6.0 BLENDING STUDY (TASK 4)

UOP used a proprietary Catalytic Condensation process (oligomerization) to upgrade C_3/C_6 by-products of the Fischer-Tropsch reaction to obtain a more valuable distillate product. The blending characteristics of this material, as well as those of the hydrocracked wax, with other straight-run Fischer-Tropsch synthesis products were evaluated.

Laboratory analyses were obtained for these blends and used to adjust computer based blending correlations. Also, laboratory analyses were obtained for blends of Fischer-Tropsch products with low value refinery LCO. LCO was used to represent the potential of blending high aromatic components. Corrections were made to the traditional blending correlations to account for the blending characteristics of the LCO. These studies maximized the use of blending components available in a Fischer-Tropsch upgrading complex, for production of more valuable, high quality transportation fuels.

Specifically, key diesel properties such as cetane number, pour point, flash point, viscosity, API and distillation were determined for components and blends to evaluate the accuracy of normal blending correlations. All the pilot plant work, component blending and laboratory analyses were done at the Engineered Materials Research Center. The computer modeling of blend correlations and the adjustments based on laboratory analyses were performed by the Marketing Services Department at UOP Inc.

6.1 FISCHER-TROPSCH COMPLEX FLOW SCHEME AND MATERIAL BALANCE

Two Fischer-Tropsch complex flow schemes are considered in this report. The base case (Figure 6.1) contains a hydrocracker that upgrades Fischer-Tropsch wax, heavy condensate and heavy polymer into transportation fuel. The alternate case (Figure 6.2) deletes the hydrocracker, and the three heavy liquids are sent to fuel oil. Upgrading units are briefly described in the following sections.

6.1.1 Catalytic Condensation Unit (Oligomerization)

The catalytic condensation unit is used to oligomerize light olefins in the Fischer-Tropsch gases into liquid products. Estimated yield and product property information for the catalytic condensation unit is presented in Table 6.1. The catalytic condensation unit is not affected by the choice between base and alternate case.

Properties of the 356°F+ C_5/C_6 oligomerized product used in the blending study are given in Appendix C. Coal-derived feedstock was oligomerized in a pilot plant study. An account of the study is included as Appendix D.

6.1.2 Distillate Hydrotreater

The primary purpose of the distillate hydrotreater is to saturate the heavy distillate olefins from the catalytic condensation unit to obtain cetane number improvement in the hydrotreated product. Since the only impurities present may be very small amounts of oxygenates or organic acids, the hydrotreater severity is set by the olefin saturation requirements. Yields in this hydrotreater are essentially stoichiometric and are presented in Table 6.2. After hydrotreating the calculated cetane index of this distillate is increased to 57. Care must be taken, however, since the cetane index does not readily correlate with the actual measured cetane number for this highly branched stream.

6.1.3 Naphtha Hydrotreater (NHT)

The naphtha hydrotreater processes C_5/C_6 naphtha from the catalytic condensation unit along with straight run IBP-350°F Fischer-Tropsch product. For the base case, IBP-350°F material from the hydrocracker is hydrotreated as well. Again, because of the nature of the feed, the primary purpose of this hydrotreater is to saturate olefins and remove any small quantities of oxygenates or organic acids, which may be present in the Platforming unit feed. Estimated yields and product properties for the naphtha hydrotreater are provided in Table 6.3.

The IBP-350°F cuts from the Fischer-Tropsch condensate and the hydrocracked distillate had to be fully characterized to accurately complete the NHT/CCR Platforming yield estimate. Specifically, the IBP-350°F condensate material was analyzed for olefin and oxygen content to help estimate hydrogen consumption in the naphtha hydrotreater. The iso/normal ratio in the IBP-350°F naphtha cut from the hydrocracker would affect the performance of the CCR Platforming unit. The relevant properties of the IBP-350°F cuts are listed in Appendix C.

6.1.4 Naphtha Splitter

Full boiling range naphtha from the naphtha hydrotreater is fractionated into two product streams by the naphtha splitter. The purpose of the fractionation is to remove the highly paraffinic C_5/C_6 cut from the reformer charge. The resulting C_5/C_6 stream is an ideal isomerization feedstock.

6.1.5 CCR Platforming Unit

Naphtha splitter bottoms are fed to a UOP CCR Platforming unit. The unit is a moving bed system in which catalyst is continuously withdrawn, regenerated and then returned to the reactor section. Continuous regeneration allows uninterrupted operation at higher catalyst severity than is achieved in fixed-bed systems. The resulting product yields are provided in Table 6.4.

6.1.6 Penex/Molex Units, Isomerization and n-Paraffin Separation (21)

The C_5/C_6 naphtha splitter overhead is charged to a Penex* isomerization unit. The octane (RONC) of the fraction is improved as low octane normal paraffins are isomerized to higher octane iso paraffins.

Conversion of normal to iso paraffins is limited by thermodynamic equilibria. The Molex* unit separates then directs higher octane iso paraffins to the gasoline pool and lower octane normal paraffins for isomerization as a recycle stream. The Penex/Molex combination unit permits nearly complete conversion of the C_5/C_6 naphtha splitter overhead into iso paraffins (Table 6.5)

6.1.7 Hydrocracker (Base Case Only)

The hydrocracker provides a means of upgrading heavy material, primarily Fischer-Tropsch wax, into transportation fuel. Commercial hydrocracking is described in Section 5.1. Table 6.6 provides an analysis of the unit's product yield and specifications.

6.2 DEVELOPMENT OF BLENDING CORRELATIONS

Once the flow scheme was set, the next step was to examine the diesel fuel quality produced by the various process units. Straight run Fischer-Tropsch condensate (Appendix C) and pilot plant derived oligomerized Fischer-Tropsch C_5/C_6 material (Appendices C and D) were separated into the appropriate boiling range fractions for blending with distillate produced by catalytic hydrocracking of Arge Fischer-Tropsch wax (Section 5). This blend made up the diesel pool in the blending study. Blend description is given in Appendix F.

The physical properties of the individual diesel pool components suggested that the diesel pool in the blending study would be of exceptional quality. The quality is a result of high cetane and low aromatics (high smoke point). The diesel pool may be of exceptional quality, but it will not have a higher selling price than a diesel fuel that just meets specifications.

In order to capitalize on the high quality of the diesel pool in the complex, an external LCO stream was considered for blending. The

LCO has low cetane (~20) and appreciable aromatics (~70 wt-%). By increasing the size of the diesel pool while still maintaining specifications, value is added to the LCO just by blending.

In order to determine the impact of blending the LCO into the diesel pool, a set of blending correlations had to be developed. The blending correlations are needed to predict the ASTM 50% point, cetane index, flash point, pour point and viscosity of the final diesel pool.

It is economically attractive to blend the LCO into the higher value diesel pool as long as the overall diesel pool still meets specifications. Four situations are considered:

1. No LCO blended into the diesel pool
2. Add LCO so that the diesel pool contains 20 wt-% LCO
3. Add LCO so that the diesel pool contains 40 wt-% LCO
4. Add LCO so that the diesel pool contains 60 wt-% LCO

A set of generalized correlations were used to produce paper blends (predictions). These paper blend properties were compared to actual laboratory results for two situations, 0 wt-% and 60 wt-% LCO. Notice that laboratory results confirm that the blend without the LCO far exceeds specifications and that the LCO blending to capitalize on this strength is justified. It must be noted that LCO represents a source of aromatics and may be substituted by a similar aromatic and low cetane blending component, depending on market availability.

The next step was to fine tune the generalized correlations. Correction factors were determined that generated paper blends matching the actual laboratory results. In other words, the corrected correlations would be identical to the laboratory data for 0 and 60 wt-% LCO blends.

The final step of the paper blend study was to test the modified correlations on an intermediate blend. Close agreement at an intermediate composition would allow use of the modified correlations over the entire interval with reasonable certainty. A 40 wt-% LCO blend was chosen as the intermediate point. Results listed in Table 6.7 verify that the modified correlations apply over the entire interval of 0 to 60 wt-% LCO addition. The variation between laboratory and paper blend (predicted) values of ASTM 50% point and pour point are within expectations.

The corrected generalized correlations are presented in Appendix E.

6.3 BASIS FOR DIESEL BLENDING STUDY

The original concept behind the diesel blending study was to calculate diesel blends for two cases: 1. maximum diesel, and 2. maximum diesel plus jet fuel. The F-T complex produces a diesel product with a very high cetane number. Another part of the study was to increase the diesel product volume by blending low cetane LCO into the diesel pool and determine the effect on the diesel pool properties. All of the diesel blending work refers to the base case (includes hydrocracker). All blend derivations are described in Appendix F.

6.3.1 Results for Case 1: Maximum Diesel

The diesel pool is composed of three streams, as shown in the schematic diagram for the complex (Figure 6.1):

1. Olefinic LPG is oligomerized in the catalytic condensation unit. The poly diesel is hydrotreated in the diesel hydrotreater and sent to the diesel pool.

2. The 350-650°F F-T condensate material can be used directly as "straight-run" diesel. The 650°F+ cut has a very high pour point and can not be used. It is sent to the HC Unibon unit for conversion into better quality blend stock.

3. The 350°F-EP distillate from the HC Unibon unit is sent to the diesel pool.

Both the F-T condensate and hydrocracked distillate contain substantial amounts of IBP-350°F material. These materials cannot be blended into the diesel pool because they have very low flash points.

Four diesel blends were made. The first was without LCO. The LCO was then blended into the pool so that the total diesel product contained 20, 40 and 60 wt-% LCO. Three different types of LCO were used. Properties of the LCO's are given in Section 3.0 as well as in Appendix C. Equal amounts of the three types were used in all of the blends with LCO. Three LCO's were used so that the composite would be generic and have a wide distribution of LCO components. Also, the relative contribution of any of the three components could be adjusted if desired. As it turned out, this adjustment was not necessary.

The results of the four blends are shown in Table 6.8. These blends are referred to in Table 6.8 as paper blends since all relevant properties were calculated from correlations developed in Appendix E. All of the blends meet the 2-D specifications that are shown at the bottom of the table. The primary effect of the LCO is to depress the cetane number, but the LCO also affects the other diesel properties.

Diesel fuel stability is discussed at the end of this section. As the diesel blend is coal derived, the distillate stability must be determined. Also, addition of a fluid catalytic cracking (FCC) derived LCO stream will compound the stability problems of the diesel blend. The blend must be treated to enhance fuel stability.

6.3.2 Results for Case 2: Maximum Diesel + Jet Fuel

The purpose of Case 2 was to increase the total distillate product volume by producing both diesel and jet fuel product. As discussed in the preceding section, all of the distillate streams in the complex were blended into the diesel pool. The only way to increase the total distillate volume for the maximum diesel + jet fuel case is to use the IBP-350°F streams in a distillate product. However, the IBP-350°F cuts from the HC Unibon and F-T condensate are too light to be used as jet fuel. The API gravities for these streams are 69.9 and 62.8, respectively. The lightest jet fuel type, JP-4, has a maximum API specification of 57. Therefore, the distillate volume cannot be increased by making jet fuel out of these naphtha streams.

Another possibility to increase the distillate volume is to combine the IBP-350°F stream cuts with other materials to form a jet fuel product. However, the next section of this report will show that this is not possible.

Hence, any jet fuel would have to be formed from the light diesel fractions. The total volume of distillate products will be the same for the two cases.

6.4 JET FUEL BLENDING STUDY

The diesel blending correlations developed in Section 6.3 for flash point, pour point and viscosity were also used for the jet fuel blending study. The jet fuel blending study was done entirely using the paper blend properties generated by the modified generalized correlations. No laboratory blends were generated. The freeze point for jet fuel blends was assumed to be equal to the calculated pour point. This assumption is not entirely correct, but it is sufficiently accurate for this study.

Two main types of jet fuel were considered; Jet A and JP-4. The specifications for the two jet fuel types are compared in Table 6.9.

6.4.1. Jet A Product

The first jet fuel blends were made in an attempt to make a Jet A product. The blend that was closest to the Jet A specifications is shown in Table 6.10. The blend calculations are included in Appendix E.

The Jet A product meets all specifications, except for the gravity. Component viscosity data are only available at 100°F. Data at -4°F would be required to determine if the blend meets the viscosity specification.

There are no other streams in the complex that could be blended into the Jet A product to meet the gravity specification without adversely affecting the other properties, so the conclusion is that a Jet A product cannot be made from the streams in the upgrading complex. The reason for this may be that the hydrocracked distillate and F-T condensate cuts are too paraffinic.

The API's of these streams are too high relative to their pour points. Materials which contain aromatics, such as heavy FCC gasoline or straight-run kerosine, would have to be blended into the Jet A blend to make an "on-spec" product. The hydrocracked distillate and F-T condensate cuts have high smoke points due to such low aromatics content. Therefore, they have significant capacity to accept aromatics to provide lubricity without reducing the smoke point below the 25-mm specifications. The LCO cannot be added because it has an unacceptably high boiling range. Also, the LCO will adversely affect the freeze point of the jet fuel blend.

6.4.2 JP-4 Product

The next series of blends were aimed at meeting the JP-4 specifications. Several blends were made but the JP-4 specifications could not be met. Different combinations of components can be assembled to meet the API specification, but then the distillation, particularly the front end distillation, is always too high. The blends could not meet JP-4 freeze point specifications.

The idea of adding IBP-350°F naphtha into the JP-4 product to decrease the front end distillation was explored, but without success. Two sets of JP-4 blends, with and without naphtha are shown in Table 6.11.

The two base blends, without naphtha, were set up so they would meet the JP-4 API specifications. Blend A contains the 350-400°F and 400-450°F cuts from the HC Unibon and F-T condensate along with the DHT product. Blend B contains only the two 350-400°F distillate streams. Sufficient naphtha (IBP-350°F material from the HC Unibon) was then added into the two blends so that the distillations would meet the JP-4 specifications. In both cases, both the API and freeze points of the resulting blends are too high.

Although jet fuel cannot be made from blends comprised solely of material from the complex, it could be blended with an external stream to make an acceptable product.

6.5 DISTILLATE BLEND STABILITY

Fuel stability is an important consideration during production and blending of middle distillates. Typically, three separate reactions cause instability in middle distillates: salt formation from acid-base reaction, oxidation and/or polymerization of unsaturates and esterification leading to sediment formation (22).

The 60 wt-% LCO diesel blend was analyzed for instability using a UOP test method. In this method, the sample is maintained at 212°F under oxygen atmosphere for 16 hours. Color and sediment are then determined. As seen in Table 6.12, the 60 wt-% diesel blend was unstable with both color and sediment formation exceeding allowable limits. Blend stability can be improved by hydrotreating, application of stabilizers and chelating agents, and occasionally accompanied by caustic scrubbing. The stability problem seen in the 60 wt-% LCO diesel blend is expected due to the presence of olefins and oxygenates (from hot and cold condensate) and unsaturates, sulfur, nitrogen compounds (from the FCC derived LCO's).

In a commercial Fischer-Tropsch upgrading complex, the distillate blend will have to be stabilized, especially when an external LCO stream is blended. In a refinery, distillate treatment to improve stability is very common as more and more supplemental blending components from different processes and sources are added to straight-run distillate. These blend components are derived from high severity cracking operations or from conversion of bottom-of-the-barrel fractions to lighter components. Also, coal-derived substitutes in the diesel blend pool will compound the instability problem and the blend must be treated to remove sediment precursors.

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* Penex and Molex are registered trademarks and/or service marks of UOP Inc.

Table 6.1

Catalytic Condensation Unit Yields

	Net Charge MT/D	Net Products MT/D
C_3=	123.9	10.8
C_3	123.9	123.9
C_4=	129.8	14.4
C_4	129.8	129.8
C_5=	86.4	19.2
C_5	172.9	172.9
C_6=	74.7	22.8
C_6	167.2	167.2
C_7-320°F (Gasoline)	--	100.7
320°F-500°F (Diesel)	--	243.4
500°F+ (Heavy Polymers)	--	3.5
Total	1008.6	1008.6

Estimated Liquid Product Properties

Stream	Gasoline	Distillate	Heavy Polymer
Specific Gravity	0.71	0.78	0.87
Distillation			
IBP°F	97	329	509
EP°F	320	482	680
RONC	93		
MONC	82		
After Hydrogenation			
Cetane Index		57	
Smoke Point, mm		>25	
Freeze Point, °F		<76	

Table 6.2

Distillate Hydrotreater Yields

Net Charge	MT/D	Net Product	MT/D
Poly Diesel	243.4	Distillate	246.8
Hydrogen	3.4		

Distillate Product Properties	
API	49.9
Specific Gravity	0.78
50% Point, °F	406
Cetane Index	57
Flash Point, °F	126
Pour Point, °F	-60
Viscosity, cSt @ 100°F	1.20

Table 6.3

Naphtha Hydrotreater Yields

	Base Case, MT/Day	Alternate Case, MT/Day
Feedstock		
C_5/C_6 from Cat. Con.	382.2	382.2
C_5/C_6 from HC Unibon	169.1	0.0
F-T Condensate, IBP-350°F	283.2	283.2
HC Unibon, C_7-350°F	757.7	0.0
Hydrogen	9.3	4.7
Products		
C_5/C_6 to Isomerization	551.2	382.1
Naphtha to Reformer	1042.2	284.6
Fuel Gas	8.0	3.3
Product Properties (C_6+)		
API Gravity	67.76	67.76
Sulfur, ppm	<0.5	<0.5
Total Nitrogen, ppm	<0.5	<0.5
Diene Value	<50	<50

Table 6.4

CCR Platforming Unit Yields

	Base Case, MT/Day	Alternate Case, MT/Day
Feedstock		
Naphtha from NHT	1042.2	284.6
Products		
Hydrogen	23.6	6.4
Fuel Gas	172.3	47.0
LPG	104.0	28.4
Reformate	742.4	202.7
Product Properties		
Specific Gravity	0.77	0.77
API Gravity	52.3	52.3
Reid Vap. Press., psia	6.6	6.6
Molecular Weight	93.3	93.3
RONC	95.0	95.0
MONC	84.5	84.5

Table 6.5

UOP Penex/Molex Combination Unit Yields

	Base Case, MT/Day	Alternate Case, MT/Day
Feedstock		
C_5/C_6 from Naphtha Splitter	551.2	382.1
Hydrogen	0.1	0.1
Products		
Fuel Gas	0.3	0.2
LPG	2.6	1.8
Isomerate to Storage	548.4	380.2
Product Properties		
Specific Gravity	0.641	0.641
API Gravity	89.2	89.2
Reid Vap. Press., psia	14.4	14.4
Molecular Weight	78.4	78.4
RONC	89.0	89.0
MONC	87.3	87.3

Table 6.6

Hydrocracker Yields

Feedstock	MT/Day
F-T Wax	2537.0
Heavy Polymer from Cat. Con.	3.5
F-T Condensate, 650°F-EP	601.8
Hydrogen	26.9
Products	
Fuel Gas	4.1
LPG	82.0
C_5/C_6 to NHT	169.1
C_7-350 to NHT	757.7
350-EP to Diesel Pool	2156.3

Product Properties*

Cut, °F Boiling Range	IBP-350	350-400	400-450	450-500	500-650	650-700	Total
Specific Gravity	0.70	0.75	0.76	0.77	0.79	0.80	0.78
API Gravity	69.9	56.6	53.7	51.4	48.2	44.3	48.4
ASTM 50% Point, °F	237	370	421	475	575	675	
Cetane Index	46.2	62.8	68.5	73.3	77.7	73.1	74**
Flash Point, °F	30	136	174	210	260	360	135
Pour Point, °F	<-70	<-70	<-70	-35	-10	15	+10
Freeze Point, °F	<-65	<-65				+68	
Viscosity, cSt @ 100°F	0.57	1.15	1.55	2.09	3.59	8.52	3.58
Wt. Fraction	0.26	0.06	0.07	0.06	0.2	0.3	1.0

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* Lab Analysis

** Cetane Number

Table 6.7

Comparison Between Paper and Laboratory Blends

Blend	LCO Content, Wt-%	API	ASTM 50% Point, °F	Cetane Number*	Flash Point, °F	Pour Point, °F	Viscosity, cSt @ 100°F
Paper or Laboratory**	0	48.2	559	>74	186	13	3.5
Paper Blend	40	36.2	555	55	194	5	3.3
Laboratory	40	36.5	540	55	187	10	3.2
Paper or Laboratory**	60	30.2	541	45	184	0	3.2

---

* Cetane Index for Paper Blends and Cetane Number for Laboratory Blends.

** Paper blends for 0 and 60 wt-% LCO use corrected correlations. Corrections forced convergence at endpoints of interval, the reason for paper and lab properties being the same at 0 and 60%.

Table 6.8

Diesel Paper Blends

LCO Content, Wt-%	Flow Rate, MTD	API	ASTM 50% Point, °F	Cetane Index	Flash Point, °F	Pour Point, °F	Viscosity, cSt @ 100°F
0	3,288	48.8	548	76	188	13	3.6
20	4,110	42.5	553	66	187	8	3.5
40	5,480	36.1	558	56	186	3	3.4
60	8,221	29.8	564	45	185	-2	3.3
Specifications				40 Min	125 Min	20 Max	1.9-4.1

Table 6.9

Jet Fuel Specifications

	Jet A	JP-4
API	37-51	45-57
Smoke Point, mm, min	25	20
Flash Point, °F, min	100	Report
RVP, psi, max	Report	2-3
Freeze Point, °F, max	-40	-72
Viscosity, cSt @ -4°F, max	8	Report
Distillation		
10% Over °F, max	400	--
20% Over °F, max	--	293
50% Over °F, max	Report	374
90% Over °F, max	Report	473
EP, max	572	--

Table 6.10

Jet A Product

Analysis*	Jet A Product	Jet A Specifications
API, min	53.2	37-51
Smoke Point, mm, min	>50	25
Flash Point, °F, min	156	100
RVP, psi, max	<1	Report
Freeze Point, °F, max	-51	-40
Viscosity, cSt @ -4°F, max	7	8
cSt @ 100°F, max	2	--
Distillation		
10% Over °F, max	378	400
50% Over °F, max	405	Report
90% Over °F, max	456	Report
EP, max	515	572

---

* Calculated from Correlations in Section 6.3.

Table 6.11

JP-4 Products

Analysis*	JP-4 Blend A	JP-4 Blend A w/Naphtha	JP-4 Blend B	JP-4 Blend B w/Naphtha	JP-4 Specs.
API	53.6	59.0	56.6	61.1	45-57
Smoke Point, mm, min	>50	?	>50	?	20
Flash Point, °F, min	152	60	146	60	Report
RVP, psi, max	<1	<3	<1	<3	2-3
Freeze Point, °F, max	-53	-62	-61	-67	-72
Viscosity cSt @ -4°F, max	--	--	--	--	Report
cSt @ 100°F	1.9	1.5	1.8	1.5	--
Distillation					
20% over, °F, max	380	275	360	270	293
50% over, °F, max	399	367	367	357	374
90% over, °F, max	424	410	386	378	473

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* Calculated from Correlations in Section 6.3.

Table 6.12

Blend 4 (60 wt-% LCO) Stability
(UOP Test Method)

	Test Results	Maximum Allowable Limit
Color	8.0	6.0 (Mid-American Pipeline Specifications)
Sediment mg/100 ml	6.3	1.6 (UOP Test Method Limit)

Test Conditions: 16 hour at 212°F, O_2 media, sediment and color determined

FIGURE 6.1

FISCHER-TROPSCH PRODUCT UPGRADING COMPLEX BASE CASE FLOW SCHEME

(FLOW RATES IN METRIC TONS PER DAY)

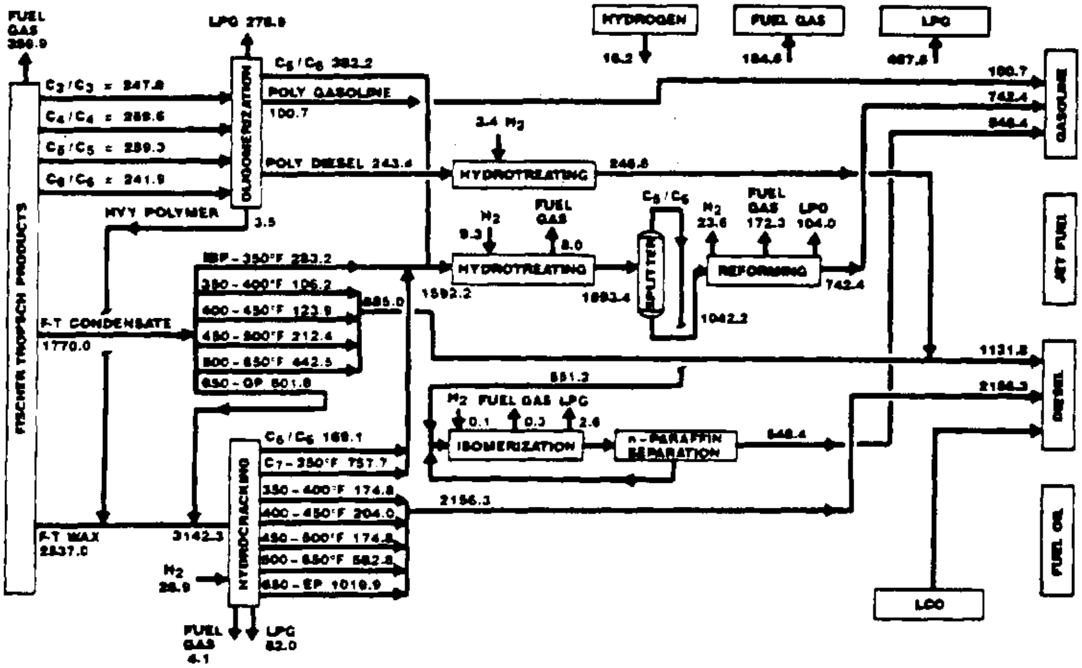

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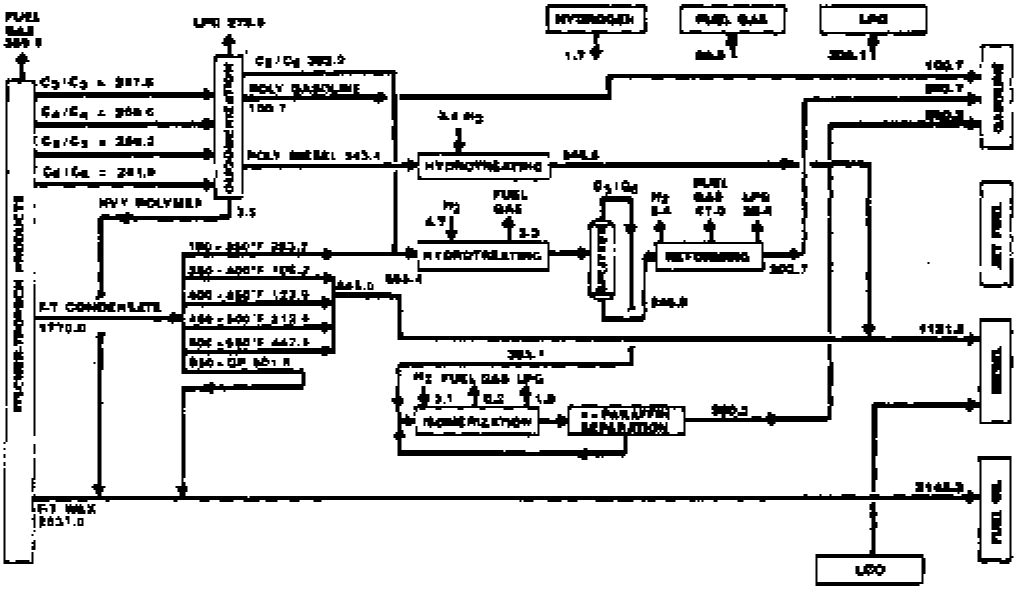
FIGURE 6.2

FISCHER-TROPSCH PRODUCT UPGRADING COMPLEX ALTERNATIVE CASE FLOW SCHEME

(FLOW RATES IN METRIC TONS PER DAY)



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