BASE CASE II 4.2 PRODUCT YIELDS AND QUALITY

Stream numbers are given below for reference to the material balance sheets in Appendix B and process diagrams in Sub-Section 4.4.

4.2.1 SNG (49)

Quantity	19,023.3	lb-mol/hr
	315.4	Mlb/hr
	173.3	MMSCF/SD

Composition (Only compounds greater than 0.1% are listed; see Appendix B for detailed composition.)

	Percent
Hydrogen	3.8
Methane	89.7
Ethene	1.0
Ethane	2.3
Propene	1.0
Propane	0.1
Carbon dioxide	0.5
Inerts (N ₂ + Ar)	$\frac{1.6}{100.0}$
	100.0

Other

Heat of combustion (HHV)	1,003 Btu/SCF
Carbon monoxide (0.1% max.)	0.07%
Water	0.01%
Sulfur	None

Compatibility Indexes (versus pure methane)

Index	Calculated	<u>Preferable</u>	<u>Objectionable</u>
Lifting, I ₁	0.99	under 1.0	above 1.06
Flash-back, I _f	1.06	under 1.15	above 1.2
Yellow-tip, I _y	0.97	above 1.0	under 0.8

The SNG product is of satisfactory quality and is interchangeable with pure methane. The olefin nature of the Fischer-Tropsch light gases, however, gives rise to a yellow-tip index value slightly below the preferable value. If the olefins prove troublesome in actual tests, an expensive hydrogenation step for olefin saturation could be added.

4.2.2 Gasoline (50)

Quantity 13,580 Bb1/SD 140.9 Mlb/hr

Blending

Properties

Estimated properties and a comparison with unleaded gasoline specifications are presented in Table 4.2.1.

This gasoline meets all specifications. Compared to typical present-day gasolines, it is slightly lower in gravity and contains fewer aromatics.

Heavy polymer gasoline hydrogenation has been added in order to meet the olefin target of 20 vol. % max. Without hydrogenation, the following are estimated:

(Research + Motor)/2 = 88.5Olefin, vol. % = 28

Mobil and industry experience with high olefinic gasolines is limited. Consequently, marketing such a gasoline would require extensive testing and, perhaps, additive package reformulation.

TABLE 4.2.1

COMPARISON OF PRINCIPAL UNLEADED GASOLINE SPECIFICATIONS
WITH ESTIMATED FISCHER-TROPSCH GASOLINE PROPERTIES CASE II

	Estimated F-T Unleaded Gasoline Properties	Specifications
Gravity, ^O API	67.2	
Octane Numbers	01	
Research	91	
Motor	83	82 min.
(Research + Motor)/2	87	87 min.
Volatility		
Reid Vapor Pressure, 1b Distillation, OF	10.0	
IBP	86.5	
10%	108.9	158 max.
30%	137.3	
50%	186.0	170/250 min./max.
70%	249.6	2.0/200 11.21./ 11.021.
90%	335.2	374 max.
EP	420.6	437 max.
	120.0	TOI MAX.
V/L Ratio (=20), OF	@127.3	@140 max.
Sulfur, wt. %	Nil	0.10 max.
Composition, vol. %		
Paraffins	60.5	
Olefins	19.9	20 max. (target)
Naphthenes	3.1	(+
Aromatics	16.5	
Molecular Weight	93.1	

4.2.3 Diesel Fuel (117)

Quantity

2,307 Bbl/SD 25.4 Mlb/hr

Properties

Estimated properties and a comparison with diesel fuel specifications are shown in Table 4.2.2.

This product could be marketed as a premium diesel oil, Grade No. 1-D, for engine service requiring frequent speed and load changes. Its relatively high estimated cloud point, however, could preclude it being marketed in cold weather regions.

4.2.4 Heavy Fuel Oil (118)

Quantity

622 Bb1/SD 7.4 Mlb/hr

Properties

Estimated properties and a comparison with gas turbine fuel oil specifications are shown in Table 4.2.3.

Because of the non-existant sulfur and metals contents, this product could be marketed as a premium gas turbine fuel.

4.2.5 Alcohols (156)

Quantity

2,025 B/SD 510 Mlb/hr

Composition

Composition of the mixed alcohol product is:

	<u>Wt. %</u>
Ethanol	59
I-propanol	14
N-propanol	14
2-butanol	4
I-butanol	1
N-butanol	5
2-pentanol	1
N-pentanol	1
C ₆ plus	1
-0 F	100

The alcohol product is essentially free of acids, aldehydes, ketones and water.

TABLE 4.2.2

COMPARISON OF PRINCIPAL DIESEL FUEL SPECIFICATIONS WITH ESTIMATED FISCHER-TROPSCH DIESEL FUEL PROPERTIES - CASE II

	DIESEL FUEL-	DIESEL FUEL-ASTM D975(1)		: - -
	Grade No. 1-D	Grade No. 2-D	Отве	Estimated F-T Diesel Fuel Dronerties
			70170	110001
Gravity, ^O API Cetane Number, min. (D613 or D976)	- 40	- 40	45(2)	√ 50 √
Volatility))
90% min./max., OF (D86)	-/550	540/640(5)		520
Flash Point, F min. (D93)	100	125		123
Cloud Point, Fr (D2500)	(3)	(3)		10-01
Viscosity, Kin. @ 100°F min./max.	•			01
(D445)	1.4/2.5	2.0/4.3		8
Sulfur, wt. % max. (D129)	0.50	0.50	(4)	None
Corrosion, max. (D130)	No. 3	No. 3		N 1
Carbon Residue on 10% Resid.,))		H
max. (D524)	0.15	0.35		Trace

-99-

1976 Annual Book of ASTM Standards.

Various engine builders' requirements.

£36£6

Varies with marketing region; maps included in ASTM D975. Varies in individual states, some as low as 0.3%. 540/680 90% min./max. proposed but currently not accepted by industry.

TABLE 4.2.3

COMPARISON OF PRINCIPAL FUEL OIL AND GAS TURBINE FUEL OIL SPECIFICATIONS WITH ESTIMATED FISCHER-TROPSCH HEAVY FUEL OIL PROPERTIES - CASE II

Estimated F-T Hvy. Fuel Oil Properties	4. L	150	Trace	Satisfactory	None	Trace 0 0
Gas Turbine F.D. No. 3 - GT ASTM D2880*	ı	130 or Legal	0.03	45	ı	10 n
Fuel Oil No. 5 (Light) ASTM D396*	1	130 or Legal	0.10	150	Lega1	1 1 1 1
Fuel 011	Gravity, OAPI	Volatility Flash Point, ^O F min. (D93) Distillation	Ash, wt. % max. (D482)	Viscosity, SSU at 100°F, min. (D445)	Sulfur, wt. % (D129)	Metals, ppm (wt.) max. Vanadium Sodium + Potassium Calcium Lead

*1976 Annual Book of ASTM Standards.

4.2.6 Butane LPG (139)

Quantity

146 Blb/SD 1.2 Mlb/hr

Properties

Estimated properties and a comparison with LPG specifications are shown in Table 4.2.4.

This product is a satisfactory commercial butane fuel.

4.2.7 Propane LPG (138)

Estimated properties and a comparison with LPG specifications are shown in Table 4.2.4.

This product is a satisfactory commercial propane fuel.

4.2.8 Byproducts

Sulfur (29)

Quantity Impurities 61 T/SD 0.5 wt. %

Anhydrous Ammonia (17)

Quantity

Impurities (mainly water)

Grade

103 T/SD

0.5 wt. % max. agricultural

Excess Power (6,000 volts)

 $7.01 \, MW(e)$

TABLE 4.2.4

COMPARISON OF PRINCIPAL LPG SPECIFICATIONS WITH ESTIMATED FISCHER-TROPSCH LPG PROPERTIES - CASE II

	Commercial Propane ASTM D1835*	Est. F-T C3 LPG Properties	Commercial Butane ASTM D1835*	Est. F-T C4 LPG Properties
Vapor Pressure at 100°F, max., psig (D1267)	208	178	70	37
Volatile Residue Butane and Heavier, max. vol. % (D2163) Pentane and Heavier. max. vol. %	2.5	Ħ	I	i
	•	ı	2.0	- 1
Corrosion, max. (D1838)	No. 1	No. 1	No. 1	No. 1
Sulfur, grains (D2784)	15	None	15	None

*1976 Annual Book of ASTM Standards.

BASE CASE II 4.3 THERMAL EFFICIENCY

Table 4.3.1 is a summary of the overall plant thermal efficiency, which is defined as the combustion heat of the products, byproducts and excess power divided by the combustion heat of the total coal feed. The efficiency has been calculated using both the high and low heating values.

TABLE 4.3.1

FISCHER-TROPSCH CASE II - THERMAL EFFICIENCY

Percent of Input	1 1	34.6 0.9 14.0 2.5 52.8	00.1 00.1 1.0 1.0 1.0 1.0
Total LHV MMBtu/hr	$\frac{18,894}{3} \frac{11}{18,897}$	6,531 162 2,649 480 138 9,984	263 $ 19 $ $ 69 $ $ 10,355$
Low Heating Value (LHV)	12,236Btu/lb 8,610Btu/lb	904.7Btu/SCF 3.514MMBtu/Bbl 3.991MMBtu/Bbl 4.682MMBtu/Bbl 4.994MMBtu/Bbl 5.326MMBtu/Bbl	12,380Btu/lb 3,780Btu/lb 8,020Btu/lb 3,415Btu/kWH
Percent of Input	1 1	36.9 0.9 0.1 14.5 2.6 0.7	1.5 0.1 0.4 0.1 57.8
Total HHV, MMBtu/hr	19,642 3 19,645	7,243 176 2,842 514 10,949	290 19 83 20(2) 11,361
High Heating Value (HHV)	12,720Btu/1b 9,790Btu/1b	1,003.3Btu/SCF 3.815MMBtu/Bbl 4.321MMBtu/Bbl 5.023MMBtu/Bbl 5.345MMBtu/Bbl 5.682MMBtu/Bbl	13,630Btu/lb 3,780Btu/lb 9,693Btu/lb 3,415Btu/kWH
Quantity, Unit/SD	18,530 T	173.26MMSCF 1,107Bbl 146Bbl 13,580Bbl 2,307Bbl 622Bbl	510M1b 61 T 103 T 6.01MW(e)
	Input Coal, DAF Methanol	Output SNG C3 LPG C4 LPG 10 RVP Gasoline Diesel Fuel Hvy. Fuel Oil Sub-Total	Alcohols Sulfur Ammonia Power Total

(1) If LHV of as mined coal used (7,893 Btu/lb), overall LHV thermal efficiency becomes 56.8%.

(2) Direct thermal conversion used.

BASE CASE II 4.4 PROCESS DESCRIPTIONS

The discussions below follow the block flow diagram (BFD) or the process flow diagram (PFD) as noted. These diagrams are placed at the end of the discussion. The gasification, raw gas treating and byproduct recovery units, however, are identical to those in Base Case I; consequently, their PFD's are found in Sub-Section 3.4. Detailed compositions and flows of the numbered streams are found on the material balance sheets in Appendix B.

4.4.1 General (BFD ZO-GEM-6988)

Sized coal is received from the offsite Coal Handling Unit 228 (see Sub-Section 4.5), and is gasified in Gasification Unit 201. A portion of the raw gas generated is converted in Raw Gas Shift Unit 202 to meet the H2/CO ratio requirements of F-T Synthesis Unit 250. The raw gas and shifted gas are cooled in Raw Gas Cooling Unit 203 and Shifted Gas Cooling Unit 204, respectively, before flowing to Gas Purification Unit 205. This unit removes the H2S, CO2 and naphtha from the raw gas. The H2S contained in the purification unit offgas is converted to sulphur in Sulphur Recovery Unit 206. The purified gas (synthesis gas) is sent to F-T Synthesis Unit 250 where it is converted to hydrocarbon products.

The gas liquor condensed in Units 201, 202, 203, 204, and 205 flows to Gas Liquor Separation Unit 207 in which dusty tar and oil are recovered. The gas liquor is further processed in Phenol Recovery Unit 208 and Ammonia Recovery Unit 209 before flowing to Waste Water Treatment Unit 235.

The products from the F-T synthesis are upgraded and recovered in the following units: F-T Product Fractionation Unit 252, F-T Product Hydrotreating Unit 253, Hydrotreated Product Fractionation Unit 254, Catalytic Reforming Unit 255, C5/C6 Isomerization Unit 256, Catalytic Polymerization Unit 257, HF Alkylation Unit 258, Poly Gasoline Hydrogenation Unit 259, Light Ends Recovery Unit 260 and Alcohol Recovery Unit 262. The final products produced in these units are gasoline, diesel fuel oil, heavy fuel oil, n-butane LPG, propane LPG and alcohols.

In addition to the liquid products, SNG is produced in the SNG-upgrading train from the light gases produced in F-T Synthesis Unit 250. This train consists of Hydrocarbon Recovery Unit 210, Methanation Unit 212, where unreacted CO, $\rm H_2$ and hydrocarbons are converted to methane, $\rm CO_2$ Removal Unit 213, and SNG Drying and Compression Unit 214.

The hydrogen required for hydrotreating the F-T synthesis products and the naphtha from gasification is produced from hydrogen containing offgases in Hydrogen Recovery Unit 211 and Hydrogen Purification Unit 261.

4.4.2 Gasification Area (BFD ZO-GEM-6988)

Because the study basis calls for the same synthesis gas production in both base cases, the units in the coal gasification area, including gas treating and product recovery, are identical.

Unit PFD ZO-GEM

201-Gasification 6895 & 6896 (In Base Case I, Lock Gas Compressor 101-C-41 recompresses the syngas compressor losses. In Base Case II, these losses have been neglected.)

202-Raw Gas Shift	6897
203-Raw Gas Cooling	6898
204-Shifted Gas Cooling	6899
205-Gas Purification	6900
206-Sulfur Recovery	6901
207-Gas Liquor Separation	6902
208-Phenol Recovery	6903
209-Ammonia Recovery	6904

Consequently, descriptions of these units are not repeated in this sub-section.

4.4.3 Hydrocarbon Recovery Unit 210 (PFD ZO-GEM-6973)

Purpose of the Unit is to remove and recover heavy hydrocarbons from the Fischer-Tropsch synthesis purge gas to meet methanation feedstock specifications.

Technology Used

The commercial process used is a low temperature heptane wash. This process is conventionally used to handle a gas containing $\rm CO_2$ because the operating temperature is high enough to prevent freezing of the $\rm CO_2$.

Process Description

The feedgas is cooled against the product gas and by refrigeration in 210-E-01, 02, and 03 to condense the bulk of the higher hydrocarbons before being charged to Wash Absorber 210-D-01. To prevent freezing of water, a small alcohol stream is injected into the feedgas. In the absorber, the feed gas flows counter-currently to the heptane solvent which is pumped from Heptane Regenerator 210-D-02 through Heat Exchanger 210-E-05 and Chiller 210-E-04 to the top of the absorber.

The rich heptane leaving the absorber is fed to the heptane regenerator in which the absorbed hydrocarbons are removed by fractionation. The regenerator overhead product vapor is compressed by 210-C-01, cooled and combined with the liquid stream which is condensed from the feed gas in front of the absorber. The combined stream is sent to F-T Product Fractionation Unit 252.

The absorber overhead product gas flows to Methanation Unit 212.

4.4.4 H2 Recovery Unit 211 (PFD ZO-GEM-6974)

Purpose of the Unit is to recover hydrogen for use in the plant hydrogenation/hydrotreating units. The feedstock is a slip stream of the product gas from hydrocarbon recovery.

Technology Used

Because of the relatively high ${\rm CO_2}$ content of the feedgas, the Pressure Swing Process of Union Carbide Corp. is used.

Process Description

The unit consists of four parallel pressure-swing absorbers, 211-D-01, with one onstream and the other three undergoing regeneration. During operation, essentially all of the non-hydrogen components and a portion of the hydrogen are absorbed. The remaining hydrogen leaves the absorber at a purity of over 98%.

Regeneration is by pressure reduction in 3-stages with the final pressure being nearly atmospheric. The system is controlled automatically by motor values. An absorption/ regeneration cycle requires several minutes.

The desorbed gases, called pressure-swing offgases, are recompressed by Compressor 211-C-01 and returned to the SNG upgrading train as feed to Methanation Unit 212. Gas Holder 211-F-01, on the suction side of the compressor, is required for buffering the non-static, pressure-swing

offgas flow from the regenerating absorbers.

For clarity purposes, the hydrogen-source streams and the hydrogen-feed streams are shown as part of the PFD for Units 211 and 251. Hydrogen compressors 211-C-03 and 04 are also included.

4.4.5 Methanation Unit 212 (PFD-ZO-GEM-6975)

Purpose of the Unit is the production of SNG meeting the specifications for interchangeability with existing pipeline gases. In addition, the CO content must be lowered to less than 0.1%.

Technology Used

The Lurgi Methanation Process is used. (For addition comments, see Paragraph 3.4.13.)

Process Description

The feedgas is the purge gas from F-T Synthesis Unit 250, from which the bulk of the higher hydrocarbons has been removed in Hydrocarbon Recovery Unit 210 in order to prevent fouling of the methanation catalyst.

The methanation unit consists of two down-flow, fixed-bed reactors in series. The feedgas is heated in 212-E-03, 04, and 05 against the second reactor, 212-D-02, product. Steam is injected in the feedgas, and the gas is also diluted with a portion of the methanated gas from the first reactor, 212-D-01. The dilution gas is compressed by Recycle Compressor 212-C-01, after having been cooled by 212-E-01 and 02. MP steam is generated in 212-E-01.

The net reactor effluent from the first reactor flows to the second, or clean-up, reactor in which final methanation takes place. The clean-up reactor effluent is heat exchanged against the gas feed and cooled in Exchangers 212-E-06 and 07.

Process water condensed from the reactor effluent stream is collected and routed to BFW preparation Unit 231.

The methanated gas leaves the unit for further treating CO₂ Removal Unit 213.

4.4.6 <u>CO₂ Removal Unit 213</u> (PFD ZO-GEM-6976)

Purpose of the Unit is to lower the CO₂ content in the SNG to about 0.5%, thereby improving its quality.

Technology Used

The Amine Guard Process of Union Carbide Corp. is used. (For additional comments, see Paragraph 3.4.14.)

Process Description

The Methanation Unit 212 product gas and the light gases from F-T Product Fractionation Unit 252 are charged to Absorber 213-D-01, in which the CO₂ is removed by a countercurrent stream of lean MEA solution. In the top of the absorber, the gas is scrubbed with a small flow of BFW to recover trace amounts of MEA solution. The purified gas then flows to SNG Drying and Compression Unit 214.

The absorber bottoms product (rich MEA solution) is expanded after heat exchange in 213-E-01 into MEA Regenerator 213-D-02, where the CO₂ and other co-absorbed compounds are stripped from the MEA solution. The steam in the regenerator overhead is condensed in Condensers 213-E-04 and 05, and the remaining offgases are sent to Boiler Unit 222 for incineration. The steam condensate is refluxed to the top of the regeneration. The lean solution from the bottom of the regenerator is pumped back to Absorber 213-D-01 after being cooled in 213-E-01, 02 and 03.

4.4.7 SNG Drying and Compression Unit 214 (PFD ZO-GEM-6976)

Purpose of the Unit is to dry the wet SNG to a water content of 4 lb/MMSCF and to compress the dried SNG for delivery into the SNG pipeline system.

Technology Used

The TEG Wash Process, a commercial process for drying natural gas, is used.

Process Description

The drying agent is a mixture of triethylene glycol (TEG) and other ethylene glycols.

The SNG is contacted countercurrently with lean TEG in Water Absorber 214-D-01. The water-rich TEG flows from the absorber to TEG Regenerator 214-D-02 which is heated by fuel gas. The steam stripped from the TEG is discharged to the atmosphere. The small reflux stream required is condensed within the vent tube by air cooling.

The regenerated TEG is stored in 214-F-01, where it is cooled by the rich TEG before being pumped into the top of Water Absorber 214-D-01.

The dried SNG is compressed by 214-C-01 for delivery into the SNG pipeline system.

4.4.8 Fischer-Tropsch Synthesis Unit 250 (PFD ZO-GEM-6977)

Purpose of the Unit is to synthesize hydrocarbons by reacting hydrogen and carbon monoxide.

Technology Used

Since the early 20's when Fischer and Tropsch produced higher hydrocarbons from carbon monoxide and hydrogen, the amount of research and development in the field of carbon monoxide hydrogenation has been overwhelming. Today, this chemistry can produce a full range of petrochemical and oil products, including methane (methanation), methanol, and liquid hydrocarbons and waxes (Fischer-Tropsch). Before 1940, commercial Fischer-Tropsch plants were operating in Germany, France and Japan. Low price crude oil after World War II precluded any further commercial use of F-T technology, the exception being Sasol in Sasolburg, South Africa. This plant, completed in 1955, is still in operation (Sasol I) and a large expansion is currently in progress (Sasol II). It is the Sasol technology, as reported in the literature, which is the technical basis for Unit 250 development.

Although a typical F-T product is a complicated mixture, the following overall equations illustrate the process:

nCO +
$$2nH_2$$
 (-CH₂-)n + nH₂O hydrocarbon

2nCO + nH_2 (-CH₂-)n + nCO₂ hydrocarbon

and linkage water gas shift reaction
$$CO + H_2O \longrightarrow H_2 + CO_2$$

These equations do not indicate the reaction mechanism, but they do show the stoichiometric relationship between reactants and products. Except for the water gas shift reaction, all reactions are highly exothermic. The F-T product includes paraffins, mono-olefins, aromatics, alcohols, aldehydes, ketones and fatty acids with carbon numbers from 1 through 35+. Small amounts of diolefins and esters can also be produced. Branching does occur but it is predominantly a single-methyl branched structure. Yield selectivity and composition is highly dependent upon the catalyst, reaction conditions and reactor type.

Commercial catalysts include cobalt (fixed-bed) and iron (fixed-and fluid-bed.) Both are promoted for improved activity and selectivity. Operating conditions range from 200 to 325°C and from atmospheric to 25 atm pressure, depending upon products desired, catalyst and reactor design. For example, conditions for the Sasol I medium pressure units are reported to be (15):

Type	Fixed-Bed	<u>Fluid-Bed</u>
Catalyst Base	Fe	Fe
Temperature, ^O C	220-255	320-330
Pressure, psig	360	330

Although iron is the base for both units, catalyst preparation and formulation are entirely different and very specific for each unit type.

The principal problem in designing the reactor is heat removal. Fixed-bed reactor designs are some form of a heat exchanger with catalyst being cooled by boiling water or circulating oil. Fluid-bed reactors include internal tube bundles for reaction heat removal.

As stated previously, Unit 250 is based on Sasol-type fluid-bed technology, derived mainly from references cited which include both Sasol articles and those reporting on Sasol operation. The projected commercial fluid-bed process design conditions and yields are as follows:

1. Feed Ratio $H_2/(2CO + 3CO_2) = 1.03$ Ratio is critical.(9) (12)

2. Basic yields (7) (8)

	<u>C_atoms</u>	H atoms*	H ₂ O atoms*	
C ₁ C ₂ = C ₂ C ₃ = C ₃ C ₄ = C ₄ C ₅ plus light oil	10	40.00	-	
$C_2^+=$	4	8.00	_	
C2	6	18.00	-	
C3=	12	24.00	_	
Co	2	5.33		
C ₄ =		16.00	-	
C.	8 1 8	2.50		
C_{π}^{4} plus	8	16.50	_	
light oil	35	69.30	1.25	
heavy oil	7	13.84	0.08	
alcohols	6	11.28	2.70	
acids	1	0.21	0.90	
20240	100	224.96	4.93	
CO + 100	H ₂ 112.48 100.00	HC, Alc & A $H_2O = 4.93$ C = 100	Acid + H ₂ O 100-4.9	3 lb-mol
	100.00	$H_2 = 112.4$	18	
100 +	212.48	217.41	+ 95.07	lb-mol

^{*}Estimated by MRDC.

3. Yields adjusted by MRDC to obtain 85.0% conversion of (CO + $\rm H_2$) (8)

CO:
$$17,806.5 \text{ lb-mol/hr reacted} = 96.25\% \text{ conversion}$$
H₂: $\frac{37,857.6}{55,664.1} \text{ lb-mol/hr reacted} = 80.57\% \text{ conversion}$
conversion

A detailed yield breakdown is presented in Table 4.4.1.

TABLE 4.4.1

FISCHER-TROPSCH CONVERSION UNIT 250 PRODUCT COMPOSITION

Total, 1b-mol/hr		9,337.4	380.6	745.3	377.6	22.7	163.2	9 00	95.3	37.2	101.4	139.4	6.60	44.6	52.5	21.8	7.07	. o.	9.3	60	- ·	N C	6.00	463.3	78.	
Total, lb/hr	8,658.2 136,871.1 13,542.8	,824.	10,676.0 24,588.6	361.	,486. ,181.	1,273.1				4,812.4	9,837.		13 345 0	7,367	9,812.9	4,604.6	2.185.0	1,707.9	2,944.1	2,199.8	1,424.1	366.7	7 T	786	110.	958,012.8
From Heavy Oil (4), lb/hr													527.7	627.4	1	1,627.1	185	,707	,944	2,199.8	1,0	•	~			17,181.0
From Light Oil (3),1b/hr			40.2	-		134.1		-	4,337.4	1,734.9	8	,329.	343C	6,740.	812.	-	. 400,									89,397.0
From C ₅ Plus (2), 1b/hr							990,	922	684	1,473.0	,013															21,196.0
From Reaction, 1b/hr		843	16,219.0	262 285	036	$\frac{139}{612}$	·	(2)	21,196.0				(3)	89,397.0					3	0.181,71				23,744.0	301,186.1	571,297. .8)
From Feed Gas, lb/hr	658 871 542		589.0 8,329.4																					42.0		386,715.1 (958,012
Syn Gas Feed, 1b/hr	8,658.2 127,629.0 518,185.0	199,858.4	8,329.4																					42.0		958,012.8
Đ.	28.02 44.01 28.01	4 4	30.07	42.08	56.10	58,12	70, 13		84.16	86.17	97	197/199	_	165/163	107	238/232		288	315	38.0 08.0	409	440	510	51.34	18,016	
Component		,,,,,,									•												1,000 Plus			-

(1) Yields reflect shift equation equilibrium.

- 4. Light and heavy oil carbon atom distribution and distillation, alcohol yield breakdown, and acid yield breakdown are from Reference 7.
- 5. Reactor design parameters used are:
 - Heat of reaction (MRDC estimate): 4,550 Btu/lb total product
 - Fresh feed charge: 207 MNm³/hr per reactor.

The literature, (10) & (14), refers to a second generation fluid-bed reactor being from 2 to 3 times the size of Sasol I. Reference 8 used a Sasol I reactor scale-up of 2 in their study. Using Reference 8 as the basis, the above charge rate per reactor represents a scale-up of 2.1. Five reactors are employed with one being a spare.

- Recycle mole ratio (15): 2/1
- Catalyst fill (MRDC estimate from (9) (12)): 335 metric tons per reactor.
- Operating conditions (7)
 vapor feed temperature:
 catalyst and vapor outlet temperature:
 vapor outlet pressure:

 160°C
 340°C
 340°C
 300 psia
- Catalyst life (7) (8): 50 days

Process Description

The synthesis gas from Purification Unit 205 and the recycle gas are compressed together in Compressor 250-C-01, heat exchanged against a portion of the reactor effluent in Exchanger 250-E-01 and charged to the fluid-bed Reactor 250-D-01. After mixing with the circulating hot Fe catalyst, reaction takes place as the mixture flows up the reactor through tube bundles in which oil is pumped (250-G-01) for heat removal (temperature control). At the top of the reactor, the mixture enters a large vessel in which cyclones are installed for iron/vapor separation. The hot oil is circulated to Steam Generator 250-E-02 where 200 psig steam is produced.

Because of the expected fouling nature of the reactor effluent, it is washed and cooled from 645°F to 340°F in Effluent Wash Tower 250-D-02 by a recycle stream from the bottoms of Vapor Cold Wash Tower 250-D-03. A relatively clean, hot stream is withdrawn from Effluent Wash Tower 250-D-02 for cooling. Its heat is used for heating the reactor vapor feed (250-E-01), boiler feed water heating (250-E-06) and LP steam generation (250-E-07 and 08). A hot heavy oil is withdrawn from the bottom and sent to Fractionation Unit 252.

The overhead vapor is cooled in BFW Exchanger 250-E-03 and Condensers 250-E-04 and 05. It is then water washed in Wash Tower 250-D-03. The overhead vapor is split into recycle and purge gas streams. The latter is sent to Hydrocarbon Recovery Unit 210. The condensed liquid is also split into 2 streams: cold recycle to Tower 250-E-02 and light oil product to Wash Tower 250-D-04 for final water washing. The light oil is sent to Fractionation Unit 252. The used wash water, containing the alcohols and acids from the Fischer-Tropsch reaction, flows to Alcohol Recovery Unit 262.

4.4.9 Naphtha Hydrotreating Unit 251 (ZO-GEM-6974)

Purpose of the Unit is yield a clean, saturated stabilized naphtha for gasoline pool blending from the raw gasifier naphtha.

Technology Used

See Paragraph 3.4.17.

Process Description

Identical to Unit 151. See Paragraph 3.4.17.

4.4.10 F-T Product Fractionation Unit 252 (ZO-GEM-6978)

Purpose of the Unit is to separate the F-T reactor product into light gases, feedstocks for the polymerization and hydrogenation units and a 850+ residuum for boiler fuel.

Technology Used

Because of the uncertainity as to the effect of steam on the remaining alcohols and acids, a 4-tower, dry system is used.

Process Description

The heavy oil is heated in Furnace 252-B-01, flashed in Drum 252-F-01, and charged to Vacuum Tower 252-D-01. Vacuum is maintained by 252-C-01. The tower has an upper pump-around system. The overhead vapors and excess pump-around liquid are condensed/cooled in Condenser 252-E-03 and pumped (252-G-15) to the top of Absorber/Deethanizer 252-D-02. Vacuum residue (bottoms) is pumped (252-G-03) to Boiler Unit 222.

Feed to Absorber Deethanizer 252-D-02 consists of (1) light oil from Unit 250, (2) hydrocarbons recovered in Unit 210, (3) vacuum tower overhead, and (4) lean oil from Naphtha Splitter 252-D-04. The hydrocarbon stream from Unit 210 is first flashed in Drum 252-F-03. The absorber deethanizer has an upper and middle pump-around systems. The light gases are split into a fuel gas stream and a feed stream to CO₂ Removal Unit 213 in the SNG train. The deethanizer bottoms are sent to Debutanizer 252-D-03.

In 252-D-03, the propene/butene feed for Polymerization Unit 257 is obtained. The debutanizer uses a fired reboiler, 252-B-02.

The debutanizer bottoms, after cooling in Cooler 212-E-11, is charged to Splitter 252-D-04, in which naphtha is removed to obtain a heavier lean oil for recycling to Absorber Deethanizer 252-D-02. The tower bottoms (lean oil) and the overhead naphtha are recombined to become the feedstock for Hydrogenation Unit 253. The naphtha splitter also uses a fired reboiler, 252-B-03.

4.4.11 F.T. Product Hydrotreating Unit 253 (ZO-GEM-6979)

Purpose of the Unit is to saturate the olefins and to destroy the remaining alcohols and acids.

Technology Used

See Paragraph 3.4.17.

Process Description

The feed is pumped to reactor operating pressure (253-G-01), mixed with part of the hydrogen feed, heat exchanged against the reactor effluent in Exchanger 253-E-01, and finally heated to reactor operating temperature in Heater 253-B-01. Because of the high hydrogen consumption, Reactor 253-D-01 consists of multi-beds using a cold hydrogen quench for temperature A two-stage flash system is used: High Temp. Flash Drum 253-F-01 and Low Temp. Flash Drum 253-F-02. Liquid products are combined to become feed to Fractionation Unit 254. The hydrogen-rich gases from Drum 253-F-02 are split into hydrogen recycle and hydrogen feed for Poly Gasoline Hydrogenation Unit 259. The hydrogen recycle is compressed in Compressor 253-C-01, and then mixed with the make-up hydrogen. Reaction water collected in the low temperature drum is sent to Waste Water Treatment Unit 235.

Regeneration facilities for the hydrotreating catalyst are provided.

4.4.12 Hydrotreater Product Fractionation Unit 254 (ZO-GEM-6979)

Purpose of the Unit is to separate the hydrotreated product into a pentane/hexane stream for isomerization, a C7/380 naphtha for reforming, a diesel oil product and a heavy fuel oil product.

Technology Used

A conventional 3-tower system is used.

Process Description

After heating in Heater 254-B-O1, the hydrotreater product is charged to Main Fractionator 254-D-O1, in which stripping steam is introduced at the bottom. The heavy fuel oil product is withdrawn from the bottom and after cooling sent to storage. A small amount of the heavy fuel oil, Stream 173.2, has been used in the final adjustment of the plant fuel balance. A side-cut is withdrawn to Steam Stripper 254-D-O2 from which the diesel oil product, after cooling, is pumped to storage.

The light gases, butanes, pentanes/hexanes, naphtha and steam in the overhead product are cooled in Condensers 254-E-01 and 02, and separated in Reflux Drum 254-F-01. Light gases become a feed to Light Ends Recovery Unit 260. Water is pumped (254-G-09) to Waste Water Treatment Unit 235. The hydrocarbon liquid is split into reflux for the main fractionator and feed for Debutanizer 254-D-03.

In the debutanizer, essentially all the butanes are recovered and sent to Light Ends Unit 260. The debutanizer bottoms are charged to Naphtha Splitter 254-D-04. In the splitter, the pentanes and hexanes are fractionated from the heavy naphtha, or reformer charge and after cooling pumped (254-G-07) to Isomerization Unit 256. The cooled heavy naphtha is pumped (254-G-08) to Reforming Unit 255.

4.4.13 Catalytic Reforming Unit 255 (ZO-GEM-6980)

Purpose of the Unit is to increase the anti-knock quality of the $C_7/380$ naphtha.

Technology Used

Since its commercial introduction in 1950, catalytic reforming with platinum-based catalysts has become the major process for naphtha octane improvement (and aromatics production) in the petroleum industry. Reactions include: (1) dehydrogenation of naphthenes, (2) cyclization of straight-chain paraffins and subsequent dehydrogenation, (3) isomerization of paraffins and cyclopentane derivatives and (4) hydrocracking of paraffins and naphthenes. The formation of aromatics is the principal objective.

Catalytic reforming is carried out over a wide range of reaction conditions, the most important being pressure. Other variables include recycle gas rate, temperature, space velocity and catalyst particle size. Thermodynamically, dehydrogenation is favored by low pressure and high temperatures. These conditions, however, also favor the formation of coke. Fortunately, coke formation can be substantially suppressed by operating in an atmosphere of hydrogen without significant retardation of the dehydrogenation reactions. Typical reactor conditions are:

Pressure, psig 100-700
Recycle gas, SCF/Bbl 2,500-10,000
Temperature, °F 850-1,000
Space velocity, wt/hr/wt 1-3

In recent years, bimetallic catalysts - platinum plus other metal promotors, such as rhenium - have been commercialized. Their improved selectivity and activity permit reforming at lower pressures and higher severities, without shortening regeneration cycle times, than when using the previous standard platinum-on-alumina catalyst.

The principal problem in the design of catalytic reformers is heat balance. Reactions which produce aromatics are very endothermic. Although the exothermic hydrocracking reactions are partially offsetting, large amounts of heat must be supplied to the reaction zone. In fixed-bed units, the heat is supplied by employing multiple reactors in series with intermediate reheating of the reactants. As conditions dictate, a unit may be designed to operate either in a cyclic-or semi-regenerative mode of operation.

Most feedstocks are hydrotreated first to remove arsenic, sulfur and nitrogen compounds. Otherwise, these materials would poison the platinum catalyst. The cost of hydrotreating is easily justified by the extension of the reforming catalyst life.

Commercial processes are licensed by IFP, UOP Process, Houdry, Exxon, Chevron Research and Standard Oil (Indiana).

Process Description

The naphtha feed is pumped (255-G-04) to reactor operating pressure, mixed with the hydrogen-rich recycle gas, heat exchanged against Reactor 255-D-03 effluent in Exchanger 255-E-01 and heated to reactor operating temperature in Heater 255-B-01. The naphtha/hydrogen mixture then flows through three reactors in series, 255-D-01, 02 and 03, and is reheated before the second and third reactors in Heaters 255-B-02 and 03.

The third reactor effluent is cooled in 255-01, 02 and 03 and flashed in Drum 255-F-01. The hydrogen-rich overhead is split into a recycle gas stream and a feed stream to H₂ Purification Unit 261. The bottoms are pumped (255-G-03) to Stabilizer 255-D-04 for light ends fractionation. The butanes and lighter are sent to Light Ends Unit 260. After cooling, the stabilized reformate is sent to Gasoline Blending Unit 270.

Off-stream regeneration facilities are provided.

4.4.14 <u>C₅/C₆ Isomerization Unit 256</u> (ZO-GEM-6981)

Purpose of the Unit is to increase the anti-knock quality of the pentanes and hexanes. Besides raising the pool octane, increasing the octane of the lighter gasoline constituents improves the octane balance between the front and back ends of the gasoline blend.

Technology Used

The first commercial isomerization units for the improvement of motor gasoline were announced in 1957. Isomerization requires the use of a catalyst. There is little heat evolved, and the reaction is limited by equilibrium and rate considerations. An economic balance is made between higher branched-chain ratios at low temperatures and higher reaction rates at high temperatures. Side reactions also must be considered in the selection of conditions.

Platinum-containing catalysts are favored in current commercial processes. They are promoted by the injection of trace amounts of organic chloride. The addition of a small amount of hydrogen suppresses the polymerization of the traces of olefins formed during the isomerization reaction and the formation of coke during hydrocracking reactions. Specifications for feedstock impurities, e.g., sulfur, water, benzene and C7's, vary considerably between the commercial processes. Licensors, however, have in recent years improved significantly impurity tolerances. Although operating conditions chosen generally allow a catalyst life of two or more years, should accidental deactivation occur, the catalyst can be easily regenerated and reactivated to full activity.

Typical reaction conditions are:

Temperature, OF	250-550
Pressure, psig	200-500
Space velocity, vol/hr/vol	1-5
H ₂ /hydorcarbon mole ratio	0.5 - 4

Processing conditions are generally milder for butane isomerization than for pentane or hexane isomerization.

Commercial processes are licensed by BP Trading, Shell Research and UOP Process.

Process Description

To maximize the octane improvement, Isomerization Unit 256 includes n-pentane recycling. The C_5/C_6 product from Unit 254 and the pentane products from isomerization are fed to Deisopentanizer 256-D-01. The overhead product, pentane isomerate, also contains the butanes and isopentane in the fresh feed and from 3 to 5 vol. % of n-pentane. After cooling, it is sent to Gasoline Blending Unit 270.

The n-pentane/hexane bottoms are mixed with recycle and make-up hydrogen, heated via Exchanger 256-D-04 and Heater 256-D-01 and passed over the catalyst in Reactor 256-D-02. The reactor effluent is cooled and flashed in Separator 256-F-02. A hydrogen-rich offgas is obtained for recycling via Compressor 256-G-01 and for hydrogen recovery in Unit 211.

The separator liquid is sent to Stabilizer 256-D-03 where the butanes and lighter are fractionated. The stabilizer offgases from Reflux Drum 256-F-03 after caustic washing are sent to H₂ Purification Unit 261, and the excess reflux to Light Ends Recovery Unit 260.

The stabilizer bottoms are charged to Depentanizer 256-D-04. The overhead product is pumped (256-G-04) to the deisopentanizer for recovery of the recycle n-pentane The tower bottoms, hexane isomerate, after cooling, are sent to Gasoline Blending Unit 270.

4.4.15 Catalytic Polymerization Unit 257 (ZO-GEM-6982)

Purpose of the Unit is to polymerize the propene/butene mixture from the Fischer-Tropsch reaction into higher molecular weight compounds which are suitable for gasoline blending.

Technology Used

Catalytic polymerization has been a commercial process since about 1934 for the conversion of C₃ and C₄ olefins into a higher molecular weight poly gasoline. With a propene feed, trimers predominate and with a butene feed, dimers are the major products. Since the advent of catalytic reforming yielding a source of iso-butane, however, polymerization has generally been replaced by alkylation.

Olefin polymerization is catalyzed by acids and conversions are 85% or better. There is a large exothermic heat of reaction - about 400 Btu/lb of butene and about 670 Btu/lb of propene -, and a recycle stream is often used for temperature control. Commercial catalysts are mainly phosphoric acid on solids, such as kieselguhr and quartz chips.

The water content of the feed is critical. Optimum concentration, however, differs with the catalyst type, reactor operating conditions and feed composition. The olefin feed can be either "dried", saturated with water at a controlled temperature, or mixed with injected water.

The principal reactor design problem is temperature control. Multi-beds with liquid quench or tubular heat exchanger reactors generating steam are used. Typical operating conditions are:

Temperature, ${}^{O}F$: 300 - 425 Pressure, psig: 400 - 1,500

Space velocity,

Gal/hr/lb; 0.1 - 0.5

UOP Process and Chevron Research offer processes for licensing.

Process Description

The cat poly feed is pumped (257-G-01) to water saturation pressure and saturated in Water Settler 257-F-01. Because of the high concentration of olefins, only a portion of the fresh feed is mixed with the low olefin containing recycle stream, heated to reaction temperature in Exchanger 257-E-01 and Heater 257-E-02, and charged to the inlet of Reactor 257-D-01. The remaining cool fresh feed and, if needed, recycle are used as a quench for interbed cooling.

After passing through Acid K.O. Drum 257-F-02 and Heat Exchanger 257-E-01, the reactor effluent is split into the recycle stream and the feed for Debutanizer 257-D-02. The overhead product, consisting of unreacted olefins, iso-butane and inert propane and n-butane, is cooled and pumped to Alkylation Unit 258. The poly gasoline (bottoms) is sent to Splitter 257-D-03, where it is separated at the C9 - C10 boiling range. The light poly gasoline is pumped (257-G-03) to Gasoline Blending Unit 270 and the heavy poly gasoline is pumped (257-G-04) to Hydrogenation Unit 259.

4.4.16 H.F. Alkylation Unit 258 (ZO-GEM-6982)

Purpose of the Unit is to increase the gasoline yield by the catalytic alkylation of iso-butane and unpolymerized C₃ and C₄ olefins.

Technology Used

See Paragraph 3.4.19.

Process Description

Except for an additional iso-butane-rich feed stream, identical to H.F. Alkylation Unit 153. See Paragraph 3.4.19.

4.4.17 Poly Gasoline Hydrogenation Unit 259 (ZO-GEM-6983)

Purpose of the Unit is to saturate the olefins in the heavy cat poly gasoline.

The olefin target concentration for the 10 RVP gasoline product is 20 vol. % maximum. To meet this specification, the poly gasoline is split and the heavy gasoline is hydrogenated. Preliminary gasoline blending indicated that the Cg and higher olefins should be hydrogenated and the unit has been sized accordingly. Final blending results, however, show that Cg olefin hydrogenation is not necessary. Consequently, Unit 259 is sized conservatively.

Technology Used

See Paragraph 3.4.17.

Process Description

The heavy cat poly gasoline after mixing with the make-up/recycle hydrogen is heated via the reactor effluent in Exchanger 259-E-01 and brought-up to the operating temperature by Heater 259-B-01. Reactor 259-D-01 uses multi-beds with hydrogen quench for temperature control. The effluent is cooled in Coolers 259-E-02 and 03, and flashed in Drum 259-F-01. The overhead is split into recycle and offgas streams.

The bottoms liquid flows to Stabilizer 259-D-02. After cooling the stabilizer offgases are combined with the offgases from Flash Drum 259-F-01 and sent to H₂ Purification Unit 261. The cooled stabilized heavy gasoline is sent to Gasoline Blending Unit 270.

Catalyst regeneration facilities are provided.

4.4.18 Light Ends Recovery Unit 260 (ZO-GEM-6980)

Purpose of the Unit is to separate the light gasoline and iso-butane from the hydrocarbon-rich offgases.

Process Description

Offgas streams from Units 254, 255 and 256 are first flashed in Drum 260-F-02. The overhead vapors are compressed (260-C-01) and the liquid is pumped (260-G-01) to the operating pressure of Deethanizer 260-D-01.

The low-pressure offgas from Unit 254 is first compressed and then flashed with the offgas from Unit 261 in Drum 260-F-01. The drum liquid is charged to Deethanizer 260-D-01.

The deethanizer overhead is combined with Drum 260-F-01 overhead and Stabilizer 255-D-04 uncondensed gases and sent to the fuel gas header. The feed to Debutanizer 260-D-02 is the deethanizer bottoms. In the debutanizer, the additional iso-butane feed for Unit 258 is fractionated from the light gasoline which is sent to Gasoline Blending Unit 270.

4.4.19 H₂ Purification Unit 261 (ZO-GEM-6984)

Purpose of the Unit is to obtain from the hydrogen-rich offgases a hydrogen make-up stream of 90% purity.

Technology Used

Commercial cryogenic technology, such as offered by Linde Div. of Union Carbide Corp., is used.

Process Description

Two of the three feed streams require compressing (261-C-01 and 02) before charging to the system. The combined feed is first cooled in Cooler 261-E-01 by the +32°F refrigerent from Refrigeration Unit 241 and flashed in Drum 261-F-01 for heavy hydrocarbon and water removal. The gases then pass through the Molsieve Section 261-D-01 for final drying and CO₂ removal. In Cold Box Section 261-D-02, the make-up hydrogen is recovered and sent to Unit 211 for final compression. The cold box hydrocarbon gases are compressed in Compressor 261-C-03 and mixed with the liquids separated in Flash Drum 261-F-01. The resultant mixture is a feed for Light Ends Recovery Unit 260.

4.4.20 Alcohol Recovery Unit 262 (ZO-GEM-6985)

Purpose of the Unit is to prepare a marketable alcohol mixture product and to recover methanol for make-up to Rectisol Unit 205.

Technology Used

Because of the limited alcohol information available to MRDC, the design of this unit is general in nature. Distillation is used to separate the bulk of the water and acids from the raw alcohols. Methanol is then fractionated from the alcohol mixture. A benzene azeotropic system is used for final water removal. The final step is the hydrogenation of the aldehydes and ketones to improve the marketing value of the alcohol mixture.

Process Description

The alcohol/acid water mixture from F-T Synthesis Unit 250 flows to Fractionator 262-D-01 in which the alcohols are distilled from the acidic water. Because alcohol-water azeotropic mixtures occur, a portion of the water distills overhead with the alcohols. The alcohols, together with a heavy alcohol recycle stream from Methanol Tower 262-D-03, are next charged to Alcohol Splitter Tower 262-D-02 from which a crude methanol overhead product is obtained. The crude methanol is redistilled in the methanol tower to obtain an acceptable make-up material for Gas Purification Unit 205. The higher boiling alcohols (bottoms) are returned to the alcohol splitter tower.

The bottoms stream from Alcohol Splitter Tower 262-D-02 is fed to Heavy Alcohol Tower 262-D-04 into which benzene is added to remove, via the benzene-water azeotrope, the remaining water. The azeotropic overhead is pumped to Tower 262-D-05, where 50 psig steam is used to strip the benzene which is then returned to Tower 262-D-04.

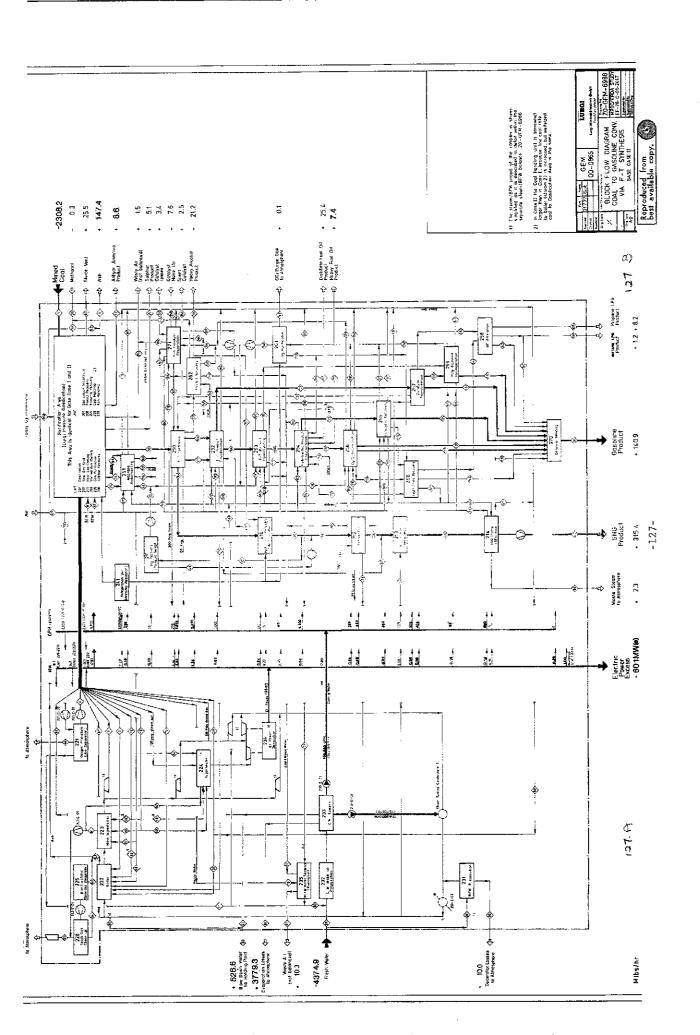
The alcohol bottoms stream from Alcohol Tower 262-D-04 is pumped to Hydrogenation Section 262-D-06 where the aldehyde and ketone impurities are hydrogenated to their corresponding alcohols. Make-up hydrogen is supplied from H₂ Recovery Unit 211 and the purge gas is returned to the same unit. A small portion of the upgraded alcohol mixture is sent to Hydrocarbon Recovery Unit 210 for the prevention of ice formation during the cold hydrocarbon washing operation.

The waste water streams from Towers 262-D-01 and 05 are pumped (262-G-02 and 09) after cooling (262-E-13) to Waste Water Treatment Unit 235.

4.4.21 Unit Capacity Summary

The capacities of the principal process units are summarized below in conventional flow rates:

		Capacity, Uni	
Unit No.	Name	Input	Output
201	Gasification	22.8 MT coal	1,755 MMSCF
202	Raw Gas Shift	331 MMSCF	_
205	Gas Purification 1,	,062 MMSCF	742 MMSCF
210	Hydrocarbon		
	Recovery	277 MMSCF	235 MMSCF
250	F-T Synthesis	742 MMSCF	18.1 MBbl
251	Naphtha Hydro-		
	treating	1.3 MBbl	•
25 3	F-T Prod. Hydro-		
	treating	11.4 MBbl	
255	Catalytic Reforming	4.3 MBb1	_
256	C ₅ /C ₆ Isomerization	4.0 MBbl	_
257	Polymerization	6.5 MBbl	-
25 8	Alkylation	2.4 MBbl (550	Bbl/SD alkylate)
259	Poly Gaso. Hydro-		
	genation	1.2 MBbl	_
260	Light Ends Recovery	1.0 MBbl	_
261	H ₂ Purification		6 MMSCF
262	Alcohol Recovery		
	SNG Train	235 MMSCF	173 MMSCF



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