3.0 DESIGN BASES AND PERFORMANCE EVALUATION FOR THE MOBIL TWO-STAGE CONCEPTUAL COMMERCIAL PLANT

3.1 Introduction

In this section of the report, data from the Mobil bench-scale unit (BSU) is used as the basis for the preparation of conceptual commercial Fischer-Tropsch plant designs. Two case studies are examined, based on BSU data from two runs at different operating conditions. The first case represents a low-wax option where the slurry-phase F-T unit is operated in a regime to minimize reactor wax. This operation results in a significant production of methane, ethane, and ethylene (C_1/C_2 hydrocarbon gases). The second case represents a high-wax option where operation of the slurry-phase F-T unit is such that about 40 to 50 weight percent of the synthesized hydrocarbons is reactor wax. Because of milder temperature and higher pressure conditions, this case results in a much lower production of C_1/C_2 hydrocarbon gases. For a commercial plant operating in an all-liquid output mode, lower gas production is an efficiency advantage. The slurry F-T unit can be operated in such a manner as to produce about 80 to 85 weight percent of reactor wax. This case was not considered here as a viable option since only non-wax components of the product stream are reacted over the zeolite stage. When the zeolite only treats 20 percent of the output, its advantages in reducing conventional refining operations is virtually eliminated.

The conceptual commercial scale basis for the production of clean synthesis gas from coal using BGC/Lurgi gasification is taken from a prior publication.[1] Wyoming coal (27.8 thousand tons per day as-received) is processed in British Gas Corporation (BGC) slagging Lurgi gasifiers to produce 96,160 lb. mols of clean synthesis gas per hour. The coal analysis is shown in Table 3-1. Details of the production of the clean synthesis gas are given in Reference 1 and Section 4.0.

Two design bases are produced here for the low-wax case. In Reference 2, Mobil published a scoping study based on BSU Run CT-256-3. In this study, they used raw BSU data from two material balance periods as their design base. Mobil performed detailed elemental, material, and overall energy balances on this data to arrive at a modified product distribution and efficiency. This they scaled to produce an estimated commercial plant output slate. MITRE has used this data from the Mobil scoping study as one design base for the low-wax case. This is referred to as the Mobil design in this section. Additionally, MITRE performed an independent material and energy balance from the Mobil raw BSU data to arrive at a separate estimate of product distribution and efficiency. This is referred to as the MITRE design in this section. The interpretation and processing of the raw data, both by Mobil and by MITRE, has produced two sets of process flows for the low-wax case with slightly different product distribution and overall efficiencies. The Mobil estimate is extremely optimistic with respect to overall efficiency and

TABLE 3-1

COAL ANALYSIS

	Wyoming Subbituminous
Proximate Analysis (weight percent) (As-received)	
Moisture	28.0
Ash	5.1
Fixed Carbon	33.8
Volatile Matter	33.1
Ultimate Analysis (weight percent) (DAF)	
C	74.45
H	5.10
O	19.25
N	0.75
S	0.45
Cl	-
Calorific Value (Btu/lb)	
HHV (as-received)	8,509
HHV (DAF)	12,720
LHV (as-received)	7,893
LHV (DAF)	12,236

selectivity to gasoline, whereas the MITRE estimate is more conservative and results in a product distribution more closely matching the raw BSU data.

Table 3-2 shows the plant inputs of coal, oxygen, and steam for the MITRE design basis. The total input coal to the plant is split between coal sent to gasification and coal sent to boilers for steam generation. The high pressure steam generated is used to drive turbines for air separation and oxygen compression, for gasification, and for downstream plant requirements. Details of steam utilization are given in Reference 1 and are not reproduced here. In the MITRE design, the raw gas from the BGC gasifier is shifted from a molar H_2:CO ratio of 0.49 to 0.67. This latter ratio was used at the Koelbel pilot plant and has been used in all the Mobil Bench-Scale unit (BSU) runs to date.

In their scoping study, Mobil used the same design basis as the MITRE report[1] except that no external shift was employed. Feed gas to the slurry Fischer-Tropsch reactor was augmented with sufficient steam to produce an internal gas shift of 0.67. It should be noted that the proposed addition of steam has not been successfully demonstrated by Mobil to date. Because of this, MITRE opted to use external shift in the preparation of its conceptual commercial design cases. The Mobil scoping study design basis is shown in Table 3-3.

3.2 Low Wax Case Design Basis

In the MITRE design, material balance Periods 3-11 and 3-34 from BSU Run CT-256-3 (refer to Section 2) were used for the first stage

TABLE 3-2

MITRE DESIGN BASIS FOR MOBIL SLURRY-PHASE F-T COMMERCIAL PLANT

Based on BGC Gasification/Koelbel Synthesis Case in MITRE Report

Coal Input to Plant	2,316,557 #/hr	(27.8 M tons/day as received)
Coal Split to Steam Plant	216,600 #/hr	(Plus tars, oils, phenols)
Coal Split to Gasification	2,100,000 #/hr	
Oxygen for Gasification	553,000 #/hr	
Steam for Gasification	456,000 #/hr	

Gasifier Output: (Clean Shifted Gas)*

	Moles per hour	Pounds per hour
CO	57,650	1,614,200
H_2	38,510	77,020
CH_4	7,490	120,139
C_2H_4	26	729
C_2H_6	341	10,270
Naphtha	178	17,300
	104,195	

Total moles of clean synthesis gas = 96,160 Lb. Moles per hour.

*Mobil Scoping Study uses clean, unshifted BGC gas; MITRE Study shifts gas to 0.67 H/CO.

TABLE 3-3

MOBIL DESIGN BASIS FOR MOBIL SLURRY F-T COMMERCIAL PLANT

Design Basis: BGC Lurgi Gasification (MITRE Basis)
Internal SFT shift assumed.

Input to Slurry Fischer-Tropsch/ZSM-5 Reactor System

Component	Clean Syngas		Steam	
	Moles	Pounds	Moles	Pounds
CO_2	2,360	103,864		
C_2H_4	26	729		
CO	64,319	1,801,575		
H_2	31,841	64,000		
CH_4	7,490	120,140		
C_2H_6	342	10,281		
N_2	365	10,224		
H_2O			6,738	121,351
Totals:	106,743	2,111,070	6,738	121,351

TOTAL: 2,232,421 pounds per hour.

slurry-phase F-T reactor and the second stage zeolite reactor, respectively.

Period 3-11 was chosen because of the good material balance achieved and because, after 13 days onstream, the system was operating in a stable mode. Period 3-34 was chosen because the severity factor was close to 1.0* which would maximize the yield of alkylate. Table 3-4 shows the raw data corresponding to these two material balance periods.

The material balance and thermal inputs and outputs derived from these operating periods are shown in Table 3-5. This operation represents a high-methane, low-wax case where C_1 and C_2 hydrocarbon gas production is approximately 12 weight percent and reactor wax production is about 8 weight percent. The output data from Table 3-5 can now be directly scaled to determine the expected outputs from a conceptual commercial plant employing this technology. The scaling factor is simply the ratio of the commercial gasifier output to the gas rate used in the BSU material balance period.

Figure 3-1 shows the total material balance for the conceptual commercial design. Clean shifted synthesis gas, including methane, ethylene, and ethane, produced in the gasifier is fed to the slurry phase F-T reactors. Total hydrogen and carbon monoxide conversion of 86.85 mole percent is obtained in a single pass, with CO conversion

*Severity factor defined as ratio of isobutane to C_3 and C_4 olefins.

TABLE 3-4

BSU TEST DATA EMPLOYED IN MITRE DESIGN BASIS FOR LOW-WAX CASE

	First Stage Only	First and Second Stage
MB Number	3-11	3-34
Days on Stream	13	35
First Stage Conditions		
H_2/CO	0.68	.695
Pressure MPa	1.48	1.48
Temperature, °F	260	259
Space Vel. NL/g Fe-hr	2.622	2.273
Feed Superficial Vel. cm/sec	4.038	3.480
N_2 in feed, Mol %	7.4	6.9
H_2 Conversion	79.38	80.74
CO Conversion	91.94	92.26
H_2 + CO Conversion	86.85	87.54
Yields Wt. % of Products		
Hydrocarbons	21.87	23.00
CO_2	68.80	67.74
H_2O	0.71	1.43
H_2	0.96	0.87
CO	7.66	6.96
Balance Recovery, Wt. % Charge	100.33	105.75
gHC/Nm^3 (H_2 + CO)	197	215
Selectivities, Wt. % of HC		
CH_4	6.78	7.69
C_2H_4	1.58	1.06
C_2H_6	2.83	3.25
C_3H_6	7.53	3.90
C_3H_8	1.82	9.03
C_4H_8	6.16	4.37
$i\text{-}C_4H_{10}$	0.07	9.26
$n\text{-}C_4H_{10}$	1.78	7.61
$C_5\text{-}C_{11}$	18.64	44.46
Light HC	14.31	1.70
Heavy HC	27.62	---
Slurry Wax	9.88	7.66
Second Stage Conditions:		
Temp. °C Inlet		373
Outlet		415
Pressure MPa		1.411
GHSV litre/hour		2,832
Days on Stream		17.6
($i\text{-}C_4/C_3^= + C_4^=$) Molar		0.93

TABLE 3-5

MATERIAL AND ENERGY BALANCES FROM RUN CT 256-3
(MITRE DESIGN BASIS LOW-WAX CASE)

INPUT:	Moles/Hr	Pounds/Hr	MMBtu/Hr (LHV)
CO	55.15	1,544.8	6.715
H_2	37.50	75.6	3.903
	92.65	1,620.4	10.618

OUTPUTS:

F-T Reactor (MB # 3-11)			
Hydrocarbons		355.86	
CO_2	25.44	1,119.50	-
H_2O	0.64	11.55	-
H_2(79.36%)	7.74	15.62	.806
CO (91.93%)	4.45	124.64	.542
		1,627.2	

ZSM-5 Reactor (MB # 3-34)			
Hydrocarbons		Pounds/Hr	MMBtu/Hr
CH_4	24.13	25.83	.556
C_2H_4	5.62	3.55	.072
C_2H_6	10.07	10.94	.224
C_3H_6	26.80	13.10	.258
C_3H_8	6.48	30.30	.603
C_4H_8	21.92	14.67	.286
$i\text{-}C_4H_{10}$	0.25	31.10	.622
$n\text{-}C_4H_{10}$	6.33	25.56	.505
$C_5\text{-}C_{11}$	70.78	158.25	3.036
LHC/C_{12}^+	56.37	5.71	.108
HHC	99.79	-	-
Wax	27.26	27.26	.518
H_2O	-	9.5	-
	355.86	355.86	6.788

SFT/ZSM-5 Reactor Section

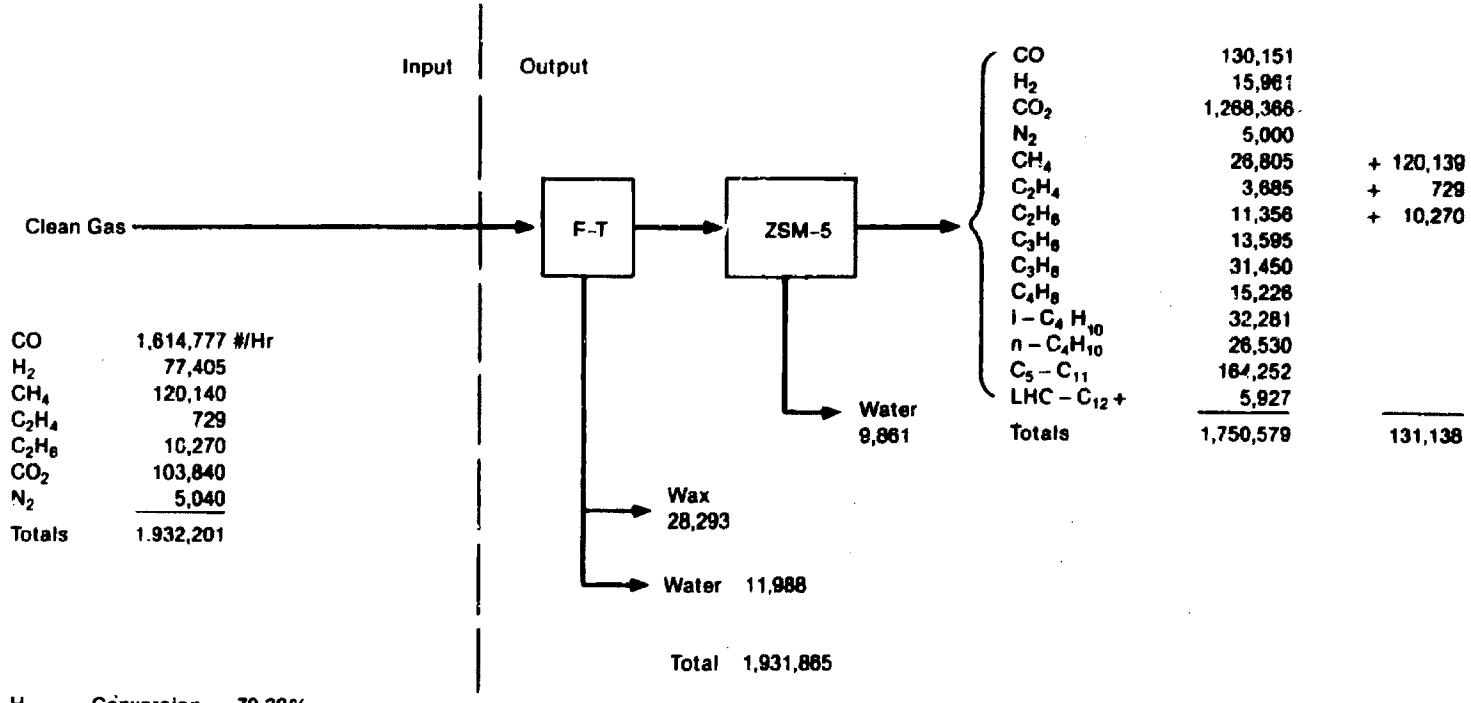

FIGURE 3-1

MATERIAL BALANCE, POUNDS/HOUR (MITRE ESTIMATE)

being as high as 92 percent. This high conversion reflects the actual conversion levels achieved at the BSU scale during this material balance period. Reactor effluent from the first stage F-T reactor, excluding reactor wax, is passed to the second stage zeolite fixed-bed reactors. The effluent from the second stage is listed on the right of Figure 3-1. Gasifier-produced methane and ethane are assumed to pass through the system as inerts.

Figure 3-2 shows a simple schematic of the two-stage synthesis process and the initial product separation stage. Wax/catalyst separation removes the excess reactor wax from precipitated F-T catalyst and returns the catalyst to the reactor. Excess reactor wax is then withdrawn. Fresh catalyst from catalyst preparation is slurried in reactor wax, activated and pumped into the slurry reactors to maintain a constant level of catalyst activity. It should be noted that the ability to withdraw wax and separate the fine catalyst particles and return them to the reactor without deactivation has not been satisfactorily demonstrated by Mobil to date. The ability to do this becomes even more important in cases where reactor wax is a substantial part of the output. Research on improved methods of catalyst separation and recycle are currently underway. Two product streams emerge from the separator. These are the hydrocarbon vapor stream No. 1 and the hydrocarbon liquid stream No. 2.

These two streams are sent to the product recovery section illustrated schematically in Figure 3-3. Carbon dioxide removal is necessary at this stage, since the product of internal shift is carbon

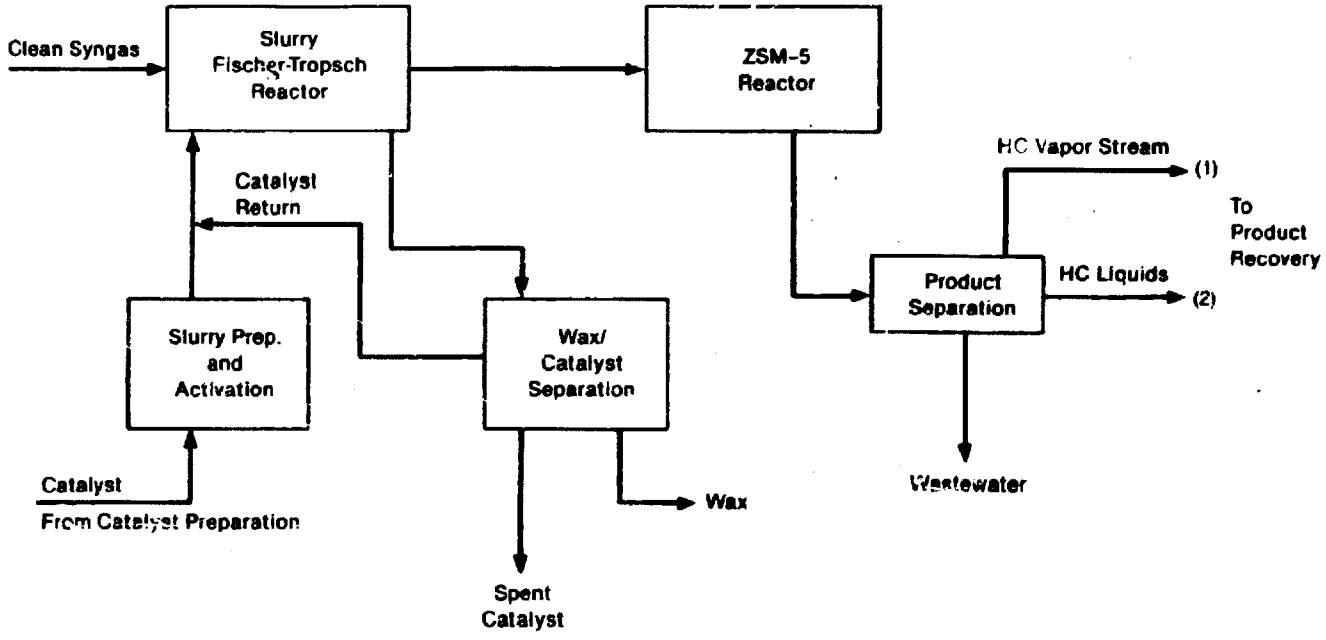

FIGURE 3-2

SYNTHESIS REACTOR SECTION

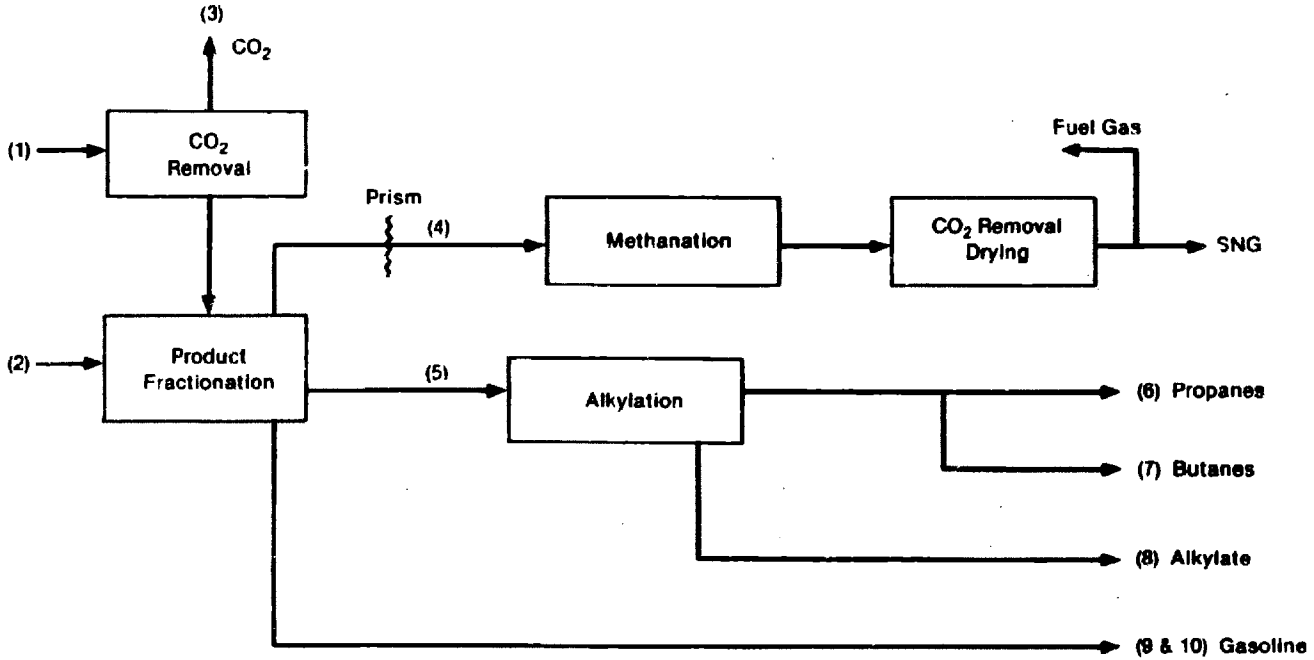

FIGURE 3-3
PRODUCT RECOVERY SECTION

dioxide (Stream No. 3). The product streams (identified by numbers) are then processed as indicated in Figure 3-3. C_3 and C_4 hydrocarbons (Stream No. 5) are sent to the alkylation unit where isobutane is reacted with propene and butene to produce C_7 and C_8 gasoline boiling range hydrocarbons. Output from the alkylation unit is then alkylate (Stream No. 8) which is blended with the zeolite effluent gasolines, propanes (Stream No. 8) and butanes (Stream No. 9). C_1 and C_2 hydrocarbons and unreacted synthesis gas (Stream No. 4) are sent to methanation to produce synthetic natural gas (SNG). In this configuration, the plant is operating in the mixed-output mode, where SNG is produced in addition to the gasoline and other hydrocarbon liquids. In the alternative all-liquid mode, the C_1 and C_2 hydrocarbons are reformed to syngas and recycled to the F-T reactor so that only liquid products are produced by the plant. In this case, an autothermal reformer[3] is substituted for the methanation unit.

Table 3-6 shows the product recovery material balance for the MITRE estimate. Streams 1 and 2 are the two inputs to the product recovery section. Stream 3 represents removed carbon dioxide. Stream 4 is the overhead gases from product fractionation. This gas serves both as a source of hydrogen for hydrotreatment of the gasifier naphtha that is produced by the BGC slagging Lurgi system and as internal plant fuel gas. The remainder of this gas is methanated and reports to SNG product. Stream 5 is the feed stream to the alkylation unit. Here, i-butane is reacted with propene and butene to produce

TABLE 3-6

PRODUCT RECOVERY MATERIAL BALANCE (POUNDS/HOUR) LOW-WAX CASE
(MITRE ESTIMATE)

Component	STREAM NUMBER								
	1 and 2	3	4	5	6	7	8	9	10
CO_2	1,268,366	1,268,366							
C_2H_4	4,414		4,414						
CO	130,151		130,151						
H_2	15,961		15,961						
CH_4	146,944		146,944						
C_2H_6	21,626		21,626						
N_2	5,000		5,000						
C_3H_6	13,595		832	12,763					
C_3H_8	31,450			31,450	33,376				
$i\text{-}C_4H_{10}$	32,281			32,281	232	756	465		
C_4H_8	15,226			15,226					
$n\text{-}C_4H_{10}$	26,530			26,530		23,364	3,138		
C_5^+	170,170						56,794	142,344	27,835
TOTALS	1,881,723	1,268,366	324,928	118,250	33,608	24,120	60,397	142,344	27,835

C_7 and C_8 gasoline range hydrocarbons. Table 3-7 shows the alkylation unit material balance. Conversion of i-butane is taken as 95 percent. Streams 6, 7, and 8 are the outputs from the alkylation unit, i.e., propanes, butanes and alkylate. Streams 9 and 10 are the gasoline products from the zeolite reactor. The Mobil estimated finished 10-RVP gasoline, including the alkylate, is a reasonably high-octane material having the properties shown in Table 3-8.[2] Actual measured properties of the second stage effluent are also shown in Table 3-8.

During the BSU Run CT-256-3, the measured properties of the second stage effluent varied considerably with the severity factor ($i\text{-}C_4/(C_3^= + C_4^=)$. This is reflected by the range of properties shown in Table 3-8. Table 3-9 is indicative of hydrocarbon properties and selectivities for operation at 23 days onstream. This table illustrates dramatically the effect of the zeolite on the first stage raw F-T product.

Table 3-10 shows the energetics of the MITRE estimate for the whole system from clean synthesis gas to finished products. It should be noted that the value of the SNG is net of internal plant fuel gas requirement (327 MMBtu/hr) for zeolite reactor heating and hydrogen requirement for gasifier naphtha treatment (168 MMBtu/hr). Overall LHV efficiency based on total plant input coal is therefore 54 percent at this stage, but an additional 1,630 barrels per stream day (BPSD) of naphtha will be added to the gasoline pool as the contribution from

TABLE 3-7

ALKYLATION UNIT BALANCE

	FEED		ALKYLATE		BUTANES		PROPANES	
	Lbs.	Lb. Moles	Lbs.	Lb. Moles	Lbs.	Lb. Moles	Lbs.	Lb. Moles
C_3H_6	12,763	303	-	-	-	-	-	-
C_3H_8	31,450	713	-	-	-		33,376	757
i-C_4H_{10}	32,281	555	465	8	756	13	232	4
C_4H_8	15,226	271	-	-	-	-	-	-
n-C_4H_{10}	26,530	456	3,138	54	23,364	402	-	-
C_5+	-	-	-	-	-	-	-	-
			30,894					
			25,900	530				
	118,250	2,298	60,397	592	24,120	415	33,608	861

Alkylation Reactions

(i-butane) $C_4H_{10} + C_4H_8 \rightarrow C_8H_{18}$

Moles 271 271

$C_4H_{10} + C_3H_6 \rightarrow C_7H_{16}$

259 259

i-butane conversion yield (Mobil) = 0.95 = 530 moles i-C_4-H_{10} converted to C_5+

TABLE 3-8

ESTIMATED PROPERTIES OF MOBIL 10-RVP GASOLINE

Research Octane Number (RON), Clear	89
Motor Octane Number (MON), Clear	83
RVP PSIA	10

Distillation °F	ASTM	TBP
10 Vol. %	109	84
30	139	141
50	199	161
70	240	197
90	286	319

*PONA (Vol. %) 67/13/4/16

Range of Measured Properties of Second-Stage Reactor Effluent

	RON	85.1 - 92.7
	MON	75.6 - 83.4
PONA (Wt. %)	Paraffins	22.4 - 36.8
	Olefins	4.6 - 50.2
	Naphthenes	6.8 - 13.1
	Aromatics	14.5 - 54.8
ASTM Distillation °F		
	IBP	88 - 108
	50 vol. %	248 - 271
	90 vol. %	361 - 378
	EP	460 - 505

*Paraffins, olefins, naphthenes, and aromatics.

TABLE 3-9

HYDROCARBON SELECTIVITIES BEFORE AND AFTER ZSM-5 REACTOR

(Run CT-256-3, TOS = 555 Hours)

	Before Second Stage	Before Alkylation	After Alkylation
C_1	6.5	6.8	6.8
$C_2^=/C_2$	1.7/2.7	1.0/2.9	1.0/2.9
$C_3^=/C_3$	7.1/1.9	2.0/5.6	0.3/5.6
$C_4^=$	5.9	4.7	0.5
iC_4/nc_4	0/1.8	6.6/6/1	0/6.1
C_5-C_{11}	27.1	51.5	64.0
$C_{12}+$ (Liquid)	33.3	0.8	0.8
Reactor-Wax	12	12	12
C_5-C_{11} PONA (Wt.%)			
P		49.4	59.3
O		22.8	18.3
N		4.5	3.6
A		23.3	18.8

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	RON	85.1 - 92.7
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	Olefins	4.6 - 50.2
	Naphthenes	6.8 - 13.1
	Aromatics	14.5 - 54.8
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(Run CT-256-3, TOS = 555 Hours)

	Before Second Stage	Before Alkylation	After Alkylation
C_1	6.5	6.8	6.8
$C_2^=/C_2$	1.7/2.7	1.0/2.9	1.0/2.9
$C_3^=/C_3$	7.1/1.9	2.0/5.6	0.3/5.6
$C_4^=$	5.9	4.7	0.5
iC_4/nc_4	0/1.8	6.6/6/1	0/6.1
C_5-C_{11}	27.1	51.5	64.0
C_{12}+ (Liquid)	33.3	0.8	0.8
Reactor-Wax	12	12	12
C_5-C_{11} PONA (Wt.%)			
P		49.4	59.3
O		22.8	18.3
N		4.5	3.6
A		23.3	18.8

TABLE 3-10

ENERGY FLOW SCHEMATIC FOR LOW-WAX CASE (MMBTU/HR LHV)
(MITRE ESTIMATE)

Total Plant Coal Input = 18,959 MMBtu/Hr

	Clean Syngas	Raw Products	Refined Products	
CO	7,019	566		
H_2	3,996	824		
CH_4	2,582	3,159		
C_2H_4	15	89		
C_2H_6	210	442		
C_3H_6		268	SNG	4,296
C_3H_8		627	Propane	661
C_4H_8		297	Butane	475
$i\text{-}C_4H_{10}$		634	Gasoline*	4,353
$n\text{-}C_4H_{10}$		522	Wax**	538
$C_5\text{-}C_{11}$		3,154		
C_{12}^{+}		113		
Wax		538		
Naphtha		(343)		
	13,822	11,233		10,323

*Gasoline is blend of alkylate, light and heavy gasoline; weighted average 248 #/Bbl; 4,682 MMBtu/Bbl (LHV).
**Wax is assumed to contain 19,000 Btu/lb.

the hydrotreated gasifier naphtha which will further increase the total efficiency.

The Mobil scoping study[2] used material balance Periods 3-22 and 3-34 for the first and second stage reactors, respectively. That is, although they used the same period as the MITRE estimate for the second stage, they used a different first stage period. This, together with computations of material and energy balances, leads to a slightly different overall efficiency and product selectivity from that obtained by MITRE.

Table 3-11 shows the Mobil scoping study design basis from the BSU data of Run CT-256-3. Based on this raw data and after appropriate scale-up, Table 3-12 shows the product recovery material balance obtained in the Mobil case. To further enhance their yield of alkylate, Mobil opted to provide purchased isobutane in their conceptual design. This amounted to an additional 10,671 lbs/hour of iso-butane, equivalent to 210 MMBtu/hr (LHV).

Table 3-13 compares the predicted raw product yields obtained from both the MITRE and Mobil estimates. The Mobil estimate is higher with respect to efficiency than the MITRE case. Overall thermal efficiency for the Mobil case is 81 percent, based on actual synthesis of hydrocarbons from carbon monoxide and hydrogen. This is a very optimistic value for LHV thermal efficiency for a feed syngas of H:CO ratio 0.5. The MITRE estimate of 77 percent for thermal efficiency is certainly more conservative.

TABLE 3-11

MOBIL SCOPING STUDY DESIGN BASIS FROM PDU RUNS

	First Stage F-T Only	First and Second Stage
MB Number	3-22	3-34
Days on Stream	23	35
First Stage Conditions		
H_2/CO	.685	.695
Pressure MPa	1.48	1.48
Temperature, °F	260	259
Space Vel. NL/g Fe-hr	2.507	2.273
Feed Superficial Vel. cm/sec	3.829	3.480
N_2 in feed, Mol %	6.6	6.9
H_2 Conversion	78.36	80.74
CO Conversion	89.37	92.26
H_2 + CO Conversion	84.89	87.54
Yields Wt. % of Products		
Hydrocarbons	19.43	23.00
CO_2	69.41	67.74
H_2O	0.78	1.43
H_2	0.95	0.87
CO	9.43	6.96
Balance Recovery, Wt. % Charge	107.36	105.75
gHC/Nm^3 (H_2 + CO)	191	215
Selectivities, Wt. % of HC		
CH_4	7.55	7.69
C_2H_4	1.64	1.06
C_2H_6	3.13	3.25
C_3H_6	8.19	3.90
C_3H_8	2.24	9.03
C_4H_8	6.98	4.37
$i\text{-}C_4H_{10}$	0.07	9.26
$n\text{-}C_4H_{10}$	2.12	7.61
$C_5\text{-}C_{11}$	12.33	44.46
Light HC	20.13	1.70
Heavy HC	26.93	---
Slurry Wax	8.91	7.66
Second Stage Conditions:		
Temp. °C Inlet		373
Outlet		415
Pressure MPa		1.411
GHSV litre/hour		2,832
Days on Stream		17.6
($i\text{-}C_4/C_3^= + C_4^=$) Molar		0.93

TABLE 3-12

PRODUCT RECOVERY MATERIAL BALANCE (LBS/HOUR)
(MOBIL SCOPING STUDY)

	Stream Number								
Component	1 and 2*	3	4	5**	6	7	8	9	10
CO_2	1,517,117	1,495,526	21,591						
C_2H_4	4,825		4,827						
CO	161,887		161,887						
H_2	15,663		15,663						
CH_4	149,191		149,191						
C_2H_6	21,975		21,130	845	845				
N_2	10,226		10,226						
C_3H_6	15,094		955	14,143					
C_3H_8	19,369		582	18,791	21,410				
$i\text{-}C_4H_{10}$	29,548			29,054	262	785	465		
C_4H_8	16,836			16,611					
$n\text{-}C_4H_{10}$	16,424			16,175		15,181	1,953		
C_5^+	207,288			1,568		648	66,365	156,435	43,999
H_2O	16,665								
Wax	30,260								
Totals:	2,232,368	1,495,526	386,052	(97,187)	22,517	16,614	58,783	156,435	43,999

*Including water and wax.
**Alkylate Feed (10,671 lbs. $i\text{-}C_4H_{10}$ Imported).

TABLE 3-13

COMPARISON OF PREDICTED RAW YIELD STRUCTURES
FOR MOBIL AND MITRE ESTIMATES
(LOW-WAX CASE)

Components	MOBIL		MITRE	
	Pounds/Hr	MMBtu/Hr	Pounds/Hr	MMBtu/hr
CO_2	1,517,117	-	1,268,366	-
C_2H_4	4,825	98	4,414	89
CO	161,887	704	130,151	566
H_2	15,663	809	15,961	824
CH_4	149,191	3,207	146,944	3,159
C_2H_6	21,975	449	21,626	442
N_2	10,226	-	5,000	-
H_2O	16,665	-	21,849	-
C_3H_6	15,094	297	13,595	268
C_3H_8	19,369	386	31,450	627
$i-C_4H_{10}$	29,548	580	32,281	634
C_4H_8	16,836	328	15,226	297
$n-C_4H_{10}$	16,425	323	26,530	522
C_5+	207,288	3,978	170,179	3,267
Wax	30,260	575	28,293	538
Totals:	2,232,369	11,734	1,931,865	11,233
Total Efficiency (based on clean syngas, 13,822 Btu/hr	=	0.849	0.813	
Efficiency of synthesized products (based on CO + H_2 input)	=	0.81	0.77	

Table 3-14 shows the comparison of refined products for both the Mobil and MITRE low-wax case. This represents the output of conceptual commercial plants employing the Mobil technology from the Mobil and MITRE estimates. The case shown here is for the low-wax, mixed-output mode where 40 percent of the thermal output is SNG.

Table 3-15 compares the selectivities of the Mobil two-stage systems for the BSU, the Mobil scoping study, and the MITRE estimate. The selectivity obtained from the Koelbel Rheinpreussen pilot plant is shown for comparison. The Mobil scoping study assumes a higher C_5+ selectivity than was actually obtained on the BSU experiments, whereas the MITRE estimate is much closer to the BSU data.

Table 3-16 compares the predicted yields of finished products for both the Mobil and MITRE estimates for a conceptual plant producing an all-liquid output product state. Appendix B, Reference 1 details the computation of these outputs assuming that 61 percent of thermal value of the SNG appears in the liquid products after autothermal reforming.

3.3 High-Wax Case Design Basis

Originally it was intended to use the raw data from Run CT-256-4 as the basis for the high-wax design; however, because of operational problems during the run, which resulted in low syngas conversions, MITRE requested that Mobil provide additional data on which to base the design. Mobil provided the data shown in Table 3-17, together with a simulated breakdown of first and second

TABLE 3-14

COMPARISON OF PREDICTED YIELDS OF REFINED PRODUCTS
FOR MOBIL AND MITRE ESTIMATES OF LOW-WAX CASE
(MIXED-OUTPUT MODE PLANTS)

Product	MOBIL	MMBTU/HR	MITRE	MMBTU/HR
SNG	118.7 MMSCFPD	4,474	114 MMSCFPD	4,296
C_3	3,026 BPSD	443	4,515 BPSD	661
C_4	885 BPSD	147	1,285 BPSD	214
Gasoline*	28,607 BPSD**	5,581	25,283 BPSD**	4,932
Wax	2,400 BPSD	575	2,246 BPSD	538
		11,220		10,641
	(Imported isobutane)	- 210		
		11,010		
Overall Efficiency:		0.58		0.56

*For 10-RVP gasoline, 55% of $n\text{-}C_4H_{10}$ is blended into the C_5+.
**Includes 1,630 BPSD of gasifier naphtha.

TABLE 3-15

SELECTIVITIES FROM SFT/ZSM-5 SYSTEMS

Selectivities Wt. % HC	BSU	Scoping Study	MITRE	Koelbel
CH_4	7.69	7.65	7.46	2.0
C_2H_4	1.06	1.08	1.03	3.6
C_2H_6	3.25	3.08	3.16	1.2
C_3H_6	3.90	3.97	3.78	18.0
C_3H_8	9.03	5.10	8.75	4.6
C_4H_8	4.37	4.43	4.24	3.8
$i\text{-}C_4H_{10}$	9.26	7.78	8.98)	
$n\text{-}C_4H_{10}$	7.61	4.33	7.38)	1.3
C_5+	46.16	54.6	47.40	65.5
Wax	7.06	7.97	7.87	0
Pounds HC Synthesized/hr	0.8	379,660	359,400	860
HC Yield gHC/nM^3 ($CO + H_2$ converted)	215	205.2	192	198

TABLE 3-16

COMPARISON OF PREDICTED YIELDS OF REFINED PRODUCTS
FOR MOBIL AND MITRE ESTIMATES OF LOW-WAX ALL-LIQUID OUTPUT CASE

	MOBIL		MITRE	
	BPSD	MMBtu/hr	BPSD	MMBtu/hr
Gasoline	40,449	7,891*	35,569	6,939
C_3	4,351	637	6,478	948
C_4	1,275	212	1,844	907
Wax	3,452	827	3,223	772
		9,567		8,966
Overall Efficiency	0.49		0.47	

*Mobil gasoline includes imported isobutane equivalent to 302 MMBtu/hr.

TABLE 3-17

LOW METHANE + ETHANE SENSITIVITY CASE
(DATA BASED ON RUN CT-256-4)

	First Stage	Second Stage
Inlet P, MPa	2.87	Cascaded
Inlet T, °C	227(a)	371
Outlet T, °C	258	393(b)
Space Velocity	4.13(c)	1.02(d)
H_2/CO, Molar	0.67	---
Catalyst	FE/Cu/K_2CO_3	ZSM-5 Class
Heat of Reaction, kJ/g-mol (H_2+CO) in SFT Feed	53.46(e)	0.71(b)

(a) Actual gas temperature equals the slurry temperature (258°C) after the first couple of millimeters.
(b) Prorated from base case according to the quantity of hydrocarbons in the second-stage feed.
(c) NL/gFe-hr, prorated from base case assuming that the superficial gas velocity is 90 percent of that for base case (low temperature activity correction).
(d) WHSV based on feed HC, assuming the same contact time as the base case.
(e) Assumed the same as the base case.

stage Fischer-Tropsch products produced per 100 moles of hydrogen and carbon monoxide feed (not shown). Subsequent to this, Mobil has substantiated these conversion levels in an ongoing BSU run. However, it should be noted that sustained high conversions of synthesis gas for long run periods has still to be satisfactorily demonstrated by Mobil in their BSU operations. From the simulated data provided by Mobil, Table 3-18 was developed which shows the first and second stage yield data and corresponding product selectivities for this case, which produces 43 weight percent reactor wax.

The data in Table 3-18 is then scaled by the factor 961.6, since the commercial plant produces 96,160 moles/hour of clean synthesis gas. Figure 3-4 shows the total material balance for the conceptual plant design. Just as in the low-wax gas, the clean gasifier output is fed to the first stage slurry-phase synthesis reactors. The reactor wax is withdrawn from the first stage and sent to the hydrocracker. This section will be detailed later. The remaining effluent passes over the zeolite reactor. The output from this second stage is shown on the right in Figure 3-4.

Just as in the low-wax case, the effluent from the zeolite reactor is sent to the product recovery section of the plant (see Figure 3-3). The result of this is shown in Table 3-19. Stream Number 11 is the diesel fraction of the product and will be blended with the diesel obtained from the wax hydrocracking operation. In

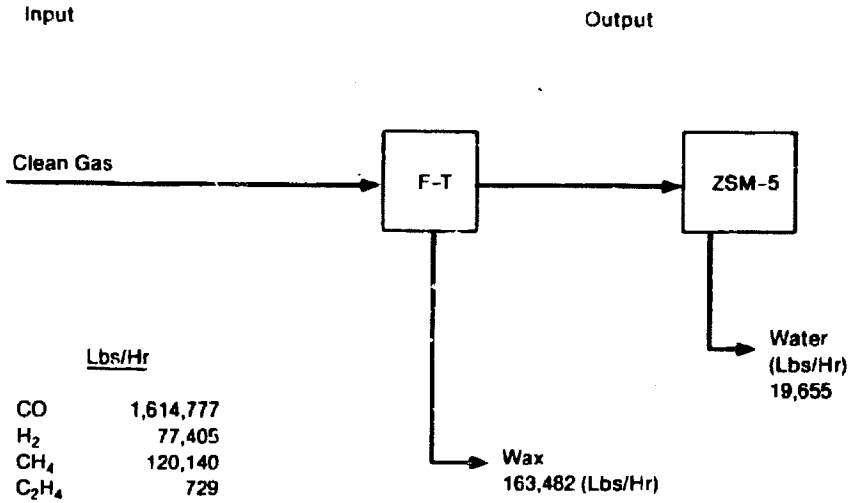
TABLE 3-18

DESIGN BASIS FOR MOBIL HIGH-WAX CASE
(BASED ON RUN CT-256-4)

	FIRST STAGE		SECOND STAGE	
Component	Wt. Percent	Lbs/100 moles H_2 + CO	Wt. Percent	Lbs/100 moles H_2 + CO
Hydrocarbons	22.48	395.20	22.25	392.04
CO_2	66.00	1,160.92	65.94	1,161.86
H_2O	0.81	14.26	1.16	20.44
H_2	1.13	19.81	1.12	19.73
CO	9.54	167.72	9.53	167.92
	99.96	1,757.91	100.00	1,761.99

SELECTIVITIES

Component	Wt. Percent	Lbs/100 moles H_2 + CO	Wt. Percent	Lbs/100 moles H_2 + CO
CH_4	4.23	16.72	4.33	16.97
C_2H_4	2.61	10.31	1.74	6.82
C_2H_6	0.77	3.04	0.83	3.25
C_3H_6	4.04	15.97	1.98	7.76
C_3H_8	0.99	3.91	1.55	6.07
C_4H_8	2.37	9.37	1.56	6.10
$n\text{-}C_4H_{10}$	1.24	4.90	1.31	5.14
$C_5\text{-}C_{15}$	30.56	120.77		
Isobutane			3.36	13.17
$C_5\text{-}C_{11}$			38.85	152.29
Oxygenates	5.62	22.21		
C_{12}^+			1.12	4.39
C_{16}^+	4.54	17.94		
Wax	43.02	170.02	43.37	170.01



Lbs/Hr	
CO	1,614,777
H_2	77,405
CH_4	120,140
C_2H_4	729
C_2H_6	10,270
CO_2	103,840
N_2	5,040
	1,932,201

Total 1,934,280

	From ZSM-5	From Gasifier
CO	161,472	
H_2	18,972	
CO_2	1,117,245	103,840
N_2		5,040
CH_4	16,318	120,140
C_2H_4	6,558	729
C_4H_8	5,866	
C_2H_6	3,125	10,270
C_3H_6	7,462	
C_3H_8	5,837	
$n-C_4H_{10}$	4,943	
$i-C_4H_{10}$	12,664	
C_5-C_{11}	146,442	
$C_{12}+$	4,221	
Totals	1,511,155	240,019

H_2 Conversion = 75%
CO Conversion = 90%
$(H_2 + CO)$ Conversion = 84%

FIGURE 3-4
MATERIAL BALANCE (LBS/HR) FOR HIGH-WAX CASE

TABLE 3-19

PRODUCT RECOVERY MATERIAL BALANCE (POUNDS/HOUR)
HIGH-WAX CASE

	Stream Numbers									
	1 and 2	3	4	5*	6	7	8	9	10	11
CO_2	1,221,085	1,221,085								
C_2H_4	7,289		7,289							
CO	161,472		161,472							
H_2	18,972		18,972							
CH_4	136,458		136,458							
C_2H_6	13,395		13,395							
N_2	5,040		5,040							
C_3H_6	7,462		472	6,990						
C_3H_8	5,837			5,837	5,837					
$i\text{-}C_4H_{10}$	12,664			12,664		639				
C_4H_8	5,866			5,866		3,590				
$n\text{-}C_4H_{10}$	4,943			4,943		4,358	581			
$C_5\text{-}C_{11}$	146,442						21,274	122,489	23,953	
C_{12}^+	4,221									4,221
	1,751,146	1,221,085	343,098	36,300	5,837	8,857	21,855	122,489	23,953	4,221

*Alkylate Feed

the mixed-output mode, Stream Number 4 is sent to combined shift-methanation, where unconverted syngas is converted into synthetic natural gas (SNG).

The large quantity of reactor wax produced in this case must be upgraded to transportation fuels. Dry[4] has reported on the hydrocracking of ARGE wax and claims that with the correct processing severity the wax will hydrocrack readily to produce a product slate consisting of 5-percent C_1-C_4 gases, 15-percent gasoline, and 80-percent high quality diesel. Initial hydrocracking studies performed by Mobil [5] have not yet achieved such a favorable product yield because of excess reaction severity. For the purposes of this conceptual design, we have assumed that an identical hydrocracker product slate to that obtained by Dry with ARGE wax was produced by the Mobil slurry-phase reactor wax.

It is important that this be substantiated by additional hydrocracking studies, as failure to selectively crack this wax with minimal gas make will adversely affect the overall plant product distribution and hence, economics. The quality and characteristics of the Mobil reactor wax may be very different from ARGE wax but insufficient analytical data on the Mobil material are available to date.

Figure 3-5 shows a mass and energy flow schematic of the wax hydrocracker section. Wax still containing about 0.01 weight percent finely divided catalyst is filtered and passed to the hydrocracker. Hydrogen is also added and the estimated hydrogen

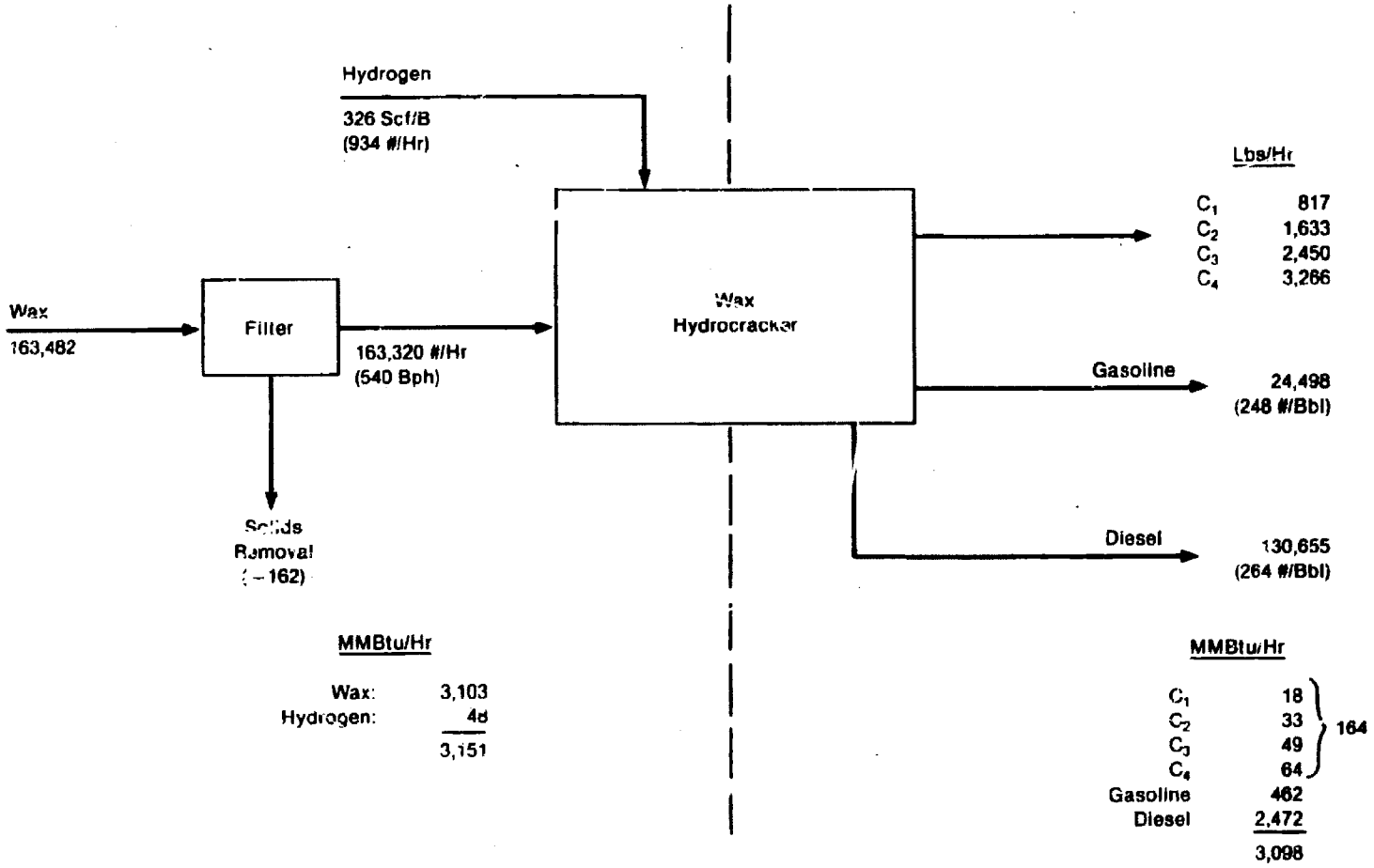


FIGURE 3-5

WAX HYDROCRACKING
MASS AND ENERGY FLOW SCHEMATIC

consumption is 326 SCF/barrel of wax feed. The estimated products from wax hydrocracking are shown on the right in Figure 3-5.

It should be noted that the assumption is made in this design that wax containing this low solids loading can be obtained. Fixed-bed hydrocracking is intolerant of solids in the feedstock and these must be removed to levels of about 200 ppm. Additionally, the low hydrogen consumption of 326 SCF/barrel of wax feedstock has been calculated from theoretical considerations and has not been demonstrated by Mobil in their hydrocracking studies.

Table 3-20 shows the contribution to the product streams from both the zeolite reactor effluent after alkylation and methanation and the wax hydrocracker effluent. The hydrocracker is expected to produce excellent quality diesel fuel[4]; however, the octane rating of the gasoline from the wax hydrocracker is expected to be low (similar in octane number to the raw Fischer-Tropsch product, about 55 RON). Since this gasoline represents about 13 weight percent of the combined gasolines and the average Research + Motor octane number of the zeolitic gasoline is only 86, the combined stream will have an intermediate octane number* of 82. This is too low for sale as high-octane gasoline. The hydrocracked gasoline must be reformed or upgraded in other ways to enhance its octane number. It is suggested that the gasoline stream from the wax

* $\frac{RON + MON}{2}$ = Intermediate octane number.

TABLE 3-20

PRODUCTS FROM HIGH-WAX CASE

	Zeolite Reactor		Wax Hydrocracker	
Product	Lbs/hr	MMBtu/hr	Lbs/hr	MMBtu/hr
SNG	-	4,671	-	51
C_3	5,837	116	2,450	49
C_4	8,587	168	3,266	64
Gasoline	168,297	3,177	24,498	462
Diesel	4,221	80	130,655	2,472
TOTALS		8,212		3,098

TABLE 3-21

OVERALL PREDICTED YIELD STRUCTURE OF REFINED PRODUCTS
FOR MOBIL HIGH-WAX CASE
(MIXED-OUTPUT MODE)

Product	Quantity		MMBtu/hr (LHV)
SNG	112.5	MMSCFPD	4,242
Propanes	1,127	BPSD	165
Butanes	625	BPSD	104
Gasoline*	20,940	BPSD	4,085
Diesel	12,264	BPSD	2,552
			11,148

OVERALL EFFICIENCY (LHV) = 0.59

*Gasoline includes 1,630 BPSD gasifier naphtha + 55 percent of n-butane.

hydrocracker be processed over the second stage zeolite reactor to enhance its octane rating. This has never been attempted and, because of the characteristics of this material, the zeolite may not enhance the octane number and hence, conventional reforming will have to be employed. For the purposes of this design, it has been assumed that the gasoline from hydrocracking has been successfully upgraded at minimal yield loss over the zeolite reactor. If this cannot be demonstrated, then this material will have to be reformed using conventional processes and yield losses will then occur, adversely affecting the overall economics.

Table 3-21 shows the overall predicted product yield structure for a mixed-output plant operating in the high-wax mode using Mobil technology. The SNG output is net of internal plant fuel requirement and hydrogen requirements for wax hydrocracking and gasifier naphtha hydrotreating. For the purposes of the analysis, both gasoline streams have been combined with hydrotreated gasifier naphtha and 55 percent of the butanes to give the overall yield of gasoline.

Table 3-22 shows the overall energy flows for the high-wax case plant, excluding the gasifier naphtha. Comparing the energetics of the Mobil low-wax case to this one, we see that both cases are very similar from the viewpoint of efficiency. For refined products excluding gasifier naphtha, the overall efficiencies for the mixed-output low- and high-wax cases are .56 and .57, respectively.

TABLE 3-22

ENERGY BALANCE HIGH-WAX CASE
(MMBTU/HR LHV)

Total Plant Coal Input = 18,959 MMBtu/hr

Component	Clean Syngas	Raw Products	Refined Products	
CO	7,019	702		
H_2	3,996	979		
CH_4	2,582	2,933	SNG	4,242*
C_2H_4	15	148	Propane	165
C_2H_6	210	273	Butane	232
C_3H_6		147	Gasoline	3,639**
C_3H_8		116	Diesel	2,552
C_4H_8		114		
$i\text{-}C_4H_{10}$		249		
$n\text{-}C_4H_{10}$		97		
$C_5\text{-}C_{11}$		2,812		
C_{12}^+		80		
Wax		3,106		
	13,822	11,756		10,830

*Net of internal plant requirements, i.e. 168 MMBtu/hr naphtha hydrotreating
48 MMBtu/hr wax hydrocracking
264 MMBtu/hr zeolite reactor heating

**Does not include gasifier naphtha.

TABLE 3-23

OVERALL OUTPUTS FROM HIGH-WAX MOBIL ALL-LIQUID CASE

Product	Quantity (BPSD)	MMBTU/hr
Propane	1,571	230
Butane	870	145
Gasoline	28,525	5,565
Diesel	17,082	3,555
		9,495

Overall Efficiency (LHV) = 0.50

Table 3-23 shows the expected outputs and product selectivity for a conceptual commercial plant producing an all-liquid output. The coproduction of gasoline and diesel from this plant appears to be a very attractive option.

Table 3-24 compares the hydrocarbon selectivities for the low- and high-wax cases with the selectivity obtained by Koelbel. Operation in the high-wax mode has enabled the Mobil BSU to match the C_1/C_2 selectivity of Koelbel. Additionally, the Mobil selectivity for C_3 and C_4 hydrocarbons is far superior o that obtained by Koelbel. The production of 18 weight percent propene, for example, in the Koelbel case means that catalytic polymerization and poly-gasoline hydrogenation is required to convert these low molecular weight olefins into gasoline boiling range materials. In the Mobil case, only alkylation of these materials is required. Although Koelbel has extremely good selectivity in the gasoline boiling range, the Mobil selectivity to C_5+ hydrocarbons is even greater (i.e., 65.6 weight percent compared to 83.3 weight percent). Assuming that the reactor wax is an excellent hydrocracker feedstock and can be upgraded to produce 80 weight percent diesel and 15 weight percent gasoline, the additional liquid fuels produced means that over 80 weight percent of the total hydrocarbons synthesized are in the liquid fuels range.

TABLE 3-24

FISCHER-TROPSCH HYDROCARBON SELECTIVITIES

	Run CT-256-4	Simulated Run CT-256-4	Run CT-256-3	Koelbel
Methane	2.7	4.33	7.55	2.0
Ethylene	2.0	1.74	1.64	3.6
Ethane	0.6	0.83	3.13	1.2
Propene	2.9	1.98	8.19	18.0
Propane	0.7	1.55	2.24	4.6
Butenes	2.2	1.56	6.98	3.8
i-Butane	0.2	3.36	0.07	1.3
n-Butane	0.8	1.31	2.12	
C_5-C_{11}	21.7	38.85	30.0	65.5
C_{12}^+ (excl. wax)	20.2	1.12	29.44	
Wax	46.0	43.37	8.91	0

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