the distillate fractions were also analyzed for their properties as mentioned in the Subsection ARD-II-A.1. The results are summarized in Tables ARD-II-7 and ARD-II-8. Note that the cetane indexes and pour points of the FCC distillate are those before distillate hydrotreating (DHT). With the conversion of the olefins to paraffins in the DHT, small changes in both the cetane indexes and pour points may be expected.

The major findings are:

- Very high (91-93 wt %) conversion and high G+D yields (75-81 wt %).
- High olefin content in light gas (75 wt % in C_4^-).
- Insensitivity of product distribution to severity (temperature variation and coked catalyst versus equilibrium catalyst).
- Very low coke yield.
- High octane (90-92 R+O) but highly olefinic (63-73 wt %) gasoline.
- Moderate cetane index (49-53) and good pour point (-23 to -34°C) distillate.

The coke yield is so low that in a commercial FCC unit, other fuels, such as a small quantite of clean synthesis gas, will be needed in the FCC regenerator to provide sufficient heat for the FCC reactor.

The highly olefinic nature of the gasoline and light gas points to a route of further upgrading the FCC product using the Mobil proprietary MOGD process (Tabak and Krambeck, 1985) for converting olefins to G+D. Table ARD-II-9 shows the MOGD can increase the G+D to 91 wt % of 344°C$^-$ product,and that potential liquid product yield (C_3^+) to 98.2 wt % of the product, which is comparable or better than that reported by Dry (1976) using hydrocracking. The MOGD yield was estimated from a Mobil proprietary mathematical model. The results with Si/Al cracking catalyst were inferior to those with zeolite (Engelhard HEZ-53). Table ARD-II-9 also compares the three upgrading processes: hydrocracking, hydrodewaxing, and FCC + MOGD. The FCC + MOGD gives the highest G+D yield and excellent gasoline octane number.

Table ARD-II-7

Fischer-Tropsch
Reactor-Wax Upgrading Using FCC(1)

Run No.	1	2	3
Catalyst	HEZ-53(2)	HEZ-53	Coked HEZ-53
Cat/Oil Ratio, wt.	4.2	4.2	4.4
Oil Res. Time, s	1	1	1
T_{max}, °C	523	478	524
T_{top}, °C	504	465	505
Oil Partial Pressure, MPa	0.11	0.11	0.11
Recovery, wt %	96.9	93.4	93.1
Conversion, wt %(3)	93.0	91.4	91.1
Selectivity, wt % (G+D+C_4^-)			
Coke	0.9	1.1	-0.6
C_1	1.1	.6	1.3
$C_2/C_2^=$	1.2/1.2	.7/.7	1.5/1.5
C_3-C_4 Olef.	17.7	13.0	16.1
C_3	1.5	1.1	1.4
iC_4	1.9	2.5	1.4
nC_4	.6	0.6	0.6
C_5^+-194°C	56.3	56.5	57.0
194-344°C	17.6	23.2	19.8
Total	100.0	100.0	100.0

(1)Unit CT-180 Riser, Run CT-256-4 Reactor-Wax

(2)Commercial Equilibrium Catalyst

(3)Based on 344°C$^-$ Product

Table ARD-II-8

Products from FCC Upgrading
of a Fischer-Tropsch Reactor-Wax

Run No.	1	2	3
Catalyst	HEZ-53	HEZ-53	Coked HEZ-53
T_{max}, °C	523	478	524
Distillate			
Cetane Index	51	53	49
Pour Point, °C	-23	-23	-34
Raw Gasoline			
Paraffin, wt %	20.7	24.9	12.9
Olefin	65.7	62.5	73.4
Naphthene	4.0	4.0	2.9
Aromatic	9.6	8.6	10.8
	100.0	100.0	100.0
Octane No. (R+O)	91.5	89.8	91.6

Table ARD-II-9

Comparison of Fischer-Tropsch
Reactor-Wax Upgrading Methods

	Hydrocracking	Hydrodewaxing	FCC (+MOGD)
Catalyst	Mobil	ZSM-5 Class	HEZ-53
Temperature, °C	329	330	465-478
Pressure, MPa	4.58	2.86	0.11
LHSV, cm^3 per hr/cm^3-cat.	0.5	1.0	4.2/1(1)
Conversion, wt %	80	32	91
H_2 Consumption, NL/L Conv.	151	0	-
Selectivity, wt %			
Coke	-	-	1.1(1.1)
C_2^-	0.4	0.6	2.0(1.8)
C_3-C_4 Olef.	0.4	3.3	13.0(2.0)
LPG	9.0	13.4	1.7(2.1)
iC_4	15.0	7.2	2.5(2.6)
C_5-177°C Gasoline	65.2	61.2	56.5(2) (38.8)
177-344°C Distillate	10.0	14.3	23.2(2) (51.6)
	100.0	100.0	100.0
Gasoline (C_5-177°C)			
PONA, wt %	90/6/4/0	56/27/3/14	25/63/4/8
Octane No. (R+O)	74	82	90
Distillate (177-344°C)			
Pour Point, °C	-36	-30	-23
Cetane Index	65	61	53

(1)Cat to oil weight ratio/oil residence time(s)

(2)C_5^+-194°C Gasoline, 194-344°C Distillate

B. Task 5 - Development of Conceptual Process Schemes

B.1. Introduction

Based on the results of F-T reactor-wax upgrading reported in the preceding Section, two reactor-wax upgrading processes are chosen for this task:

Base Case - Low Pressure Hydrocracking

Sensitivity Case - FCC + MOGD + DHT

B.2. Design Base Data for Fischer-Tropsch Reactor-Wax Upgrading - Base Case

In the base case, reactor-wax is upgraded into gasoline and distillate by low pressure hydrocracking using a Ketjen 742 hydrocracking catalyst. The data is based on scoping hydrocracking studies in a microreactor (Run 11, Tables ARD-II-3 and II-4). The process scheme is shown in Figure ARD-II-2 and the operating conditions are given in Table ARD-II-10. The product yields, expressed as mol/100 mol of feed H_2+CO are given in Tables ARD-II-11 to -13, while the overall product yields are given in Table ARD-II-14. Since the hydrocracking gasoline has very low octane, it was assumed that this gasoline can be co-fed with the overhead F-T product from the first-stage reactor into the second-stage ZSM-5 reactor.

The estimated gasoline + distillate selectivity is 87 wt % of total hydrocarbons produced, including 0.6 wt % of imported isobutane, substantially higher than the 80 wt % from the gasoline mode operation of the previous contract (Kuo, 1983); the G/D ratio is 1.2/1. The gasoline has high octane (93 R+O) and the distillate has high cetane index (72).

B.3. Design Base Data for Fischer-Tropsch Reactor-Wax Upgrading - Sensitivity Case

In the sensitivity case, reactor-wax is upgraded to gasoline and distillate by FCC using an Engelhard HEZ-53 catalyst. The data is based on scoping studies in a small riser reactor (Run 2, Tables ARD-II-7 and II-8). The highly olefinic FCC light gas and gasoline can be converted by the MOGD process into high quality gasoline and distillate. The MOGD data are estimated based on pilot plant studies with FCC olefinic feeds. The process scheme is also shown in Figure ARD-II-2 and the operating conditions are given in Table ARD-II-15. The product yields expressed as mol/100 mol feed H_2+CO are given in Tables ARD-II-16 and ARD-II-17, while the overall product yields are given in Table ARD-II-14.

Figure ARD-II-2
PROCESS SCHEME FOR HIGH-WAX MODE OPERATION

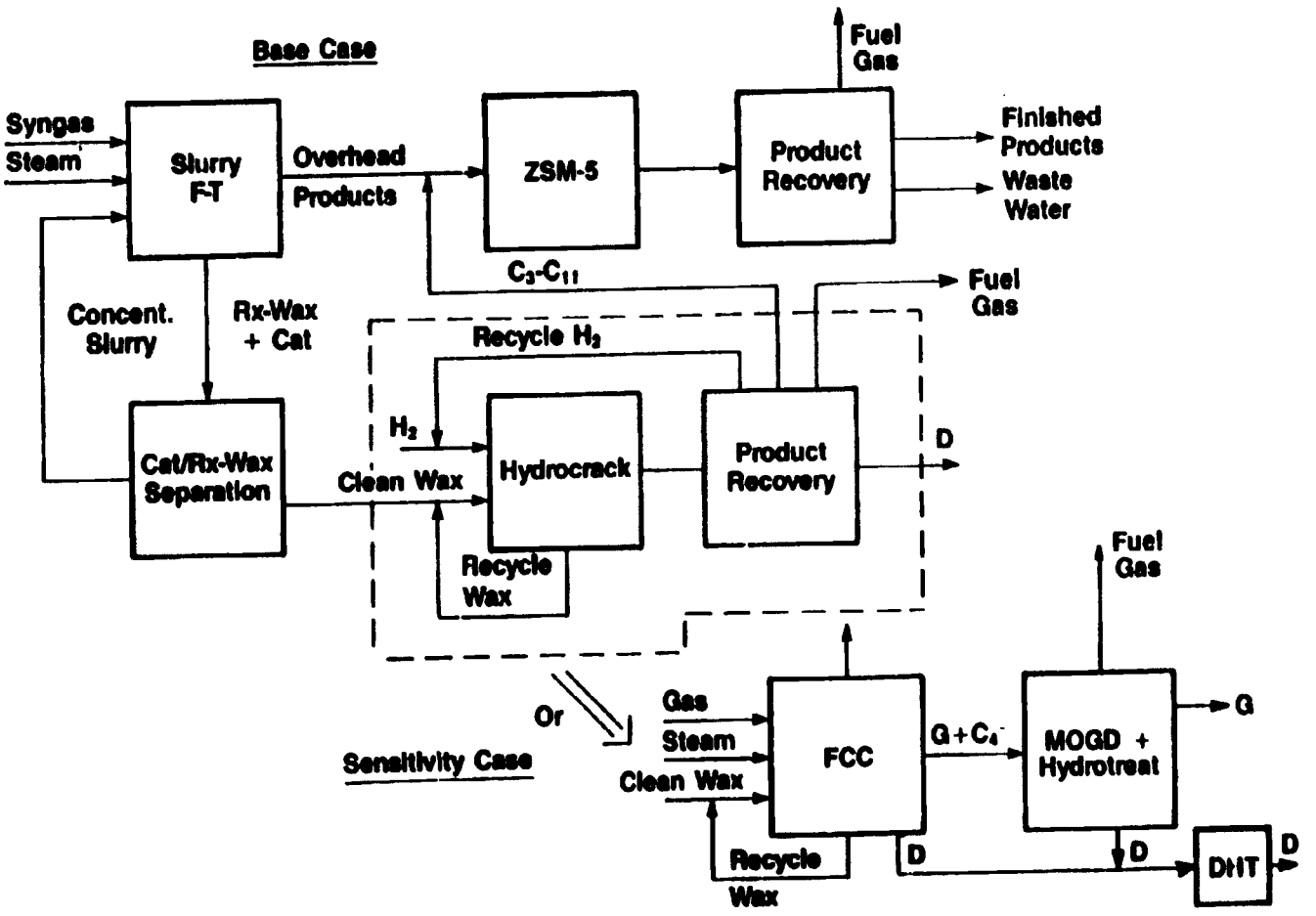


Table ARD-II-10

Process Conditions - Base Case

	First-Stage (F-T)	Second-Stage (ZSM-5)	Hydrocracker
Catalyst	I-B(Pptd Fe/ Cu/K_2CO_3)	ZSM-5	Ketjen 742
Feed H_2/CO, molar	0.5	-	-
Inlet Pres., MPa	2.87	Cascaded	4.58
Inlet Temp., °C	227	371	454(1)
Outlet Temp., °C	258	392	NA
Space Velocity	3.50 NL(H2+CO)/ gFe-hr	8.0 NL/gCat-hr	0.5 WHSV
H_2 Consumption, NL/L	-	-	110
Heat of Reaction, kJ/mol H_2+CO in Feed	56.3	0.6	NA

(1)Average temperature

Table ARD-II-11

HYDROCRACKER FEED AND PRODUCT YIELDS

(BASIS: 100 MOL FEED H2-CO)

	MOL FEED	MW	SP. GR	MOL PROD
WATER		18.02	-	0.0994
HYDROGEN	1.1185	2.02	-	0.0000
METHANE		16.04	-	0.2396
ETHANE		30.07	-	0.1445
PROPANE		44.10	0.5077	0.1053
PROPENE		42.08	0.5210	0.0071
N-BUTANE		58.12	0.5844	0.0222
I-BUTANE		58.12	0.5631	0.0058
N-BUTENE		56.11	0.6011	0.0048
N-PENTANE		72.15	0.6312	0.0106
I-PENTANE		72.15	0.6248	0.0110
CYCLOPENTANE		70.14	0.7505	0.0010
N-HEXANE		86.18	0.6640	0.0146
I-HEXANE		86.18	0.6630	0.0017
N-HEXENE		84.16	0.6805	0.0014
METHYLCYCLOPENTANE		84.16	0.7505	0.0054
CYCLOHEXANE		84.16	0.7834	0.0000
BENZENE		78.11	0.8845	0.0011
N-HEPTANE		100.21	0.6882	0.0137
I-HEPTANE		100.21	0.6830	0.0061
N-HEPTENE		98.19	0.7835	0.0037
DIMETHYL-CYCLOPENTANE		98.19	0.7496	0.0046
METHYLCYCLOHEXANE		98.19	0.7748	0.0048
TOLUENE		92.14	0.8719	0.0121
N-OCTANE		114.23	0.7068	0.0000
I-OCTANE		114.23	0.7001	0.0112
N-OCTENE		112.21	0.7212	0.0046
C8-N6		112.21	0.7786	0.0050
C8-N8		112.21	0.7922	0.0000
M-XYLENE		106.17	0.8687	0.0000
O-XYLENE		106.17	0.8848	0.0094
ETHYLBENZENE		106.17	0.8717	0.0053
N-NONANE		128.26	0.7176	0.0414
I-NONANE		128.26	0.7215	0.0101
N-NONENE		126.24	0.7334	0.0022
C9-N6		126.24	0.7500	0.0030
C9-N8		126.24	0.7977	0.0037
N-PROPYLBENZENE		120.20	0.0000	0.0016
METHYL-ETHYL-BENZENE		120.20	0.0000	0.0000
TRIMETHYL-BENZENE		120.20	0.0000	0.0018
N-DECANE		142.28	0.7341	0.0078
I-DECANE		142.28	0.7340	0.0001
N-DECENE		140.27	0.7451	0.0000
C10N6		140.27	0.7954	0.0011
C10N8		140.27	0.0031	0.0013
N-C4-BENZENE		134.22	0.0046	0.0002
TETRA-METHYL-BENZENE		134.22	0.0000	0.0000
DIETHYLBENZENE		134.22	0.8700	0.0004
C11-PARAFFIN		156.31	0.7443	0.0014
177-344°C		200.00	0.7000	0.7202
RX-WAX	0.2414	821.41	0.8700	--
TOTAL MOL	1.3599			1.0500
WT	200.55			200.55

Table ARD-II-12

HYDROCRACKER C11⁻ GASOLINE FEED TO SECOND-STAGE REACTOR

(BASIS: 100 MOL FEED H2-CO)

	MW	SP. GR	MOL
PROPANE	44.10	0.5077	0.1053
PROPENE	42.08	0.5218	0.0071
N-BUTANE	58.12	0.5844	0.0222
I-BUTANE	58.12	0.5631	0.0058
N-BUTENE	56.11	0.6011	0.0048
N-PENTANE	72.15	0.6312	0.0106
I-PENTANE	72.15	0.6248	0.0110
CYCLOPENTANE	70.14	0.7505	0.0010
N-HEXANE	86.18	0.6640	0.0146
I-HEXANE	86.18	0.6630	0.0017
N-HEXENE	84.16	0.6805	0.0014
METHYLCYCLOPENTANE	84.16	0.7505	0.0054
CYCLOHEXANE	84.16	0.7834	0.0008
BENZENE	78.11	0.8845	0.0011
N-HEPTANE	100.21	0.6882	0.0337
I-HEPTANE	100.21	0.6830	0.0061
N-HEPTENE	98.19	0.7035	0.0037
DIMETHYL-CYCLOPENTANE	98.19	0.7496	0.0046
METHYLCYCLOHEXANE	98.19	0.7740	0.0048
TOLUENE	92.14	0.8719	0.0121
N-OCTANE	114.23	0.7068	0.0508
I-OCTANE	114.23	0.7061	0.0112
N-OCTENE	112.21	0.7212	0.0040
C8-N5	112.21	0.7700	0.0058
C8-N6	112.21	0.7922	0.0060
M-XYLENE	106.17	0.8687	0.0068
O-XYLENE	106.17	0.8848	0.0094
ETHYLBENZENE	106.17	0.8717	0.0053
N-NONANE	128.26	0.7176	0.0414
I-NONANE	128.26	0.7215	0.0101
N-NONENE	126.24	0.7334	0.0022
C9-N5	126.24	0.7500	0.0030
C9-N6	126.24	0.7977	0.0037
N-PROPYLBENZENE	120.20	0.8666	0.0016
METHYL-ETHYL-BENZENE	120.20	0.8690	0.0036
TRIMETHYL-BENZENE	120.20	0.8696	0.0018
N-DECANE	142.28	0.7341	0.0078
I-DECANE	142.28	0.7340	0.0031
N-DECENE	140.27	0.7451	0.0008
C10N5	140.27	0.7954	0.0011
C10N6	140.27	0.8031	0.0013
N-C4-BENZENE	134.22	0.8646	0.0002
TETRA-METHYL-BENZENE	134.22	0.8900	0.0006
DIETHYLBENZENE	134.22	0.8700	0.0004
C11-PARAFFIN	156.31	0.7443	0.0014
TOTAL MOL			0.4412
WT			39.08

Table ARD-II-13

SECOND-STAGE PRODUCT FROM HYDROCRACKER GASOLINE

(BASIS: 100 MOL FEED H2+CO)

	MW	SP. GR	MOL
METHANE	16.04	-	0.0027
ETHANE	30.07	-	0.0019
PROPANE	44.10	0.5077	0.2253
PROPENE	42.08	0.5218	0.0047
N-BUTANE	58.12	0.5844	0.0684
I-BUTANE	58.12	0.5631	0.0430
N-BUTENE	56.11	0.6011	0.0042
N-PENTANE	72.15	0.6312	0.0181
I-PENTANE	72.15	0.6248	0.0312
N-PENTENE	70.14	0.6461	0.0007
I-PENTENE	70.14	0.6325	0.0197
CYCLOPENTANE	70.14	0.7505	0.0007
N-HEXANE	86.18	0.6640	0.0100
I-HEXANE	86.18	0.6579	0.0182
N-HEXENE	84.16	0.6780	0.0002
I-HEXENE	84.16	0.6722	0.0044
METHYLCYCLOPENTANE	84.16	0.7505	0.0041
CYCLOHEXANE	84.16	0.7834	0.0002
BENZENE	78.11	0.8845	0.0027
N-HEPTANE	100.21	0.6882	0.0049
I-HEPTANE	100.21	0.6838	0.0006
N-HEPTENE	98.19	0.7068	0.0043
I-HEPTENE	98.19	0.6992	0.0018
DIMETHYL-CYCLOPENTANE	98.19	0.7496	0.0035
METHYLCYCLOHEXANE	98.19	0.7748	0.0029
TOLUENE	92.14	0.8719	0.0169
N-OCTANE	114.23	0.7068	0.0024
I-OCTANE	114.23	0.7090	0.0046
N-OCTENE	112.21	0.7272	0.0046
I-OCTENE	112.21	0.7180	0.0014
C8-N6	112.21	0.7729	0.0036
C8-N6	112.21	0.7841	0.0020
P-XYLENE	106.17	0.8657	0.0024
M-XYLENE	106.17	0.8687	0.0130
O-XYLENE	106.17	0.8848	0.0100
ETHYLBENZENE	106.17	0.8717	0.0070
N-NONANE	128.26	0.7176	0.0009
I-NONANE	128.26	0.7250	0.0021
N-NONENE	126.24	0.7369	0.0026
I-NONENE	126.24	0.7385	0.0006
C9-N6	126.24	0.7849	0.0013
C9-N6	126.24	0.7945	0.0007
N-PROPYLBENZENE	120.20	0.8666	0.0019
I-PROPYLBENZENE	120.20	0.8690	0.0001
METHYL-ETHYL-BENZENE	120.20	0.8696	0.0114
TRIMETHYL-BENZENE	120.20	0.7340	0.0054
N-DECANE	142.28	0.7451	0.0002
N-C4-BENZENE	134.22	0.7493	0.0019
METHYL-I-C3-BENZENE	134.22	0.7954	0.0006
TETRA-METHYL-BENZENE	134.22	0.8078	0.0010
DIETHYLBENZENE	134.22	0.8780	0.0030
C11-ALKYLBENZENE	148.25	0.8000	0.0000
TOTAL MOL			0.5000
WT			39.00

Table ARD-II-14

Overall Product Yields
(Wt %)

	Base Case F-T/ZSM-5/LPHC	Sensitivity Case F-T/ZSM-5/FCC/MOGD
C_1+C_2	6.3	4.8
$C_2^=$	1.1	1.4
C_3	5.7	3.3
nC_4	0.5	-0.9
iC_4	-0.6	-0.8
10 RVP (C_4-177°C)	47.3	63.0*
177-344°C	39.7	28.6*
Total	100.0	100.0
Gasoline		
P/O/N/A, wt %	60/14/7/19	56/22/6/16
Octane, R+O	93	92
Distillate		
Pour Point, °C	-15	-25
Cetane Index	72	50

*MOGD gasoline to 166°C, distillate 166-344°C.

Table ARD-II-15

Process Conditions - Sensitivity Case

	Second-Stage (ZSM-5)	FCC	MOGD(1)
Catalyst	ZSM-5	HEZ-53	ZSM-5
Inlet Pres., MPa	Cascaded	.11(2)	5.62
Inlet Temp., °C	371	478	205
Outlet Temp., °C	393	465	NA
Space Velocity	8.0 GHSV	4.2/1(3)	1 WHSV
H_2 Circulation, NL/L	-	-	40
Heat of Reaction, kJ/mol Feed H_2+CO	.57	NA	NA

(1)80 NL/L H_2 consumption for hydrotreating MOGD distillate.
(2)Oil partial pressure.
(3)Cat-oil ratio/residence time(s).

Table ARD-II-16
FCC FEED AND PRODUCT YIELDS
(BASIS: 100 MOL FEED H2-CO)

	MOL FEED	MW	SP. GR	MOL PROD
COKE		12.01		0.2080
WATER		18.02	-	0.0994
HYDROGEN		2.02	-	0.0196
METHANE		16.04	-	0.0692
ETHANE		30.07	-	0.0429
ETHENE		28.05		0.0459
PROPANE		44.10	0.5077	0.0488
PROPENE		42.08	0.5218	0.2134
N-BUTANE		58.12	0.5844	0.0191
I-BUTANE		58.12	0.5631	0.0843
BUTENE		56.11	0.6011	0.2922
N-PENTANE		72.15	0.6312	0.0056
I-PENTANE		72.15	0.6248	0.0314
PENTENE		70.14	0.6325	0.1374
CYCLOPENTANE		70.14	0.7505	0.0002
N-HEXANE		86.18	0.6640	0.0076
I-HEXANE		86.18	0.6540	0.0577
HEXENE		84.16	0.6843	0.1996
METHYLCYCLOPENTANE		84.16	0.7505	0.0043
CYCLOHEXANE		84.16	0.7834	0.0003
BENZENE		78.11	0.8845	0.0019
N-HEPTANE		100.21	0.6882	0.0060
I-HEPTANE		100.21	0.6772	0.0495
HEPTENE		98.19	0.7068	0.1716
DIMETHYL-CYCLOPENTANE		98.19	0.7496	0.0037
METHYLCYCLOHEXANE		98.19	0.7740	0.0022
TOLUENE		92.14	0.8719	0.0187
N-OCTANE		114.23	0.7068	0.0046
I-OCTANE		114.23	0.7090	0.0291
OCTENE		112.21	0.7272	0.0991
C8-N5		112.21	0.7700	0.0075
C8-N6		112.21	0.7922	0.0075
M-XYLENE		106.17	0.8687	0.0180
O-XYLENE		106.17	0.8848	0.0065
ETHYLBENZENE		106.17	0.8717	0.0010
N-NONANE		128.26	0.7176	0.0036
I-NONANE		128.26	0.7215	0.0237
NONENE		126.24	0.7334	0.0772
C9-N5		126.24	0.7500	0.2233
C9-N6		126.24	0.7977	0.0033
N-PROPYLBENZENE		120.20	0.8666	0.0017
METHYL-ETHYL-BENZENE		120.20	0.8690	0.0117
TRIMETHYL-BENZENE		120.20	0.8696	0.0093
N-DECANE		142.28	0.7341	0.0021
I-DECANE		142.28	0.7340	0.0150
DECENE		140.27	0.7451	0.0488
C10N5		140.27	0.7954	0.0021
C10N6		140.27	0.8031	0.0021
N-C4-BENZENE		134.22	0.8646	0.0071
METHYL-C3-BENZENE		134.22	0.8624	0.0016
TETRA-METHYL-BENZENE		134.22	0.8900	0.0016
DIETHYLBENZENE		134.22	0.8700	0.0017
NAPHTHALENE		128.17	0.9800	0.0002
C11-PARAFFIN		156.31	0.7443	0.0047
C11-OLEFIN		154.30	0.7544	0.0165
C11-ALKYL-BENZENE		148.25	0.8800	0.0017
194-344°C		200.00	0.8229	0.2282
RX-WAX	0.2414	821.41	0.8700	--
TOTAL MOL	0.2414			2.4787
WT	198.26			198.26

Table ARD-II-17
MOGD PRODUCTS FROM FCC GASOLINE AND GAS
(BASIS: 100 MOL FEED H2+CO)

	MW	SP. GR	MOL PROD
WATER	18.02	-	0.0994
HYDROGEN	2.02	-	0.0196
METHANE	16.04	-	0.0692
ETHANE	30.07	-	0.0438
ETHENE	28.05		0.0322
PROPANE	44.10	0.5077	0.0556
PROPENE	42.08	0.5218	0.0298
N-BUTANE	58.12	0.5844	0.0241
I-BUTANE	58.12	0.5631	0.0888
BUTENE	56.11	0.6011	0.0426
N-PENTANE	72.15	0.6312	0.0056
I-PENTANE	72.15	0.6248	0.0314
PENTENE	70.14	0.6325	0.0275
CYCLOPENTANE	70.14	0.7505	0.0002
N-HEXANE	86.18	0.6640	0.0076
I-HEXANE	86.18	0.6540	0.0077
HEXENE	84.16	0.6843	0.0599
METHYLCYCLOPENTANE	84.16	0 7505	0.0043
CYCLOHEXANE	84.16	0.7834	0.0003
BENZENE	78.11	0.8845	0.0019
N-HEPTANE	100.21	0.6882	0.0000
I-HEPTANE	100.21	0.6772	0.0495
HEPTENE	98.19	0.7000	0.0058
DIMETHYL-CYCLOPENTANE	98.19	0.7496	0.0037
METHYLCYCLOHEXANE	98.19	0.7740	0.0022
TOLUENE	92.14	0.8719	0.0187
N-OCTANE	114.23	0.7068	0.0046
I-OCTANE	114.23	0.7000	0.0291
OCTENE	112.21	0.7272	0.0498
C8-N6	112.21	0.7700	0.0076
C8-N8	112.21	0.7922	0.0075
M-XYLENE	106.17	0.8687	0.0100
O-XYLENE	106.17	0.8848	0.0065
ETHYLBENZENE	106.17	0.8717	0.0010
N-NONANE	128.26	0.7176	0.0000
I-NONANE	128.26	0.7215	0.0237
NONENE	126.24	0.7314	0.0300
C9-N6	126.24	0.7600	0.0033
C9-N8	126.24	0.7977	0.0033
N-PROPYLBENZENE	120.20	0.8666	0.0017
METHYL-ETHYL-BENZENE	120.20	0.8000	0.0117
TRIMETHYL-BENZENE	120.20	0.8096	0.0093
N-DECANE	142.28	0.7341	0.0021
I-DECANE	142.28	0.7340	0.0150
DECENE	140.27	0.7451	0.0244
C10N6	140.27	0.7954	0.0021
C10N8	140.27	0.8031	0.0021
N-C4-BENZENE	134.22	0.8646	0.0071
METHYL-C3-BENZENE	134.22	0.8624	0.0016
TETRA-METHYL-BENZENE	134.22	0.9000	0.0016
DIETHYLBENZENE	134.22	0.8700	0.0017
NAPHTHALENE	128.17	0.9000	0.0002
C11-PARAFFIN	156.31	0.7443	0.0047
C11-OLEFIN	154.30	0.7544	0.0002
C11-ALKYL-BENZENE	148.25	0.8000	0.0017
166°C⁻ GASOLINE	100.00	0.7310	0.0290
166-344°C	200.00	0.7900	0.2650
TOTAL MOL			1.4943
WT			150.13

The G+D selectivity is 92 wt %, including 1.7 wt % of imported butanes, and the G/D ratio is 2.2. The gasoline has high octane number (92 R+O) and the distillate has high cetane index (50) before hydrofinishing. This case has the highest G+D selectivity, although the distillate yield is lower than that in the base case.

B.4. Conceptual Process Schemes and Scoping Cost Estimates and Economics

For convenience, the conventional engineering units are used throughout this Subsection.

B.4a. Conceptual Process Design

B.4a-1. Overall Material Balances

In the base case, the plant produces 17,806 BPD of 10 RVP gasoline and 12,925 BPD of diesel fuel. Import of isobutane at less than 1% the rate of finished gasoline produced is needed to maximize utilization of the light olefins. The overall material balance is summarized in Table ARD-II-18.

In the sensitivity case, the finished gasoline production increased to 23,369 BPD and the distillate production is reduced to 8,901 BPD. The total liquid fuel production, however, is about 3% higher than in the base case. The overall material balance is summarized in Table ARD-II-19.

B.4a-2. Products Quality

	Base	Sensitivity
10 RVP Gasoline		
Sp. Gr./API Gr.	0.688/74.1	0.697/71.5
Octane Number (R+O)	93	92
Distillate 350-560°F		
Sp. Gr./API Gr.	0.785/48.7	0.795/46.5
Cetane Index	72	50
Pour Point, (°F)	5	-13

B.4a-3. Process Flow Scheme

Figures ARD-II-3 and -4 are the process block flow diagrams of the base and the sensitivity cases, respectively. The process schemes for the reactors section and wax clean up for the base case is shown in Figure ARD-II-5. Figure ARD-II-6 is the process flow diagram for the distillation section and Figure ARD-II-7 is the process flow for the wax hydrocracking section.

Table ARD-II-18

Overall Material Balances
(Base Case)

Feed	Lb/hr	Sp.Gr./(MW)	BPSD/(MMSCFD)
Synthesis Gas (Slurry F-T) (1)	2,111,070	/(19.77)	/(971.0)
Synthesis Gas (Shift)	33,273	"	/(15.3)
Steam (Slurry F-T)	121,629	/(18.02)	/(61.3)
Steam (Shift)	17,822	"	/(9.0)
i-Butane	1,280	0.563/(58.12)	156/
n-Butane	272	.584/(58.12)	32/
Total	2,285,346		
Products			
Fuel Gas (2)	405,827	/(15.25)	/(242)
CO_2	1,516,043	/(44.01)	/(313)
C_3 LPG	17,703	/(44.1)	2,393/
10 RVP Gasoline	178,691	0.688/(90.5)	17,806/
Distillate	147,998	0.785/	12,925/
Waste Water	19,084	1.0/(18.02)	1,309/
Total	2,285,346		

(1) LHV = 343.7 Btu/SCF

(2) LHV = 525.0 Btu/SCF
(See Table ARD-II-21 for composition)

Table ARD-II-19

Overall Material Balance
(Sensitivity Case)

Feed	Lb/hr	Sp.Gr./(MW)	BPSD/(MMSCFD)
Synthesis Gas (Slurry F-T)	2,111,070	/(19.77)	/(971.0)
Synthesis Gas (Shift)	13,920	"	/(6.4)
Steam (Slurry F-T)	121,629	/(18.02)	/(61.5)
Steam (Shift)	7,450	"	/(3.7)
i-Butane	2,167	0.563/(58.12)	264/
n-Butane	6,969	0.58/ (58.12)	818/
Total	2,263,205		
Products			
Fuel Gas(1)	374,179	/(14.5)	/(234)
O_2	1,516,043	/(44.01)	/(313)
Propane LPG	11,789	/(44.1)	1,593/
10 RVP Gasoline	236,664	0.697/(93.2)	23,279/
Distillate	105,446	0.795/	9,065/
Waste Water	19,084	1.0/(18.02)	1,309/
Total	2,263,205		

(1)LHV = 541.0 Btu/SCF

Figure ARD-II-3
SLURRY FISCHER-TROPSCH/ZSM-5
AND REACTOR-WAX LPHC

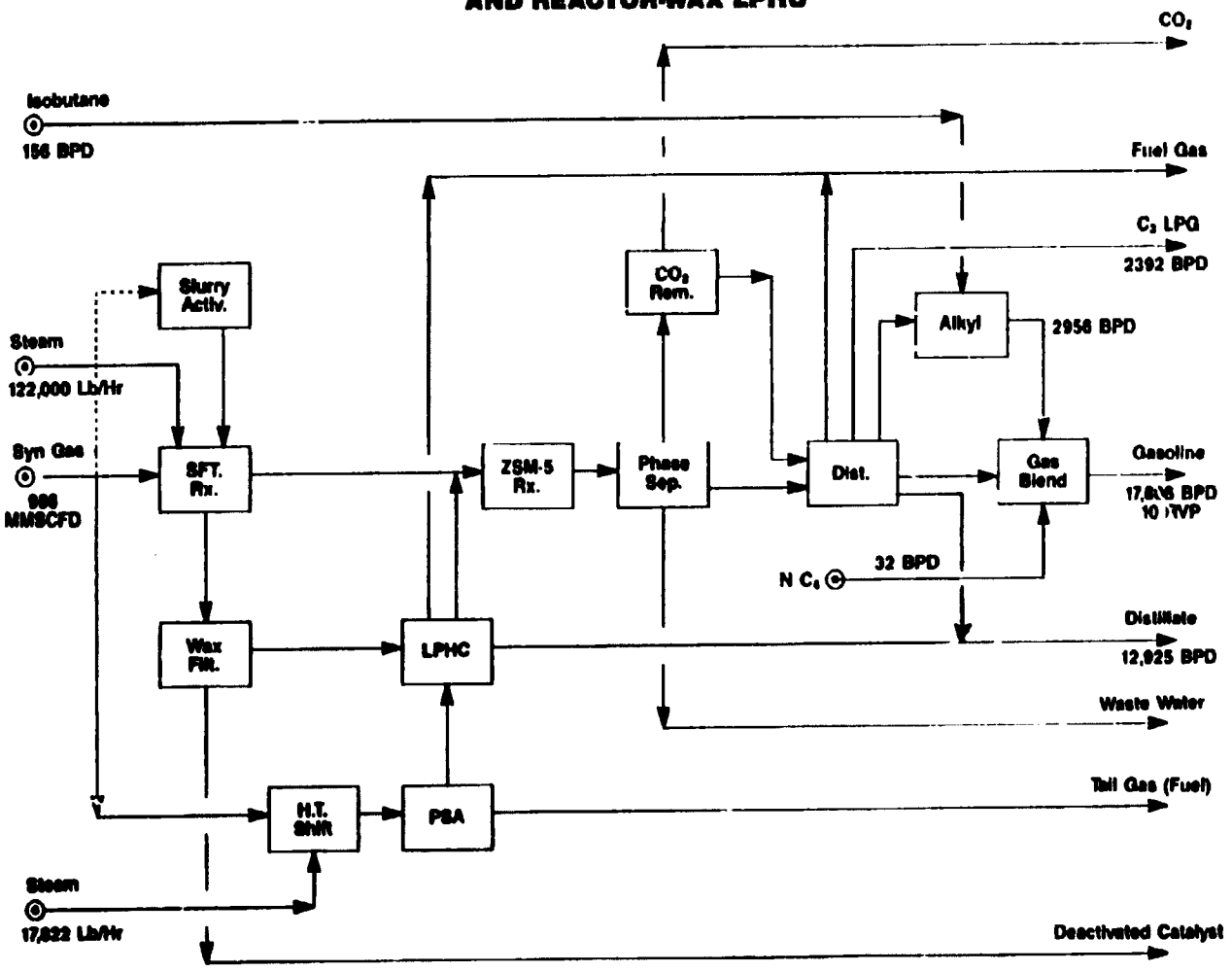


Figure ARD-II-4
SLURRY FISCHER-TROPSCH/ZSM-5
AND REACTOR-WAX FCC/MOGD

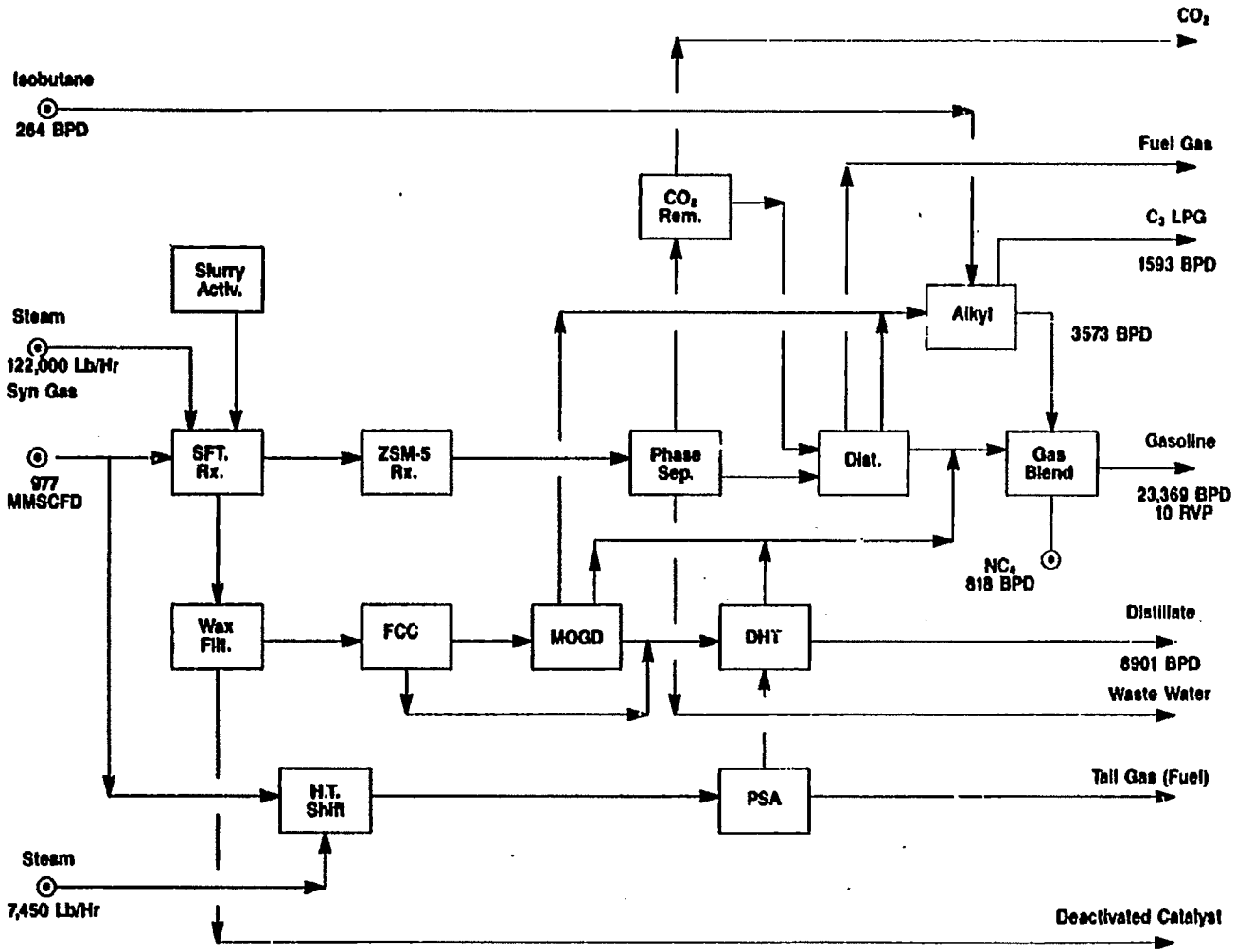


Figure ARD-II-5

SLURRY FISCHER-TROPSCH/ZSM-5 REACTORS AND REACTOR-WAX SEPARATION

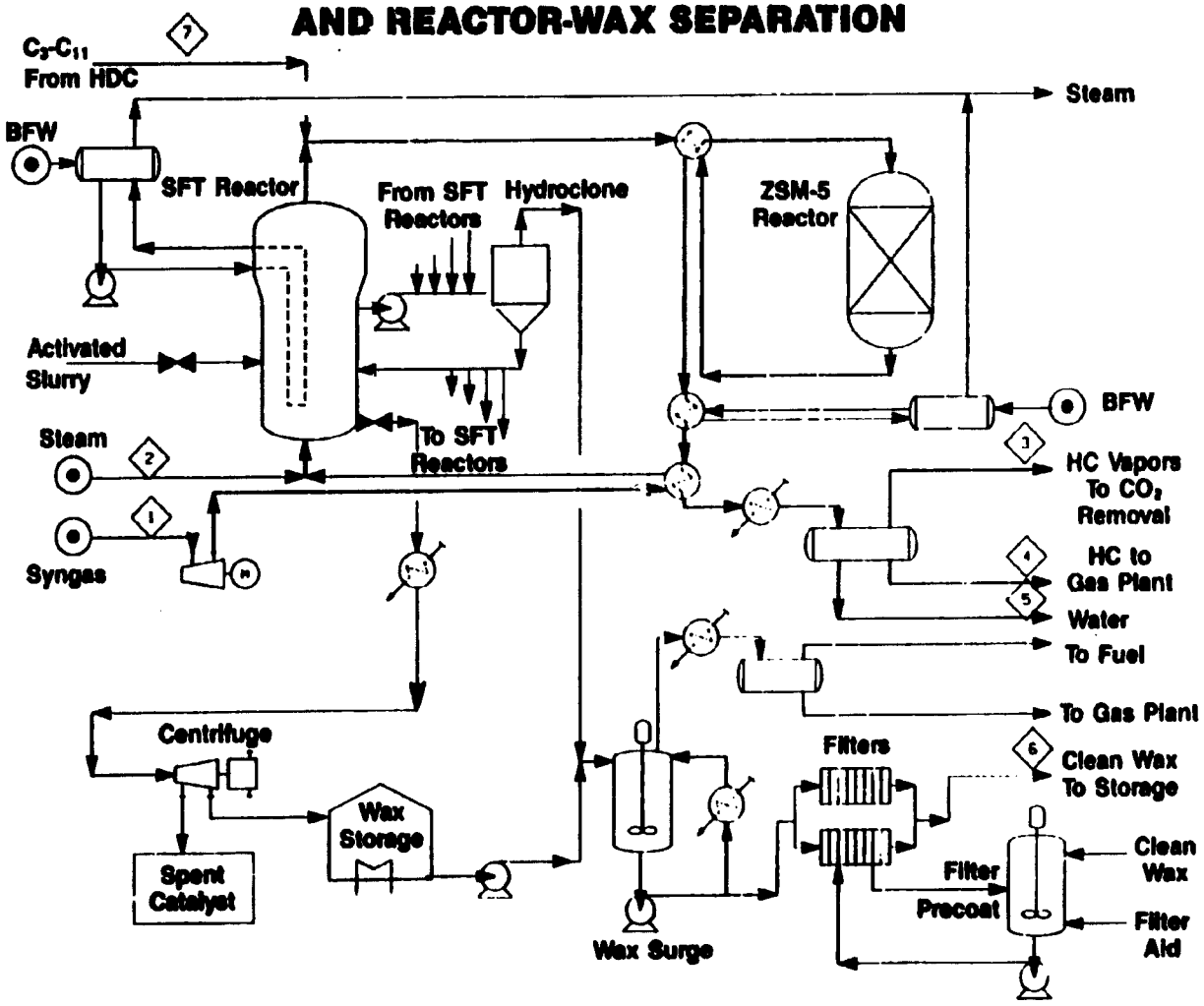


Figure ARD-II-6
PRODUCT DISTILLATION SECTION

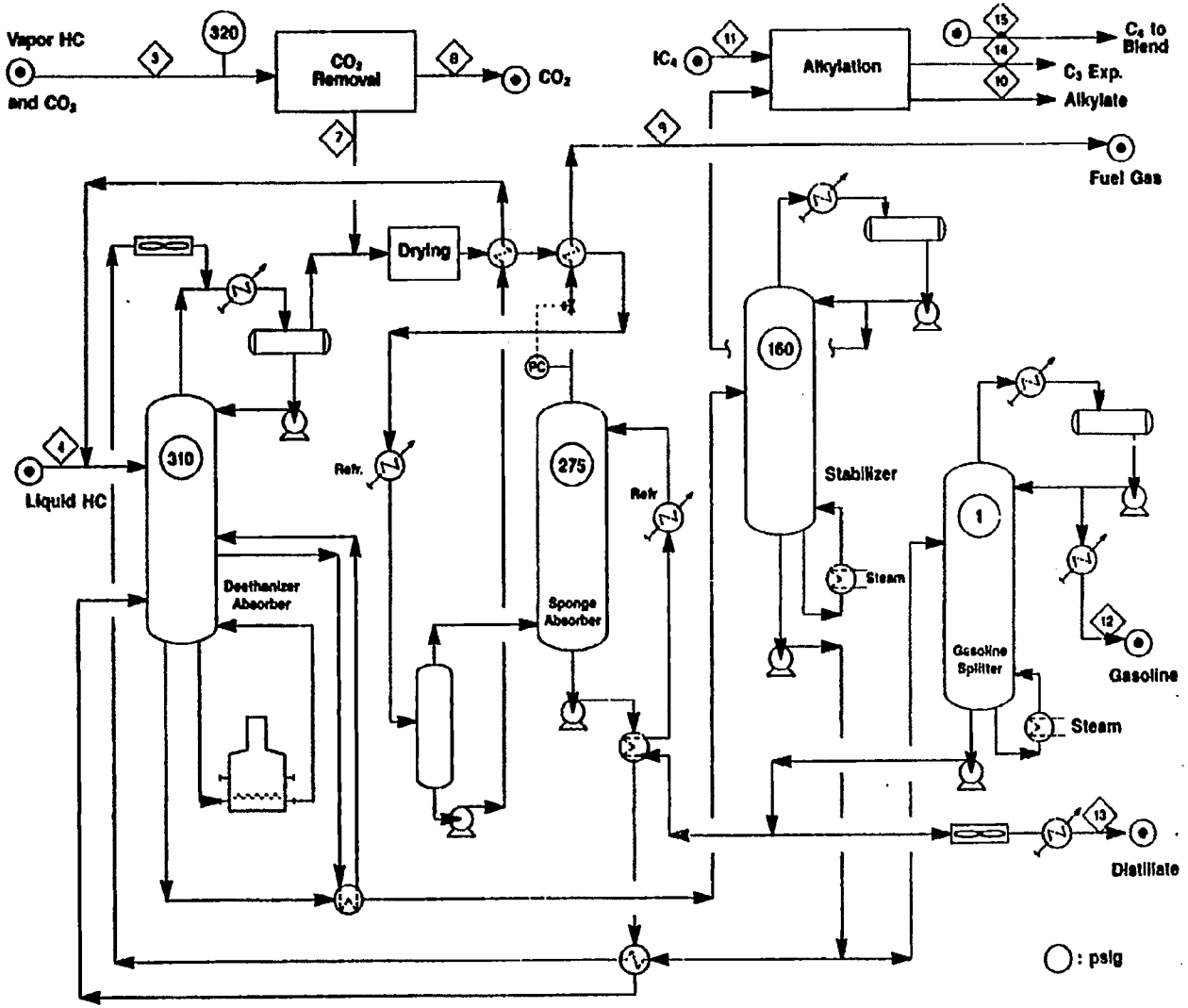
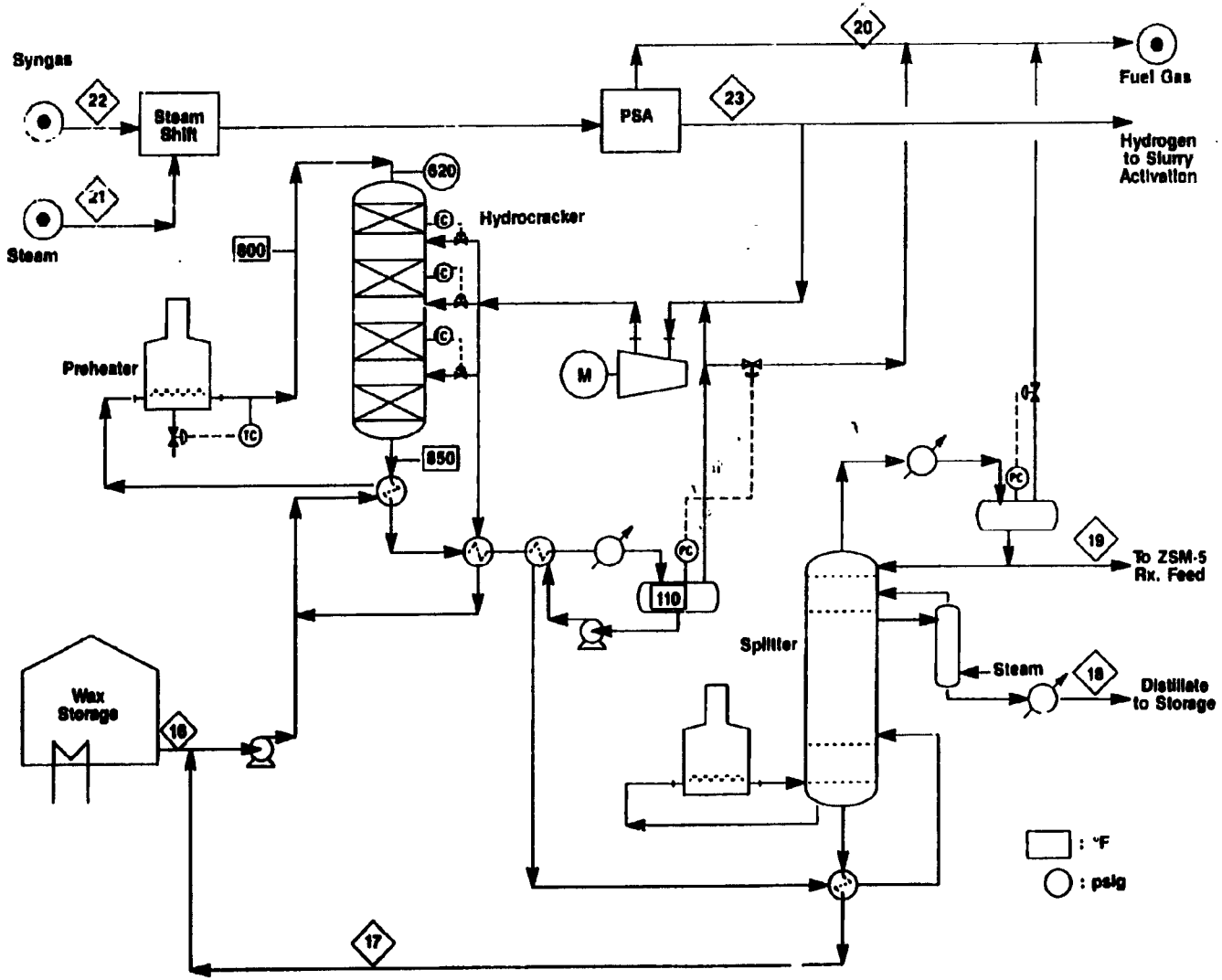


Figure ARD-II-7

LOW PRESSURE REACTOR-WAX HYDROCRACKING



Tables ARD-II-20 and -21 give the material balances for reactor section, and distillation section, respectively.

B.4b. Plant Description

The plant consists essentially of three main sections: the reactor section, the reactor-wax upgrading section and the product recovery section. Only the reactor-wax upgrading section is described here. The reactor section is described in the main report.

The reactor-wax upgrading section contains the facilities to clean up the reactor-wax from particulates of F-T catalyst and also the process units necessary to convert the clean wax into distillate and gasoline products. Two process schemes for upgrading are studied: in the base case, wax is upgraded using low pressure hydrocracking; in the sensitivity case, wax is FCC treated to produce G+D and olefins which are then converted to distillate using a proprietary Mobil MOGD process.

B.4b-1. Base Case - Low Pressure Reactor-Wax Hydrocracking

The wax hydrocracking process has the function of selectively cracking the high molecular weight hydrocarbons in the wax into distillate boiling range paraffinic hydrocarbons, in addition to saturating of the olefinic compounds produced in the cracking.

The hydrocracker design capacity is based on the rate of wax produced in the slurry F-T reactors plus recycle of the unconverted wax. Total feed rate is 21,036 BPD or 266,786 lb/hr.

The combined wax from storage plus recycle wax is mixed with preheated recycled hydrogen gas and preheated further by exchanging against the hydrocracking effluent. The mixture is then further heated in a fired heater to 800°F and fed at the hydrocracker top. The reactor consists of four fixed bed sections with intermediate quench by recycle hydrogen gas. The quench gas flow is regulated by temperature control of the bed.

The effluent from the reactor is successively cooled down by exchanging against the feed wax, the recycle hydrogen gas, the condensate hydrocarbon from the low temperature separator and finally cooled to 110°F by cooling water. The vapor liquid mixture is disengaged in the low temperature separator vessel. The vapor phase which is mostly hydrogen feeds the suction side of the recycled gas compressor. High purity

Table ARD-II-20

Slurry Fischer-Tropsch/ZSM-5 Process
Material Balance, Reactors Section

Stream No	1 Syngas Feed	2 Steam	3 HC Vap.	4 HC Liq.	5 Water	6 Reactor-Wax
H_2O		6,742.2	6.5	169.0	835.7	
H_2	31,853.0		9,574.0	1.4		
CO	64,346.5		5,758.7	1.7		
CO_2	2,360.0		34,368.7	79.1		
C_1	7,496.1		8,302.8	7.2		
$C_2^=$	21.4		170.8	0.8		
C_2	341.7		430.5	2.2		
$C_3^=$			157.9	2.2		
C_3			482.4	7.2		
$C_4^=$			137.0	5.9		
C_4			236.5	8.2		
iC_4			258.9	9.0		
C_5-C_{11}			839.8	602.4(1)		
C_{12}^+			12.5	9.0(2)		
Wax						232.2
N_2	363.1		362.0	1.1		
Total:						
lb-mol/hr	108,781.8	6,742.2	61,099.0	906.4	835.7	232.2
lb/hr	2,111,070.0	121,494.4	1,998,573.6	65,799.4	15,058.0	190,752.2
MW	19.77	18.02	32.7	72.6	18.02	821.4
BPD	-	-	-	6,300.0	1,033.0	15,040.7
MMSCFD	971.3	-	555.7	-	-	-

(1) MW = 92.4
(2) MW = 176.1

Table ARD-II-21

Slurry Fischer-Tropsch/ZSM-5 Process
Material Balance, Distillation Section

Stream No.	7 HC Vapor From CO_2 Removal	8 CO_2	9 Fuel Gas	10 Alkyl. Product	11 iC_4 Import	12 Gasoline to Blend	13 Distillate	14 C_3 LPG Export	15 C_4 Import
H_2O	0.2								
H_2	9,574.0		9,575.4						
CO	5,758.7		5,760.4						
CO_2	50.0	34,318.7	129.1						
C_1	8,302.8		8,310.0						
$C_2^=$	170.8		171.6						
C_2	430.5		432.7						
$C_3^=$	157.9		28.8						
C_3	482.4		88.1					401.4	
$C_4^=$	137.0		2.9						
C_4	236.5		4.9			239.8			4.7
iC_4	258.9		5.4		22.0				
C_5-C_{11}	839.8								
C_{12} + Gasoline	12.5					1,442.2			
Distillate							21.5		
Alkylate				279.1					
N_2	362.0		363.1						
Total:									
lb-mol/hr	26,774.0	34,318.7	24,872.4	279.1	22.0	1,682.0	21.5	401.4	4.7
lb/hr	488,094.1	1,510,366.0	353,523.0	29,877.7	1,280.5	148,350.2	3,786.2	17,703.2	272.6
MW	18.23	44.01	14.20	107.1	58.12	88.2	176.1	44.10	58.12
BPD	-	-	-	2,957.	156.0	14,748.8	190.0	2,392.0	32.0
MMSCFD	243.5	312.2	226.2	-	-	-	-	-	-

hydrogen makeup is required to replace consumption. This is produced by steam shift of synthesis gas followed by PSA purification.

The liquid hydrocarbon phase from the low temperature separator is preheated by exchange against the reactor effluent and the distillate tower bottom before feeding the tower. The distillate tower produces a small quantity of light naphtha as overhead liquid product which is mixed with the ZSM-5 reactors feed stream for the purpose of improving its octane value. The intermediate cut from this tower is the distillate product fraction which is steam stripped before sent to storage. The bottom stream is the unconverted wax which is recycled to the reactor feed.

The hydrocracking process flow diagram is shown in Figure ARD-II-7 and Table ARD-II-22 gives the corresponding material balance.

B.4b-2. Alkylation

The yields assumed for the alkylation unit are typical of Mobil experience using the HF alkylation process for C_3/C_4 olefins. The proportion of these components in the reaction products makes it necessary to import approximately 8 percent of the total iC_4 required in the case of wax hydrocracking and near 11 percent in the case of FCC-MOGD process scheme.

B.4b-3. Sensitivity Case - FCC + MOGD + DHT

The slurry F-T and ZSM-5 reactors, reactor-wax recovery, slurry F-T catalyst preparation and pretreatment and distillation sections are essentially identical for both the base and the sensitivity case.

The clean wax from the slurry F-T reactors is FCC treated, producing a highly olefinic product ranging from the light to the distillate range hydrocarbons. The FCC reactor effluent is then distilled to separate the distillate bottom products while the remaining lighter material (C_3-C_{12}) is used as feed to a MOGD unit to oligomerize the olefins into distillate and gasoline range products.

The feed to the MOGD process consists of a liquid phase light gasoline range product plus the vapor phase hydrocarbon from the FCC distillation tower overhead. The combined feedstreams are preheated and then fed to a series of fixed-bed reactors containing a proprietary Mobil ZSM-5 catalyst. The reactor effluent is cooled and sent to distillation.

Table ARD-II-22

Slurry Fischer-Tropsch/ZSM-5 Process
Material Balance, Wax Hydrocracking

Stream No.	16 Wax Feed	17 Recycle Wax	18 Distill. Product	19 C_3-C_{11} to ZSM-5	20 PSA Purge Gas	21 Steam Shift	22 Water-Gas Shift	23 Makeup Hydrogen
H_2O						987.9		
H_2					206.2		502.0	1,289.5
CO					20.2		1,014.2	6.5
CO_2					1,014.9		37.2	
C_1					118.1		118.1	
C_2					5.7		5.7	
C_3				108.1				
C_4				31.6				
C_5-C_{11}				284.7				
Distillate			698.6					
Wax	232.2	92.8						
N_2					5.7		5.7	
Total:								
lb-mol/hr	232.2	92.6	698.6	424.4	1,375.0	987.9	1,683.0	1,296.0
lb/hr	190,752.2	76,034.0	145,727.4	37,619.6	48,307.8	17,802.0	33,272.9	2,786.9
MW	821.4	821.4	208.6	88.6	35.1	18.02	19.8	2.2
BPD	15,040.6	5,995.0	12,734.7	-	-	-	-	-
MMSCFD	-	-	-	-	12.5	-	15.3	11.8

The distillation section consists of a debutanizer tower that produces an overhead product to feed the alkylation unit. The bottom product feeds the gasoline-distillate splitter. The splitter overhead is gasoline product which is mostly used for blending. The bottoms distillate product is combined with the distillate from the FCC unit and sent to the distillate hydrotreater unit (DHT). Hydrotreating is required to increase the cetane rating of the distillate to be sold as a premium diesel fuel.

B.4c. Operating Requirements

B.4c-1. Utilities for Base Case

	355 psig Steam Lb/hr	Fuel MMBtu/hr	Cooling Water GPM	Demin. Water GPM	Power KW
Slurry F-T/ZSM-5 Reactors + Activation	(2,191,210)	117	16,853	403	6,433
CO_2 Removal	1,100,000	-	-	120	17,075
LPHC + PSA	17,822	236	3,150	-	10,836
Alkylation	69,900	-	5,824	15	192
Distillation	235,000	145	17,500	50	1,300
Total	(768,488)	498	43,327	588	35,836

B.4c-2. Initial Catalyst and Chemicals Requirements (Base Case)

F-T Catalyst (Lbs.)	1,500,000
ZSM-5 (Lbs.)	188,000
Potassium Carbonate Sol., (Gal.)	500,000
Hydrocracker Catalyst (Lbs.)	380,000

B.4c-3. Utilities for Sensitivity Case

	355 psig Steam Lb/hr	Fuel MMBtu/hr	Cooling Water GPM	Demin. Water GPM	Power KW
Slurry F-T/ZSM-5 Reactors + Activation	(2,191,210)	117	16,853	403	6,433
CO_2 Removal	1,100,000	-	-	120	17,075
FCC	36,580	-	451	160	4,900
MOGD	-	50	47	-	614
DHT + PSA	7,252	13	-	-	631
Alkyl.	84,500	-	7,040	20	232
Distillation	235,000	145	17,500	50	1,300
Total	(727,878)	325	41,891	753	31,185

B.4c-4. Operating Overall Manpower

	Base	Sensitivity
Total Manpower	56	66

B.4d. Scoping Cost Estimates and Economics

The cost basis of the battery limited facilities is instantaneous 1985 and a Wyoming location. Following estimate adjustment factors for different sections of the plant are used to reflect the state of development of the proposed processing technology:

SFT/ZSM-5 Reactor Section	40%
LPHC + PSA	5%
CO2 Removal	20%
Distillation	5%
Alkylation	0%
Blending	10%
Overall	30%

These estimates do not include coal gasification, synthesis gas clean up, utilities and offsites, slurry F-T catalyst manufacture and catalyst fill and royalties.

Included in the cost are: equipment bulk materials and labor, field indirects, contractor engineering and fees, owners engineering and project management cost and capitalized spares. Because of Wyoming location, an allowance for a construction workers camp is also included. A 30% estimated cost allowance is also added in the final investments to account for imperfection in costing.

Table ARD-II-23 summarizes the cost estimates and the percent of the total investment contributed by various units for the base and the sensitivity case. The investment cost of the sensitivity case is about 4% higher than that of the base case. It, however, produces about 3 wt % more G+D per unit of synthesis gas consumed.

In order to compare the current low methane + ethane (high wax) mode design with the gasoline-mode design given in the Final Report of our earlier Contract (Kuo, 1983), the investment cost from the gasoline-mode design is also included in Table ARD-II-23. The cost estimate for that case has been revised so that its technical and economic basis are consistent with those

Table ARD-II-23

Slurry Fischer-Tropsch/ZSM-5
Conceptual Design Plant Scoping Cost Estimates
(Battery Limited Facilities)

	High Wax-Mode		
	Base Case	Sensitivity Case	Gasoline Mode
Investment Cost (Battery Limited, MM$*)	705	735	680
Investment Cost Distribution:			
Slurry F-T/ZSM-5	61	60	65
LPHC	10	-	-
PSA H_2 Plant	1	-	-
FCC, MDGD, DHT, PSA	-	13	-
CO_2 Removal	18	18	20
Distillation	5	4	7
Alkylation	4	4	7
Blending	1	1	1
	100	100	100

*Instantaneous 1985 Basis

of the current study. That plant was designed to produce 27,000 and 2,400 BPD of gasoline and wax, respectively. The investment cost for the current high-wax mode operation is about 4% higher than the gasoline-mode. This difference is small, similar to the conclusion obtained by El Sawy et al. (1984).

Based on our earlier experimental work in achieving low methane + ethane mode operation using the F-T Catalyst I-B, a F-T reactor pressure higher than that of the gasoline mode operation (365 psia versus 215 psia H_2+CO partial pressure) (see Kuo, 1983) was needed. Consequently, a higher pressure reactor section was adopted for the current conceptual process design. However, in the latter experiments, we found that a lower pressure similar to the pressure used in the gasoline-mode operation was sufficient for obtaining the similarly low methane + ethane (and high reactor-wax)yield (see Section IV.L). We, therefore, evaluate the effect of this lower reactor pressure on the process economics. A decrease of the operating pressure in the slurry F-T reactor section results in:

- An elimination of the feed-gas compressor.
- An increase in steam export.
- A decrease in the material cost for the reactor section.
- A decrease in the height of slurry F-T reactors with a corresponding increase in the total number of reactors.

We expect an overall decrease of 2-5% of the investment cost may result from this change.

C. Nomenclature

T_{max}	FCC Maximum Temperature, (°C)
T_{top}	FCC Top Temperature, (°C)

Acronyms

ARD	Appendix - Restrictive Distribution
API	American Petroleum Institute
ASTM	American Society for Testing and Material
BFW	Boiler Feed Water
BGC	British Gas Corporation

BP(S)D	Barrels Per (Stream) Day
D	Distillate
DHT	Distillate Hydrotreating
DOS	Days-on-Stream
FCC	Fluid Catalytic Cracking
F-T	Fischer-Tropsch
G	Gasoline
GC	Gas Chromatography
HC	Hydro-Carbons
HF	Hydro-Fluoric acid
LHSV	Liquid Hourly Space Velocity, (cm^3 per hr/cm^3-cat.)
LHV	Low Heating Value, (Btu/SCF)
LPG	Liquified Petroleum Gas
LPHC	Low Pressure Hydrocracking
MOGD	Mobil Olefin to Gasoline and Distillate Process
MW	Molecular Weight
PONA	Paraffins-Olefins-Naphthenes-Aromatics
PSA	Pressure Swing Absorber
R+O	Lead-Free Research Octane Number
RVP	Reid Vapor Pressure
SASOL	South African Coal, Oil and Gas Corp., Ltd.
SCF(D)	Standard Cubic Feed (per Day)
SFT	Slurry Fischer-Tropsch
WHSV	Weight Hourly Space Velocity, (g per hr/g-Cat.)

D. References

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Kuo, J. C. W., "Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline," Mobil Research and Development Corp., Final Report (DOE/PC/30022-10), DOE Contract No. DE-AC22-80PC30022, June 1983.

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

A.1. Testing of a High Gradient Magnetic Separator (HGMS) for Cleaning Reactor-Wax

To avoid probable problems in further upgrading of F-T reactor-wax containing catalyst fines, a 3.2 kg batch of Run CT-256-4 reactor-wax was cleaned up by passing it through a laboratory HGMS. The solids content was reduced from 0.13 wt % to less than 0.015 wt %.

The setup includes a heated (120°C) glass tube containing packed steel-wool across which a strong magnetic field is applied. In a batch operation the reactor-wax containing catalyst fines is poured over steel-wool in the glass tube and allowed to flow through by gravity. The high-gradient magnetic field traps the ferro-magnetic catalyst particles, and clean reactor-wax flows to the bottom where it is collected. In this laboratory setup no attempt was made to optimize the operating conditions to maximize the reactor-wax throughput. The controlling parameters are the reactor-wax temperature (i.e., liquid viscosity), feed rate, and magnetic field intensity. Continuous HGMS setups are available commercially and are used in cleaning iron-ores and clays (see Oder and Price, 1973; and Oberteuffer, 1974).

The clean reactor-wax was used as a feedstock for other upgrading processes described in the preceding Chapter.

B. Nomenclature

Acronyms

HGMS	High-Gradient Magnetic Separator

C. References

Oberteuffer, J. A., IEEE-Trans. Magnetics, Mag-10, 223 (1974).

Oder, R. R., and Price, J. R., TAPPI, 56 (10), 75 (1973).

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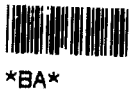

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