

THE STUDY REPORT  
ON  
THE 10,000 HEAVY OIL UPGRADING PROJECT

THE JAPAN INTERNATIONAL COOPERATION AGENCY

NO. 10000 HEAVY OIL UPGRADING PROJECT

1980

THE JAPAN INTERNATIONAL COOPERATION AGENCY



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THE STUDY REPORT  
ON  
THE ORINOCO HEAVY OIL UPGRADING PROJECT  
FOR  
THE REPUBLIC OF VENEZUELA

VOLUME II : SUPPLEMENT

NOVEMBER 1980

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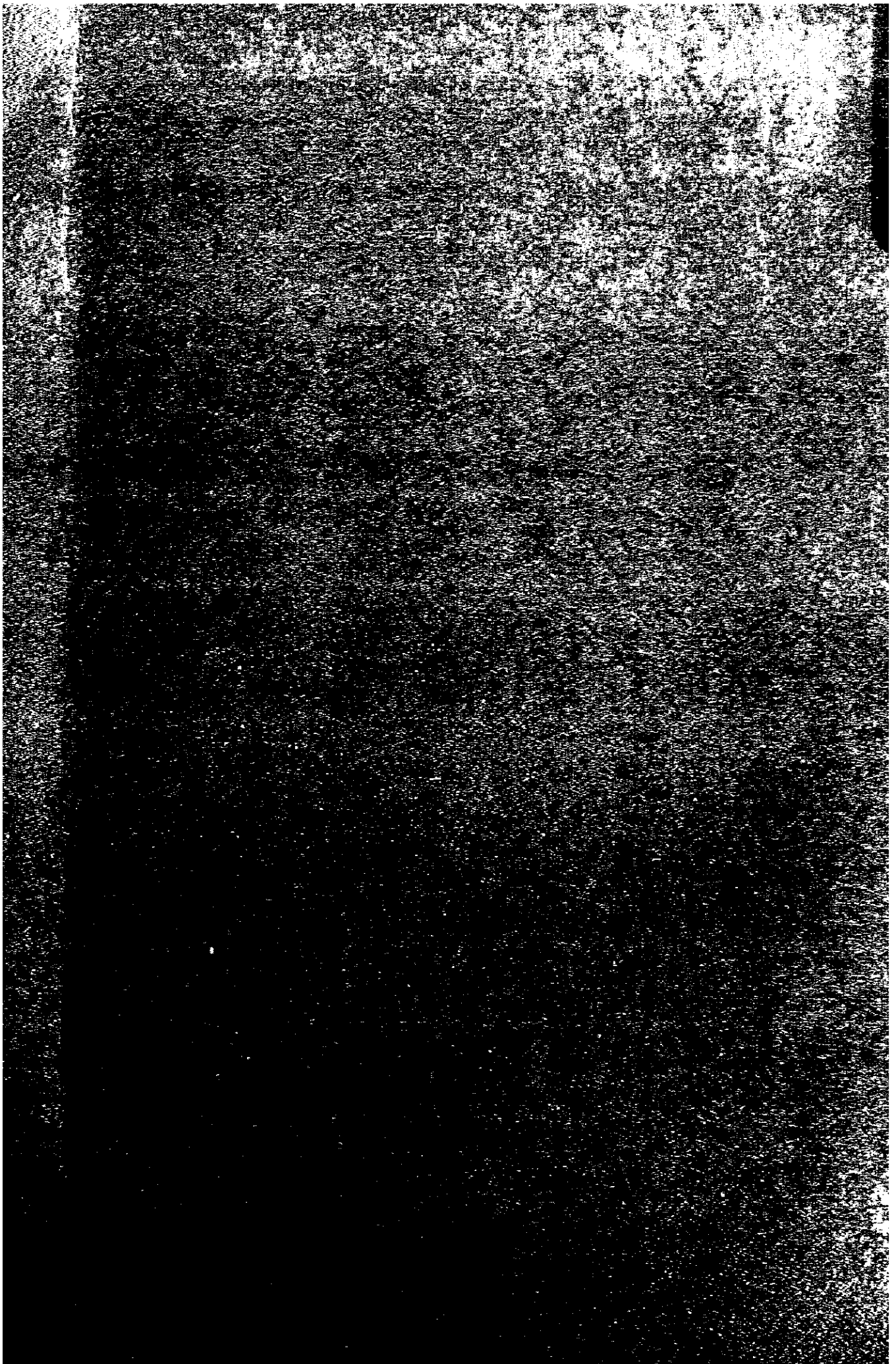
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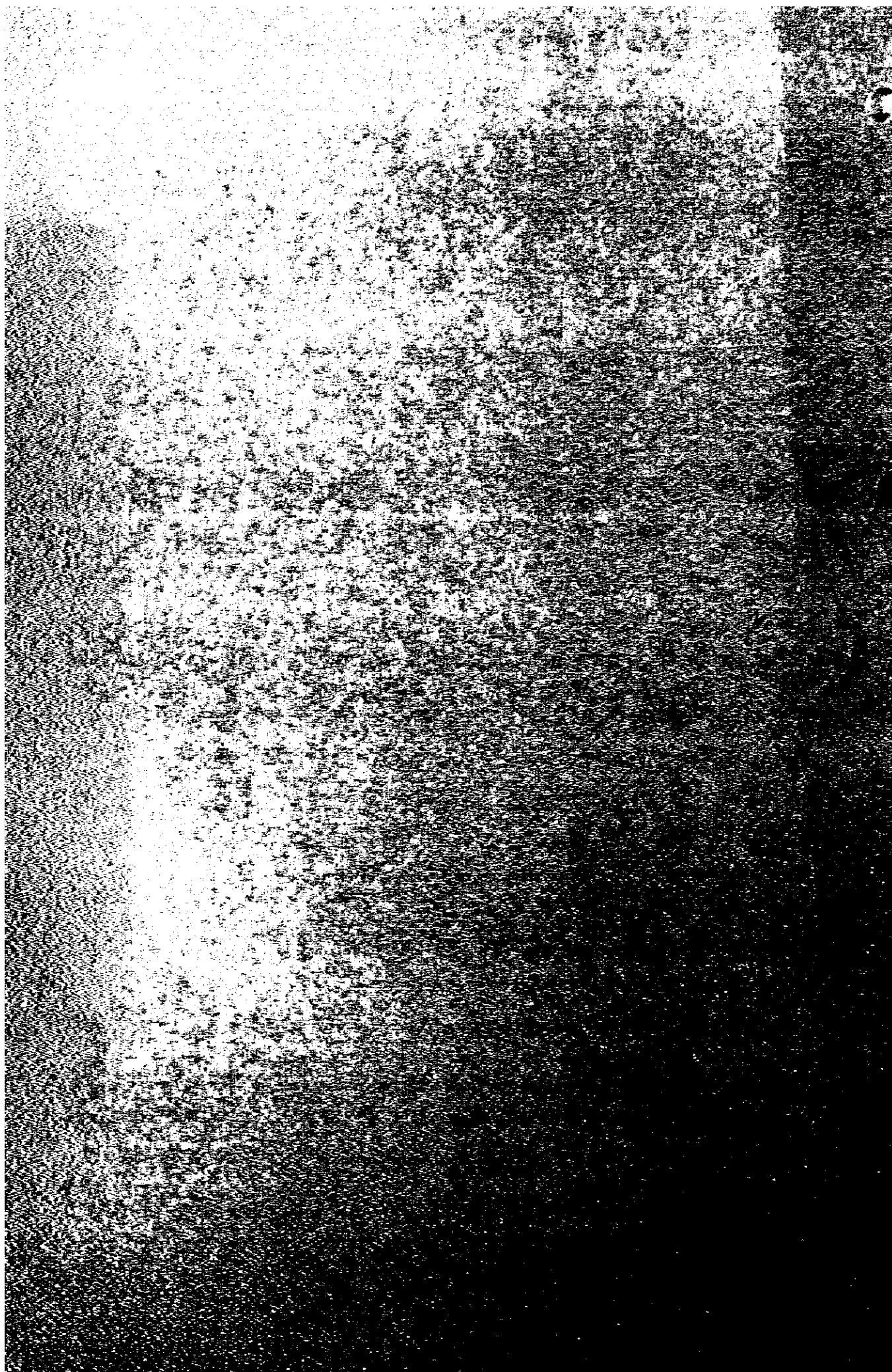
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## GLOSSARY

°API	gravity of petroleum defined by American Petroleum Institute
BBL	barrel
BPCD	barrel per calendar day
BPSD	barrel per stream day
BTU	British Thermal Unit
°C	degree centigrade
cp	centipoise
cst	centistokes
DAO	deasphalted oil
DCF	discounted cash flow
°F	degree fahrenheit
FOE	The heating value of a standard barrel of crude oil, equal to 6.24 million BTU (LHV)
Hr or H	hour
HCR	hydrocracking (unit)
HDS	hydrodesulfurization (unit)
HTR	hydrotreating (unit)
HP	high pressure
H <sub>2</sub> Plant	hydrogen generation plant
INTEVEP	Instituto Tecnológico Venezolano del Petróleo
JICA	Japan International Cooperation Agency
Kcal	kilocalorie
Kg	kilogram
LAGOVEN	Lagoven S.A.
LP	low pressure
MEM	Ministerio de Energía y Minas
m	meter
m <sup>2</sup>	square meter
m <sup>3</sup>	cubic meter
MM	million
MMBTU	million British Thermal Unit
MMKcal	million kilocalorie
MMNm <sup>3</sup> /SD	million normal cubic meter per stream day
MMSCFD	million standard cubic feet per day
MW	megawatt
MP	medium pressure

<b>m<sup>3</sup>/H</b>	<b>cubic meter per hour</b>
<b>Nm<sup>3</sup></b>	<b>normal cubic meter</b>
<b>MH</b>	<b>man-hour</b>
<b>MT</b>	<b>metric ton</b>
<b>%</b>	<b>percent</b>
<b>wt.%</b>	<b>weight percent</b>
<b>vol.%</b>	<b>volume percent</b>
<b>PDVSA</b>	<b>Petróleos de Venezuela, S.A.</b>
<b>ppm</b>	<b>parts per million</b>
<b>ROE</b>	<b>rate of return on equity</b>
<b>ROR</b>	<b>rate of return</b>
<b>SCF</b>	<b>standard cubic feet</b>
<b>SDA</b>	<b>solvent deasphalting (unit)</b>
<b>SCFD</b>	<b>standard cubic feet per day</b>
<b>Sp.Gr.</b>	<b>specific gravity</b>
<b>SR</b>	<b>sulfur recovery (unit)</b>
<b>SCF/B</b>	<b>standard cubic feet per barrel</b>
<b>Ton/H or T/H</b>	<b>tons per hour</b>
<b>Ton/SD or T/SD</b>	<b>tons per stream day</b>
<b>Ton/Y or T/Y</b>	<b>tons per year</b>
<b>UHP</b>	<b>Ultra high pressure</b>
<b>US\$</b>	<b>US dollar</b>
<b>10<sup>6</sup> US\$</b>	<b>million US dollar</b>
<b>US\$/BBL</b>	<b>US dollar per barrel</b>
<b>US\$/MMBTU</b>	<b>US dollar per million BTU</b>
<b>y</b>	<b>year</b>
<b>wt.%S</b>	<b>weight percent sulfur</b>
<b>VGO</b>	<b>vacuum gas oil</b>

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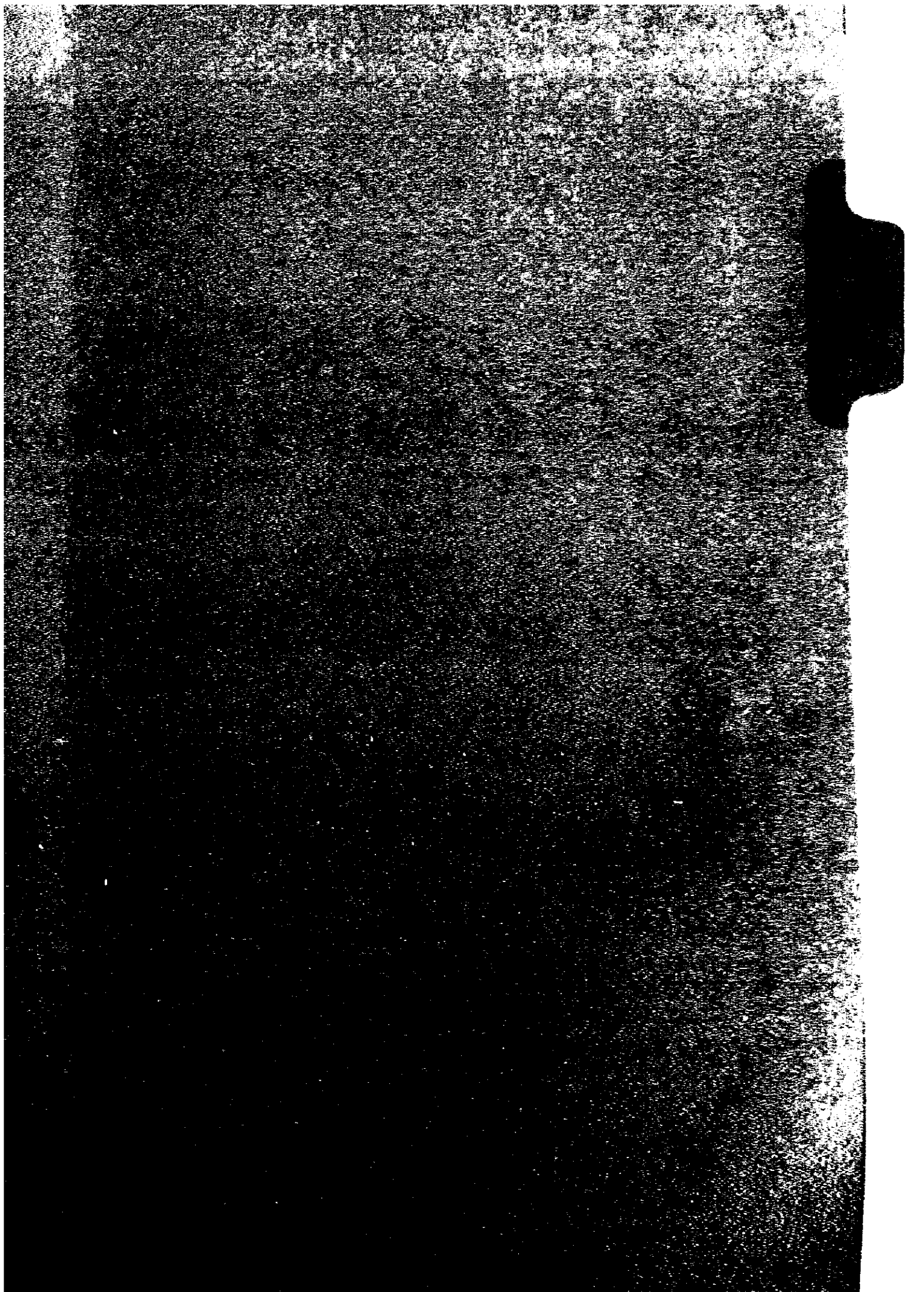
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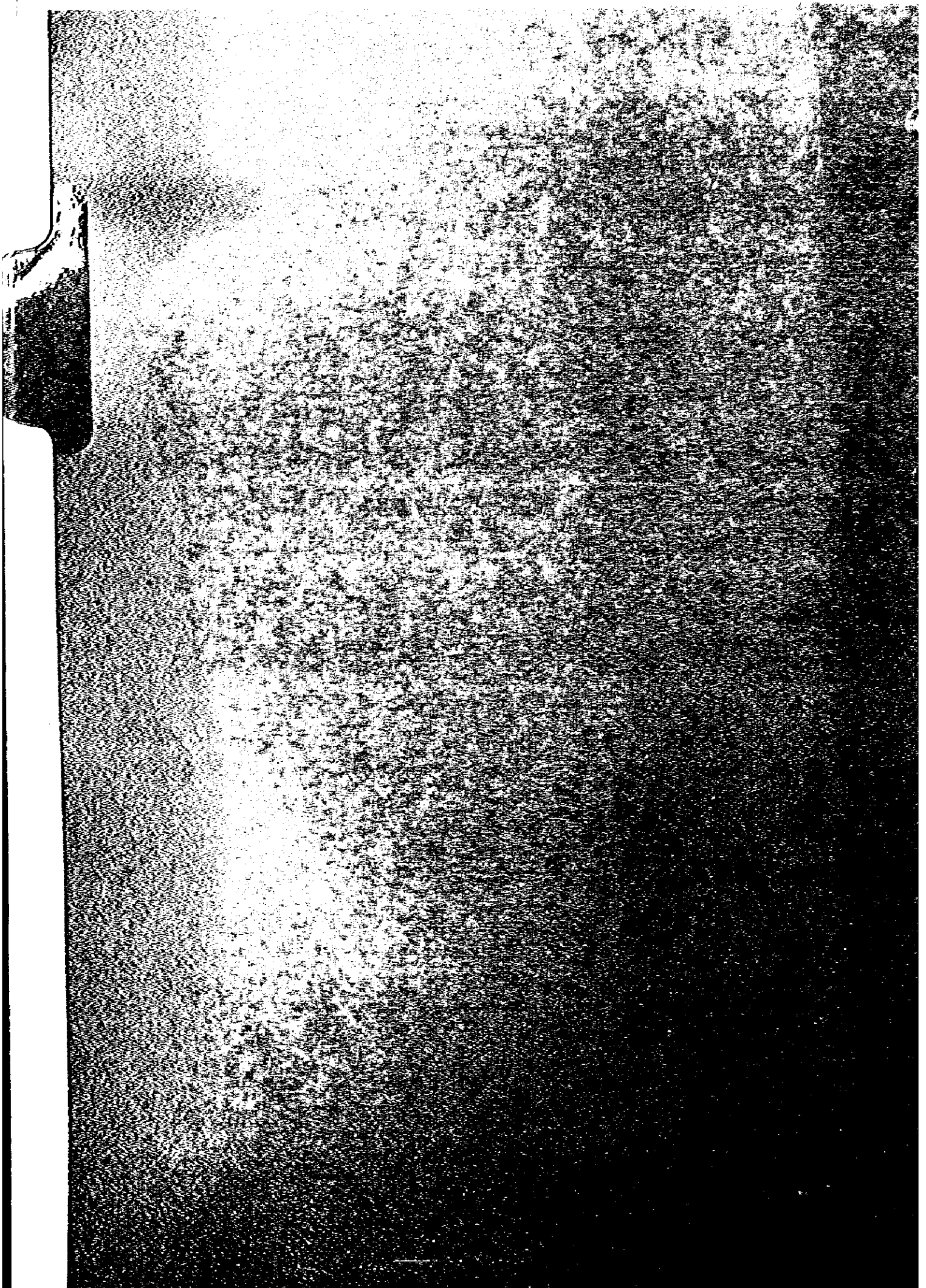
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# CHAPTER 1 DETAILED DESCRIPTION OF FLUID COKER PROCESS

(Prepared by Toa Oil Co., Ltd.)

## 1.1 TECHNOLOGY OF PROCESS

### 1.1.1 Introduction

The Orinoco crude oil has deposits in the Orinoco River basin. This crude oil is characterized by its utmost heaviness, as found from its specific gravity of 8.5° API, a pour point of 27.5°C and a residual yield of 85%. It is difficult to handle at normal temperature. Its sales in the form of a crude oil has to be limited, as long as it is sold in the original form. For its higher utilization, it is necessary to crack this heavy crude oil and upgrade it into improved crude oil having high added value.

As this upgrading process, we have studied a cracking process including the fluid coker as a main process, because fluid cokers are most widely used for upgrading. The cracked oil obtained from the fluid coker is desulfurized and mixed with other fractions as a stable blend component for improved crude oil. By-produced coke is used as boiler fuel. Steam generated by the boiler is effectively utilized for the production of raw crude oil.

### 1.1.2 Process Features

The fluid coker is a thermal cracking unit without any catalyst using coke as a heating medium. It is a very versatile unit capable of cracking any crude oil, no matter what type of crude oil it is, to give coker gas and coke. There are other thermal cracking processes such as visbreaking and delayed coking, etc. A large difference between fluid coker and these other processes is that, in the former case, crude oil is thermally cracked on the fluidized bed, using high temperature circulating coke. Because of its internal heating type, the fluid coker requires no furnace or cracking furnace. The unit is fully endurable under severe operating conditions, when it is operated to meet those product patterns requested by users.

### 1.1.3 Course of Project Development

The fluid coker was developed by Exxon Research and Engineering Co. of the U.S. The first unit operation started in 1954. Since then, more than 10 units have been constructed and are now in successful operation. ERE also developed Flexicoker units, wherein a gasifier is additionally used to convert the coke by-product into fuel gas, so that the unit can meet the varying demands of the area in which it is used. Table 1.1 gives a list of fluid coker units now in operation.

**Table 1.1 Commercial Experience of Fluid Coker**

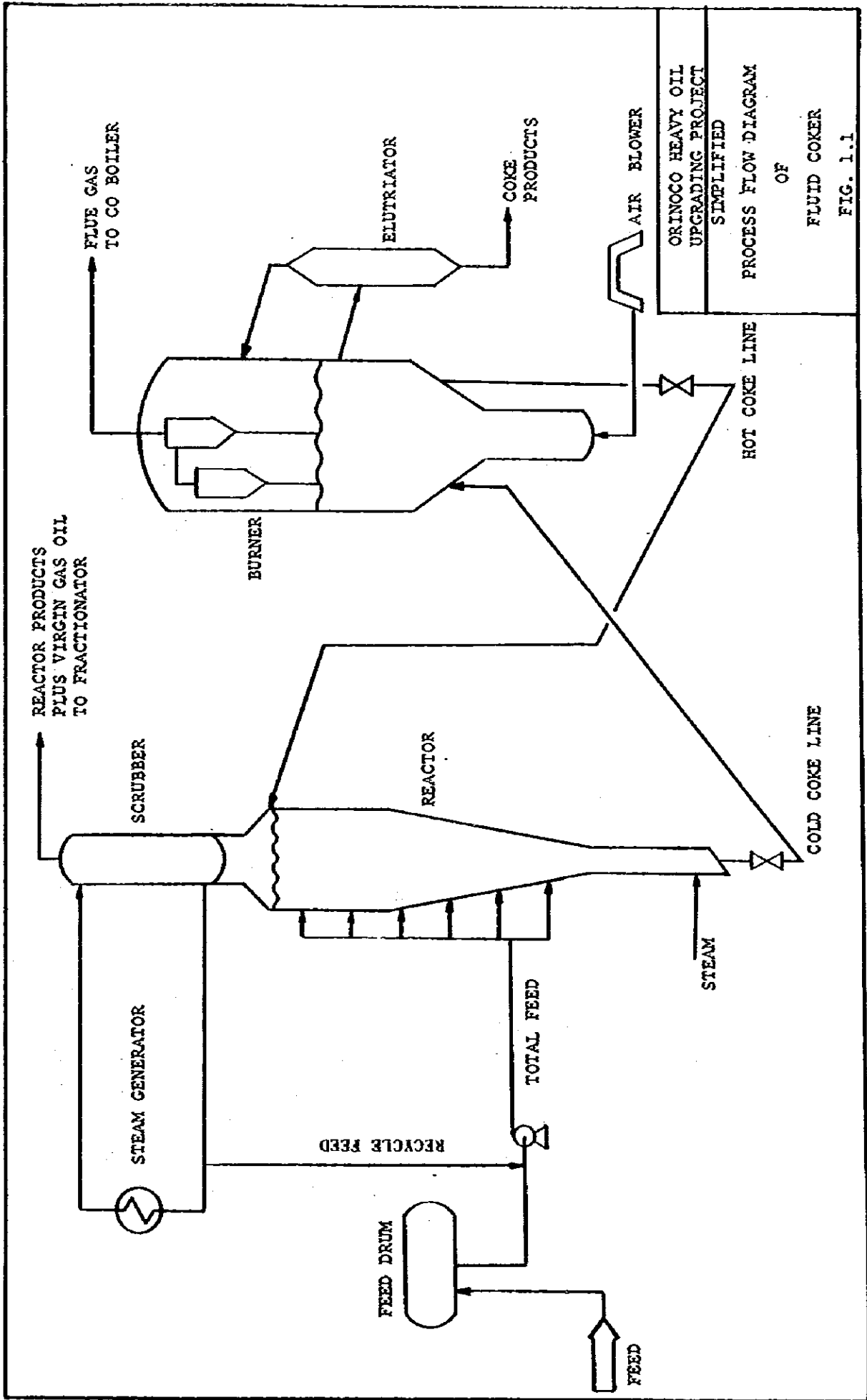
<u>Company</u>	<u>Location</u>	<u>Design Capacity (B/SD)</u>	<u>Date Onstream</u>	<u>Remarks</u>
Humble Oil Co.	Billings, Mont.	3,800	Dec. '54	
Humble Oil Co.	Baltimore, Md.	10,000	Sept. '55	Entire refinery shut down
Petrofina Canada Limited	Pointe-aux-Trembles, Quebec	3,800	Aug. '56	
Marathon Oil Co.	Detroit, Mich.	4,000	Oct. '56	Plant formerly operated by Aurora Gasoline Co.
Signal Oil Co.	Bakersfield, Calif.	4,000	Apr. '57	Plant formerly operated by Bankline Oil Co.
Phillips Petroleum Co.	Associated, Calif.	42,000	June '57	Plant formerly operated by Tidewater Oil Co.
Getty Oil Co.	Delaware City, Del.	42,000	Aug. '57	Plant formerly operated by Tidewater Oil Co.
Gulf Oil Corp.	Purvis, Miss.	4,800	Dec. '57	Plant formerly operated by Pontiac Eastern Corp.
Petroleos Mexicanos	Madero, Mex.	12,000	Feb. '68	
Imperial Oil Ltd.	Sarnia, Ontario	15,000	Apr. '68	
Humble Oil Co.	Benicia, Calif.	16,000	Apr. '69	
Syncrude Oil Co.	Mildred Lake, Alberta, Canada	73,000	July '78	
		73,000	'78	

#### 1.1.4 Process Patents

All the patents concerning the fluid coker process are owned by Exxon Research and Engineering Co.

#### 1.1.5 Feed to the Process

As the fluid coker feed, there may be used various types of oils, including crude oil, atmospheric residue, and vacuum residue. Preferably, vacuum residue is used. The fluid coker process has been originally developed for use with a wide range of heavy oils. Feed properties therefore have no restriction on its operation. Even a feed of especially



heavy and having high contents of sulfur and metals can be handled by this unit.

#### 1.1.6 Principle of Reaction

Coke, in the reactor, forms a fluidized bed along with steam taken in through the bottom of the reactor. Thermal cracking takes place at operating conditions of 510°C and 0.8 kg/cm<sup>2</sup>G. The reaction is endothermic. Heat required for thermal cracking is continuously supplied by the circulating coke. Coke gets this heat from the burner, where a part of gross coke, deposited on fluid coke at the time of cracking, is burnt by means of air supplies. Therefore, an exothermic reaction due to coke combustion takes place in the burner.

#### 1.1.7 Description of Process Flow

As illustrated in Fig. 1.1, the fluid coker unit is composed of the two vessels of reactor and burner. Coke, together with fluidizing steam, forms a fluidized bed in each of these vessels. Heat for thermal cracking is transmitted from burner to reactor by the coke circulating between them. The feed is atomized by steam and fed to the reactor, where the feed is deposited on the surfaces of fluid coke particles. When thermally cracked on the coke surfaces, the feed is converted to light hydrocarbons and coke.

Hydrocarbons thus formed go up to the scrubber through the reactor bed, where uncracked oil, is quenched for re-feeding and at the same time, entrained coke is removed. Hydrocarbons are then passed downstream into fractionator, where they are separated into coker gas and cracked oil. Newly formed coke remains on the fluid coke surfaces, and returns to the burner by way of circulating coke line (cold coke line). Large volumes of low-calorific high-temperature gas is generated at the burner. Usually this gas is introduced into CO boiler, and heat is recovered by steam generation.

Stripping steam, which is introduced into the reactor bottom, serves to strip hydrocarbons from coke surfaces, and at the same time, constitutes a part of the fluidized bed. Another type of steam is attrition steam, which is used during the coker operation, if necessary, to adjust the particle size of fluid coke and to secure stable coke circulation.

Now referring to coke circulation, heat used for thermal cracking at the reactor is supplied by circulating coke (hot coke). Necessary heat quantity is generated at the burner by introducing air and allowing a part of newly formed coke to burn. In other words, heat balance of this unit is adjusted by controlling the volume of air introduced into the burner. Surplus coke, not used for combustion, is quenched by elutriator, withdrawn from the system, and stored in coke silos for use as fuel. Coke balance of this unit is thus maintained by controlling the volume of coke withdrawn from the elutriator. Steam is used for coke transport through the circulating coke line.



### 1.1.8 Process Yields

Raw crude oil: Orinoco Crude Oil  
 Process feed: Vacuum residue

Yields (based on the weight of process feed):

	<u>Wt.%</u>
Hydrogen sulfide	0.9
C <sub>3</sub> —	10.2
C <sub>4</sub>	2.2
Coker naphtha (C <sub>5</sub> /360°F)	10.9
Coker gas oil (360°/950°F)	42.5
Coke	33.3

### 1.1.9 Products Properties

(1) C<sub>3</sub>— gas:

Molecular weight	20.9
Low heating value, Kcal/Nm <sup>3</sup>	11,050

(2) C<sub>4</sub> gas:

Molecular weight	56.8
Low heating value, Kcal/Nm <sup>3</sup>	28,100

(3) Coker Naphtha:

Specific gravity, 60/60°F	0.739 (60° API)
Sulfur, wt.%	0.84
Bromine number	130

(4) Coker gas oil:

Specific gravity, 60/60°F	0.963 (15.5° API)
Sulfur, wt.%	3.38
Nitrogen, wt.%	0.6
Bromine number	43
Conradson carbon residue, wt.%	4.0

(5) Flue gas:

Molecular weight	27.4 (day gas)
Low heating value, Kcal/Nm <sup>3</sup>	242

(6) Coke:

Sulfur, wt.%	5.8
Ni, wppm	610
V, wppm	2,460
Fe, wppm	70

### 1.1.10 Operating Conditions

	<u>Reactor</u>	<u>Burner</u>
Temperature, °F	950	1,100
Pressure, psig	12	12

### 1.1.11 Catalyst and Chemical

No catalyst is used, but seed coke is required when the unit is started up.

Seed coke:	Product coke from fluid coker.
Required quantity:	2,500 tons (43,900 BPSD for a train)

Sodium triphosphate is used as the pH control and softening agent of boiler water for both of main boiler and CO boiler.

Chemical:	Sodium triphosphate.
Required quantity:	14 kg/day (for a train)

### 1.1.12 Utilities

<u>Utilities</u>	<u>Uses</u>	<u>Requirements</u>
Steam, 49 kg/cm <sup>2</sup> G	Feed atomizing, etc.	25 tons/hr.
Steam, 15 kg/cm <sup>2</sup> G	Aeration	85 tons/hr.
Electric power	Pumping	680 kwh

### 1.1.13 Past Achievements

Table 1.1 gives a list of existing fluid coker units and their design capacities. Since 1954 when the first unit started operation, more than 10 units have been constructed and are now in successful operation.

### 1.1.14 Applicability of the Process

Orinoco Crude is so heavy that the upgrading of residual oil is inevitably required, in order to obtain the desired improved crude oil. Fluid coking is much flexible, allowing the use of a wide range of feed oils. Since the unit is run at the lower pressure, operation is easy and cost is low. The coke by-product is used for boiler fuel, and steam generated can be effectively utilized for the production of raw crude oil. Fluid coker distillate is used as the blend stock for the production of improved crude oil. It gives a yield in excess of 50%, indicating that the process is fully applicable as the main process for producing improved crude oil.

### 1.1.15 Merits/Demerits of the Process

#### (1) Merits

- (a) A wide range of oils can be used as the process feed.
- (b) Heat quantity required for the process is given by the circulating coke; and no furnace is required to pre-heat the feed.
- (c) Operation is easy.
- (d) By-produced coke is utilized as boiler fuel.
- (e) The process gives a high yield of light cracked gas oil, and therefore, it is suitable for the production of improved crude oil.

**(2) Demerits**

- (a) C<sub>3</sub> and C<sub>4</sub> products have high contents of olefines, and are often used as fuel, rather than as LPG.
- (b) A higher sulfur content of coke product makes it necessary to consider a possibility of using a flue gas desulfurization unit, if coke is to be used as fuel.

**1.1.16 Utilization of the Residual By-product**

The coke formed at the fluid coker is partly used as the fuel for the coker burner in an amount of 20-25% of gross coke. The surplus amount of coke is taken out from the system, and is used as fuel mainly for the large-capacity boiler based on the pulverized coke combustion system.

This combustion system works in the following manner. Coke is withdrawn from a coke silo, and is pulverized by a ball mill to such an extent that 70-80% thereof can be passed through a 200-mesh screen. Fine coke thus obtained is received by the fuel silo, from which the coke fuel is transported by primary air at a controlled rate to the burners. At the burner, coke is atomized into the furnace, ignited by the high temperature heat radiation and air convection, and is burnt while it is drifting in the space of the combustion chamber. Fuel oil or fuel gas is used as a supporting fuel to compensate and the load fluctuations are covered by the supporting fuel.

**1.1.17 Operability**

Unlike other coking processes, the fluid coker process is based on reaction over the fluidized bed, i.e. the reaction taking place on the surfaces of fluid coke particles. The first fluid coker unit went into operation 25 years ago. Since then, various improvements have been made, and now it is a completely established process. Abundant experiences in its operation could have eliminated any difficulty in its operation. Key points of operation are as follows:

**(1) Heat balance**

The cracking reaction is endothermic. Necessary heat is given continuously by fluid

coke coming from the burner. Therefore, heat balance is adjusted by controlling the volume of coke circulating between the reactor and the burner. This volume also controls the reactor temperature. The burner temperature is kept constant by controlling the volume of air introduced into the burner.

**(2) Coke balance**

The volume of coke circulating between the reactor and the burner is always kept constant. Any surplus coke formed is withdrawn to the silo by the quench elutriator, so that a constant volume of coke is kept in the vessels. Coke balance is thus adjusted by the volume of coke withdrawn from the system.

## **1.2 PROCESS SCHEME FOR IMPROVED CRUDE OIL PRODUCTION**

### **1.2.1 Introduction**

With recent high rises in international prices of crude oils and the reduction in crude supplies by oil producing countries, those countries consuming large amounts of petroleum feel it more and more difficult to secure their necessary amounts of crude oil. What is more, the crude oils they get tend to get heavier.

Under such circumstances, those undeveloped oil fields having deposits of heavier crude oils are attracting more and more attention. Among them, the heavy crude oil belt lying in the Orinoco River basin is expected to have a huge quantity of virgin oil deposits. Thus, a development plan on Orinoco Heavy Crude Oil is an urgent necessity.

### **1.2.2 Study Objective**

If an Orinoco heavy crude development project involves producing improved crude oil from this crude oil, it is necessary to study the properties of Orinoco heavy crude and select an optimum upgrading process. With this objective in mind, we studied the fluid coker process which is considered the most adequate for the production of improved crude oil.

### **1.2.3 Outline**

We have worked out a process scheme based on the fluid coker process for thermally cracking Orinoco heavy crude oil, because this process has the following advantages:

- (1) Those units with abundant experiences can be combined.**
- (2) The units employed give high yields of oil fractions.**
- (3) Operation is easy and flexible.**
- (4) Costs of construction and operation are less expensive.**

The related units required for this process include:

- Atmospheric distillation unit,
- Vacuum flashing unit,
- Hydrotreating unit,
- and auxiliary units, such as:
  - Hydrogen generation unit,
  - Acid gas treating unit, and
  - Sulfur recovery unit.

Fractions coming out from the fluid coker process are stabilized and upgraded by the hydrotreater and blended into improved crude oil. The blend bases for, and their proportions in, improved crude oil are as given below. An improved crude yield of 79% is obtained by a combination of units including fluid coker as the most important upgrading means. The oils coming from the fluid coker accounts for 45% of the total improved crude volume.

Atmospheric distillation:	Naphtha	0.9 vol.%
	Light gas oil	5.5
	Heavy gas oil	12.9
Vacuum flashing:	Gas oil	36.0
Fluid coker:	Naphtha	11.2
	Gas oil	33.5
	Total	100.0 vol. %

#### 1.2.4 Study Base

- (1) Crude assay data on the 50/50 mixture of Cogollar IX and Cerro Negro Crude Oil are used for the process yields and properties of oil fractions.
- (2) LGO is used as the diluent for crude oil production.
- (3) Processes are equipped with two trains of units to secure stable supply of products and safe operation. Even at the time of periodical maintenance, it is arranged that at least a train can be in operation.
- (4) Capacities of process units are determined in such a way that train of units gives 63,000 BPSD of improved crude oil production, so that a minimum of 125,000 BPSD of improved crude oil production can be secured on the whole.
- (5) The following target levels are set for the properties of improved crude oil:
  - Specific gravity: 25-30° API
  - Sulfur content: 0.7 wt.%
  - Nitrogen content: Max. 0.25 wt.%
  - Conradson carbon residue: Max. 1.0 wt.%

- (6) The heavy residual by-product is fed to the boiler, which in turn generates steam and electric power.
- (7) Off-gas from the process is treated by the sulfur recovery unit to recovery elemental sulfur.
- (8) Surplus off-gas from the refinery, together with natural gas, is used as the fuel for portable boilers which are used for crude production.
- (9) Natural gas is used as the feed to the  $H_2$  Plant, and its quantity to be required is calculated based on the supplied data concerning natural gas properties.
- (10) As regards process fuel, the atmospheric distillation unit and vacuum flashing unit make use of vacuum residue as the fuel for their furnaces. Other units utilize refinery off-gas and by-product as the fuel.

### 1.2.5 Result of Study

#### (1) Raw material

As a study base for raw crude oil, we used the crude assay data available for the 50/50 mixture of Cogollar IX and Cerro Negro Crude Oil supplied by Lagoven.

#### (2) Process scheme

A process scheme is described here, referring to Fig. 1.2. Raw crude oil is diluted with light gas oil, and the mixed crude oil is fed to the atmospheric distillation unit, where crude oil is distilled into  $C_4$  fraction, naphtha, light gas oil, heavy gas oil, and atmospheric residue. The atmospheric distillation unit is used for the purpose of securing light gas oil required to dilute raw crude oil and to wash pumps and other types of machinery.

The  $C_4$  fraction is treated by an acid gas treatment unit to get rid of  $H_2S$ , and is used as fuel gas. The fractions of naphtha, light gas oil, and heavy gas oil are fed to the hydrotreater.

Atmospheric residue is fed to the vacuum flashing unit, where vacuum gas oil is withdrawn in an amount of 30%. Use of the vacuum flashing unit is aimed at taking out as much light fractions as possible, so as to avoid reduction in light oil yields caused by thermal cracking of light fractions in the fluid coker, and at securing a necessary amount of flushing oil (such as LVGO) to be used for cleaning of instruments and pumps. Vacuum gas oil is fed to the hydrotreater and blended into improved crude oil as one of its base materials.

Vacuum residue is sent to the fluid coker, and is thermally cracked in the fluid coker reactor bed into coker gas, coker naphtha, coker gas oil and coke.

Coker gas is treated by another acid gas treating unit to get rid of  $H_2S$ , and is used as

Table 1.2 Estimated Yield of Fluid Coker Case

			APS					VPS				FLUID COKER			HTR			
	RAW CRUDE	IMPROVED CRUDE	GAS	Naphtha	LGO	HGO	RO	VGO	LVGO	HVGO	VB	GAS & COKE	UCN	CGO	FEED	WILD NAPHTHA	TVGO	
15/S CUT POINT FVT 15/S CUT POINT CVT			MW=50.62	68-380 20-193	380-510 193-266	510-650 266-343	650+ 343+	650-995 343-535	650-720 343-382	720-995 382-535	995+ 535+	C <sub>2</sub> GAS	C <sub>1</sub> -360 C <sub>2</sub> -182	360-950 182-510				
YIELD CUT POINT Vol% YIELD ON CRUDE Vol%			LHV=25700 kcal/Nm <sup>3</sup>	0.2-0.75 0.75	0.75-4.21 4.21	4.21-9.94 9.94	849	15.1-42.8 27.7	15.1-20.5 5.5	20.5-42.8 22.3	57.2	H <sub>2</sub> 16.7 mol% C <sub>1</sub> 44.8						
GRAVITY °API SPECIFIC GRAVITY 60/60	8.5 1.011	25.7 0.900	C <sub>2</sub> =6.9 mol% C <sub>3</sub> =38.9 iC <sub>4</sub> =19.8 nC <sub>4</sub> =34.4	37.2 0.839	32.0 0.365	23.0 0.916	5.4 1.034	14.2 0.971	16.9 0.9535	13.5 0.976	1.8 1.062	C <sub>2</sub> = 7.7 C <sub>3</sub> 15.6 C <sub>4</sub> = 8.1 C <sub>5</sub> 7.1	60 0.739	15.5 0.963	20.8 0.929	54.7 0.76	22.1 0.921	
TOTAL SULFUR wt%	3.67	0.70	Σ 100.0	0.65	1.16	2.43	4.04	3.28	3.24	3.29	4.32			0.84	3.38	2.86	0.1	0.77
SMOKE POINT mm FREEZING POINT °F CLOUD POINT °F POUR POINT °F ANILINE POINT °F DIESEL POINT				25								Σ 100.0 MW=20.9 LHV=11050 kcal/Nm <sup>3</sup> C <sub>1</sub> GAS C <sub>2</sub> 60 mol%						
AROMATICS FIA Vol%				323								C <sub>1</sub> 40 Σ 100.0						
VISCOSITY												MW=56.8 LHV=28100 kcal/Nm <sup>3</sup> CO GAS mol% CO <sub>2</sub> 12.0 CO 6.0 N <sub>2</sub> 56.5 H <sub>2</sub> S 0.5 H <sub>2</sub> O 25.0 Σ 100.0		29@110 18		1.0	7.0	
100°F CST 130°F CST 140°F CST 180°F CST 210°F CST	6600 10517 5944 831 (230)	4.9   2.8			2.25		303@275; 164@300	485 65@150F				7951@275 2891@300°F						
NITROGEN wt% CCR wt% H <sub>2</sub> S(DISSOLVED) wt.ppm METAL Fe wt.ppm V wt.ppm Ni wt.ppm	0.57 13.3 84 9 392 84	0.17 0.147				0.002	0.59 176	0.19 0.2	0.27	0.23	0.82 25.7		0.6 4.0	0.281	10 wppm		0.19 0.15	
WATER AND SEDIMENT Vol% SALT CONTENT NaCl PTB NEUT NO(0664) mgKOH/gm	1.0 230 1.39						324					LHV=242 (kcal/Nm <sup>3</sup> ) (DRY BASE) DUST 0.213 T/H COKE S=5.79 wt% METAL V=2460 wppm Ni=610 Fe=70 BULK DENSITY 56 lb/ft <sup>3</sup>						
Br No gBr/100 mg													130	43	29			

fuel. Coker naphtha and gas oil are sent to the hydrotreater.

Coke goes to the coke handling section, where it is pulverized to such a particle size that can be used as boiler fuel. Flue gas containing CO gas leaves the fluid coker and goes to the CO boiler, where it is used as boiler fuel.

Those distillate fractions coming out of atmospheric distillation unit, vacuum flashing unit, and fluid coker are hydrogenated at the hydrotreater, in order to stabilize cracked oils and to upgrade the blend base materials through desulfurization. Hydrogen required for hydrotreatment is supplied from the H<sub>2</sub> plant, where hydrogen is generated, using natural gas and the high-pressure purge gas from the hydrotreater. Tail gas leaving the hydrotreater is passed through an acid gas treatment unit and used as fuel.

Stabilized oils leaving the hydrotreater are stored in product tanks as improved crude oil.

**Table 1.3 Construction Costs of Process Units**

Process Unit	Capacity	No.s	Construction Cost (10 <sup>6</sup> Japanese Yen)
Atm. Distillation	102,790 BPSD	2	9,272
Vacuum Flashing	67,144 BPSD	2	6,624
Hydrotreating	60,893 BPSD	2	16,809
Fluid Coker	43,559 BPSD	2	28,711
Hydrogen Plant	0.893 MM Nm <sup>3</sup> /D as H <sub>2</sub>	2	8,496
Acid Gas Removal	68 Ton/D	2	3,218
	23 Ton/D	2	
	192 Ton/D as H <sub>2</sub> S	2	
Sulfur Recovery and Solidification	255 Ton/D as S	2	3,041
<b>Total</b>			<b>76,171</b>

Note:

- (1) Location: Chiba, Japan
- (2) As of mid. 1980 and no escalation included.



(3) Overall material balance

Fig. 1.2 shows the overall material balance for the fluid coker case. Table 1.2 gives yields and properties of oil fractions leaving respective process units.

(4) Estimated cost of construction

Table 1.3 gives the costs of process unit construction estimated under the following premises:

- The refinery is erected in Chiba area, Japan.
- Costs are estimated on the "present price" basis wherein the costs of construction materials and machinery and the labor cost are based on the price levels set as of the middle of 1980. Any fluctuations in prices, which may take place in the future, are not taken into consideration.
- Construction cost includes cost of construction materials, labor cost, costs of design and engineering, and contractor expenses.

(5) Utility requirements

Table 1.4 gives estimated utility requirements of process units.

(6) Catalyst and chemical requirements

(a) Catalyst:

Hydrotreater catalyst:

Unit cost	\$8.3/kg
Filling quantity	241,800 kg (per train)
Catalyst life	1 year (totally renewed)

Fluid coker seed coke:

Filling quantity	2,500 tons (per train)
------------------	------------------------

(b) Chemical:

$\text{Na}_3\text{PO}_4$  used as a boiler cleansing agent:

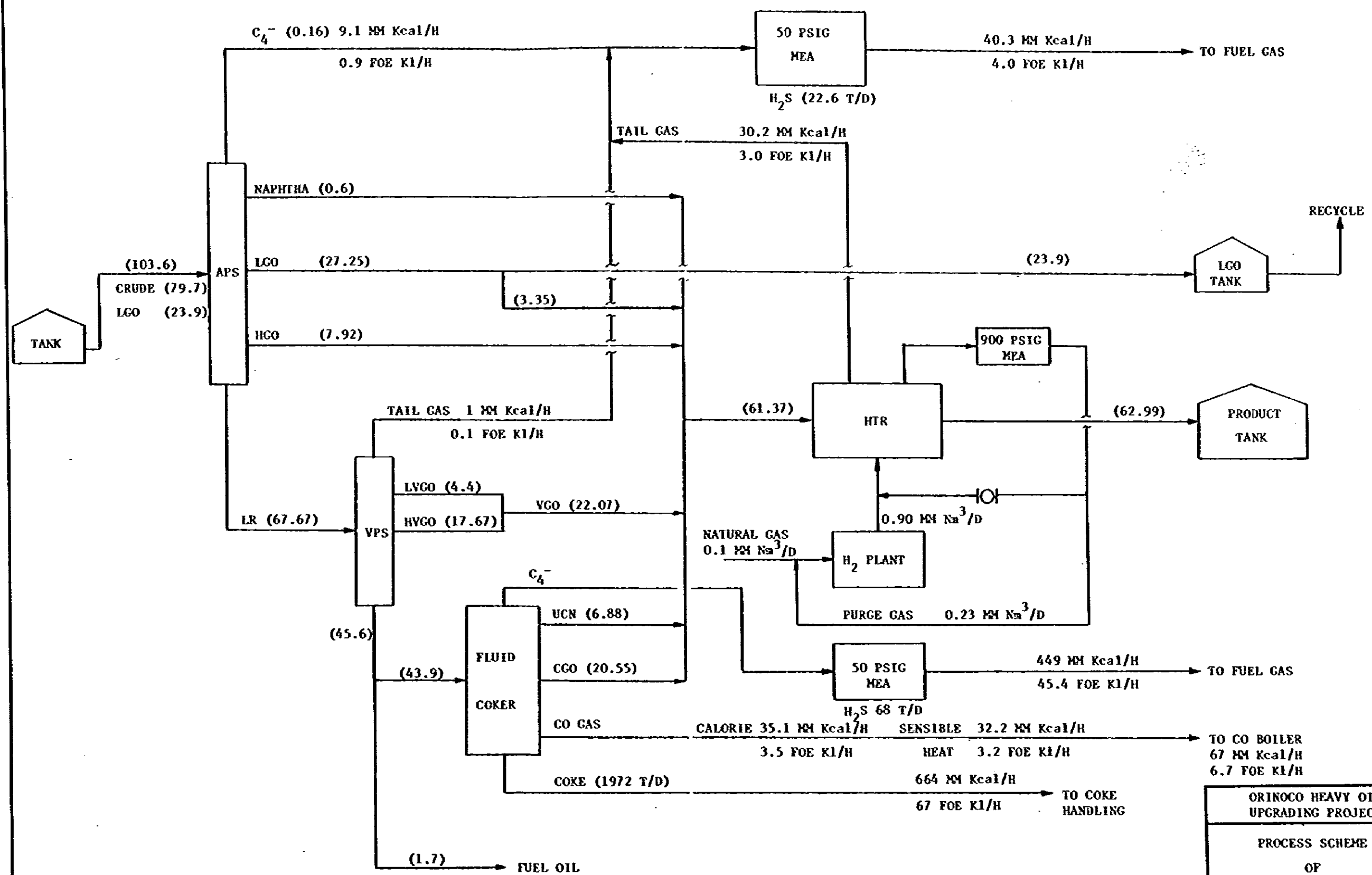
<u>Process units</u>	<u>Quantities used</u>	<u>Costs</u>	<u>Remarks</u>
Fluid coker	3 kg/day	\$0.6/kg	1,000 T/D of 49-kg/cm <sup>2</sup> G steam generated.
Hydrotreater	2.9 kg/day	\$0.6/kg	960 T/D of 15-kg/cm <sup>2</sup> G steam generated.

(7) Process wastes

(a) Wastewater

Steam condenses at the fractionation section of the fluid coker, and resultant wastewater contains  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and other wastes. If necessary, these harmful substances have to be removed. The volume of wastewater per train and its properties are as follows:

UNIT: 1,000 BPSD



ORINOCO HEAVY OIL  
UPGRADING PROJECT  
PROCESS SCHEME  
OF  
FLUID COKER CASE  
FIG. 1.2

Table 1.4 Estimated Utility Requirements

(Fluid Coker Case)

Process Unit	Capacity BPSD	Eloc. KW	Steam Ton/H			Water Ton/H					Fuel			
			49KG 400°C	15KG 270°C	3.5KG sat.	BFW	cond.	Process water	Foul water	Loss water	Cooling water	X10 <sup>6</sup> kcal/H Gas	Oil	
Atm. Distillation	205,588	1,720	21.2	20.8	-21.2		68.2	-89.0		(4) 26				110
Vacuum Flashing	134,287	1,640	7.0		-7.0	50.2		-50.2		(4) 22				110
Fluid Coker	87,118	20,000	(5)-81.6 49.0 64.5.0	102.0	8.4	150.4		-146.0	-78.6	(4) 40				
Hydrotreating	121,786	4,000	28.0	-64.0	-28.0	80.0		-16.0		(4) 70				24
Hydrogen Plant	(1) 1,786	1,780		-18.6		114.6		-60.8	-38.8	(4) 18			142	
Acid Gas Removal	(2) 560	580		5.2	85.4					(4) 10				
Sulfur Recovery	(3) 510	2,220			-56.6	79.2			-22.6	(4) 24				
Total		31,940	105.2 (5)-81.6	45.4	-19.0	474.2		-362.0	-140.0	(4) 210			142	244

Note: Negative figures indicate quantity made.

- (1) x10<sup>3</sup> Nm<sup>3</sup>/D as H<sub>2</sub>
- (2) Ton/D as H<sub>2</sub>S
- (3) Ton/D as sulfur
- (4) Mechanical cooling
- (5) Saturated Steam

Volume of wastewater:	73 tons/hr.
Properties:	
pH	7 – 7.5
H <sub>2</sub> S	1,000 – 1,500 wppm
HN <sub>3</sub>	500 – 1,500 wppm
COD	300 – 400 wppm
SS	20 wppm
Oil	400 wppm

(b) **Chunk coke**

During the fluid coker operation, coke is formed on the inner walls of the reactor. Such coke falls off in lumps and deposits on the stripper bottom. These lumps are called chunk coke. Such coke may block smooth circulation of fluid coke, and adversely affects the coker operation. The reactor is thus equipped with a chunk coke withdrawal system at the reactor bottom, through which chunk coke is periodically withdrawn during operation. Chunk coke is hard because it contains hydrocarbons, apart from its properties as bed coke. It is disposed as a waste material.

(8) **Process plot plan**

Fig. 1.3 shows a plot plan for the fluid coker case.

Major units are as follows:

(a) Reactors	10 m $\phi$ x 2 units
(b) Burners	13 m $\phi$ x 2 units
(c) Blowers	150,000 Nm <sup>3</sup> /hr x 2 units
(d) Fractionators	8 m $\phi$ x 2 units

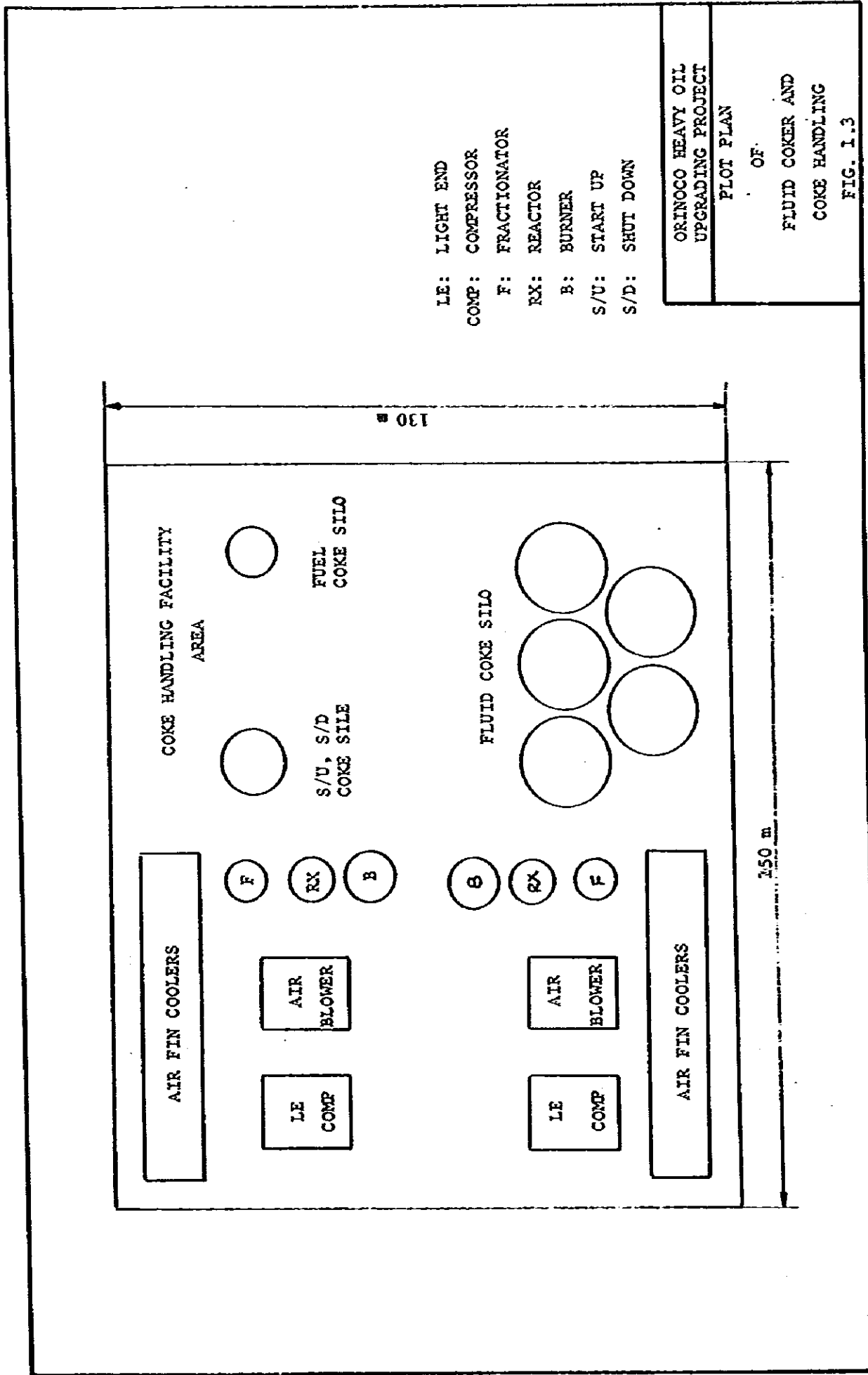
(9) **Major unit sizes and structure**

Fig. 1.4 shows the dimensions of fluid coker reactor and burner. Both of them are made of carbon steel and lined with refractory brick.

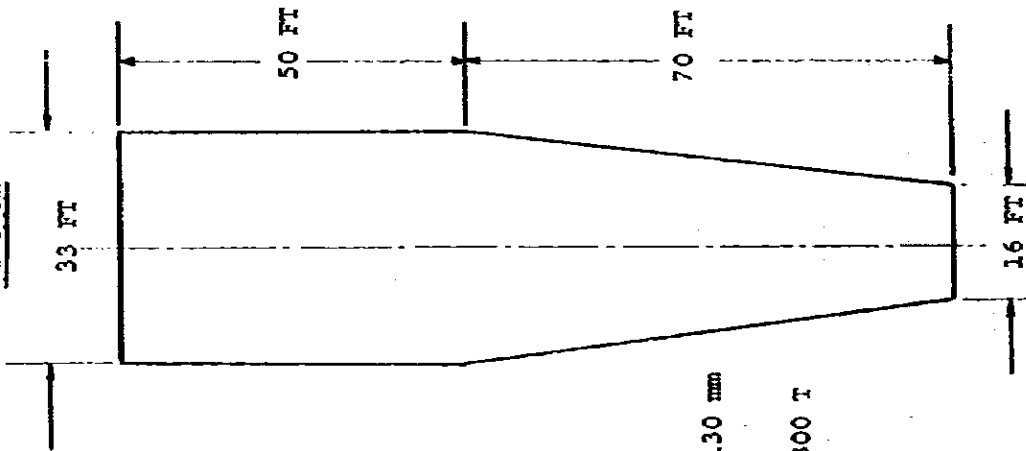
### 1.2.6 Discussion

Orinoco crude oil is a heavy crude of 8.5°API. If a study is made on process for converting it to low sulfur improved crude of a specific gravity in the range of 25-30° API, the process inevitably calls for the use of cracking and desulfurization. In that case, apart from the economic analyses of investment and operating cost, and apart from the technical study of operating performance, the key points of the feasibility study are: How can the yield of improved crude be raised, and in what way should process by-products be used effectively?

If fluid coker process is to be adopted, an improved crude yield of about 80% is

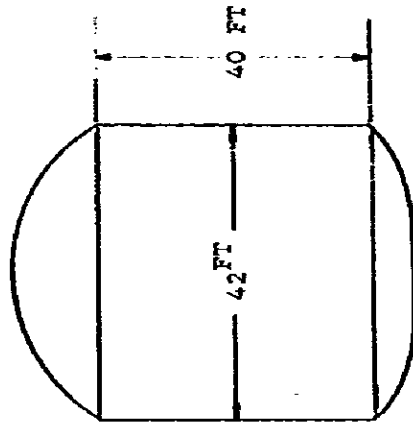


REACTOR



REFRACTORY THICKNESS 130 mm  
COKE LOADING 1,800 T

BURNER



REFRACTORY THICKNESS 100 mm  
COKE LOADING 700 T

BASE:  
45,600 BPSD FEED  
CCR 25.7 WT%

ORINOCO HEAVY OIL  
UPGRADING PROJECT

DIMENSION

OF

FLUID COKER'S

MAIN EQUIPMENT

FIG. 1.4

expected from the raw crude. This level of oil yield is higher than in other cracking processes. The coke by-product can be used as the fuel for boiler which generates steam for use in raw crude oil production. The steam consumption for this use is likely to be less initially, but will increase gradually. Therefore, it will be necessary to stockpile surplus coke in preparation for future use. From the foregoing points, we are convinced that the process including fluid coker as the most important upgrading means can fully serve as an Orinoco heavy crude oil upgrading process.

### 1.3 UTILIZATION OF BY-PRODUCT

#### 1.3.1 By-product

About 2,000 tons/day per train of fluid coke is produced by the fluid coker. Its properties and burning characteristic are described, and a combustion system is selected, in this sub-section.

##### (1) Coke properties

Bulk density:	0.897 g/cm <sup>3</sup>
Sulfur content:	5.79 wt.%
Metal contents:	
V.	2,460 ppm (weight basis)
Ni.	610 ppm ( " )
Fe.	70 ppm ( " )

##### Particle size:

<u>Mesh</u>	<u>Particle size (<math>\mu</math>)</u>	<u>Residual on mesh (%)</u>
20	841	5
50	297	15
60	250	25
80	177	55
100	149	65
140	105	75
200	74	95

Heating value: 8,080 Kcal/kg

##### (2) Burning characteristic

Coke has a volatile content as low as 2-3%, as compared with other heavy products of petroleum, such as heavy oil and asphalt, which contain much higher levels of volatile substances. Coke is therefore characterized by an ignition temperature as high as 870 to 920°C.

##### (3) Combustion system

Boilers of a vertical U-frame pulverized-coal combustion type are considered the most appropriate. This type of burners have significant experiences in the use with anthracite having similar properties.

### 1.3.2 Conceptual Scheme for Boilers

A conceptual scheme is worked out for coke boilers and coke transport facilities, wherein 1,000 tons/hr. of steam having a pressure of 100 kg/cm<sup>2</sup>G and a temperature of 500°C is generated by using two boilers each having a capacity of 500 tons/hr. and burning about 2,000 tons/day of coke produced by a train of fluid coker.

#### (1) Coke transport system

In order to improve the coke ignitability, coke is pulverized by mills to such a particle size that about 90% can be passed through 200-mesh screens. Two mills, each with a 30-ton-hour capacity, are used for each boiler. Since coke is hard (having a Hardgrove index of about 30), some measures against abrasion are required for these mills. Fig. 1.5 shows a flow diagram in which coke product is stored in an amount corresponding to about 10 days of production, with 2,000 tons of fine coke being separately stored.

Coke is transported by a blower to a cyclone separator, where coke is separated from air and stored in fluid coke silos. Coke leaving a fluid coke silo is sent to an air separator by way of a belt conveyor and a bucket elevator. Coke is then pulverized for size adjustment and passed into fuel coke silos. Each of these fuel coke silos is equipped with an automatic feeder, which supplies the boiler with a controlled amount of coke by means of primary air.

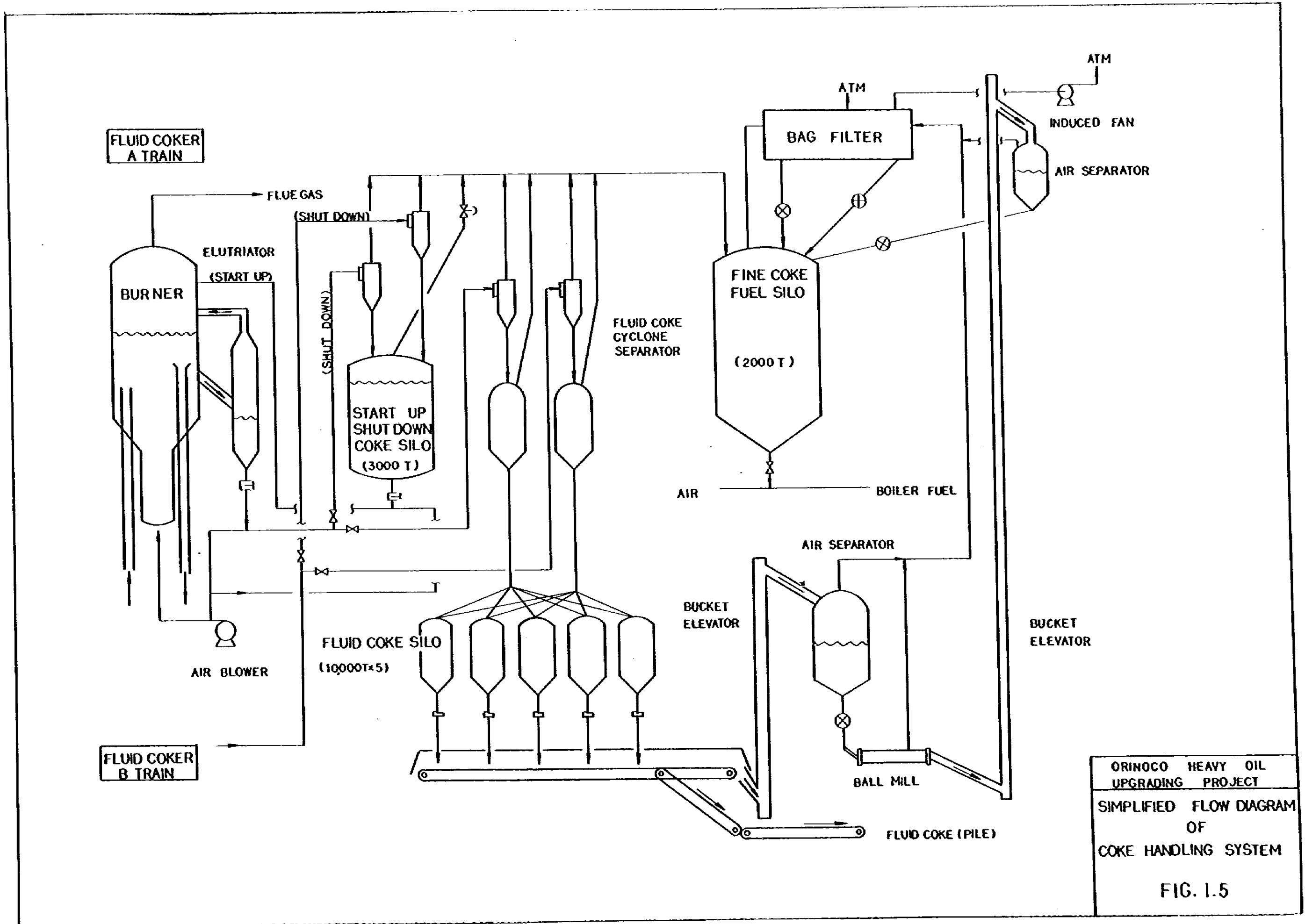
#### (2) Coke boilers

Fig. 1.6 illustrates a flow diagram for the boiler system. A constant amount of coke is withdrawn from a fuel coke silo by the automatic feeder, and by preheated primary air sent to a boiler. Boiler flue gas is passed through a dust collecting unit, where dust and soot are recovered. In working out a boiler scheme, the following points are taken into consideration.

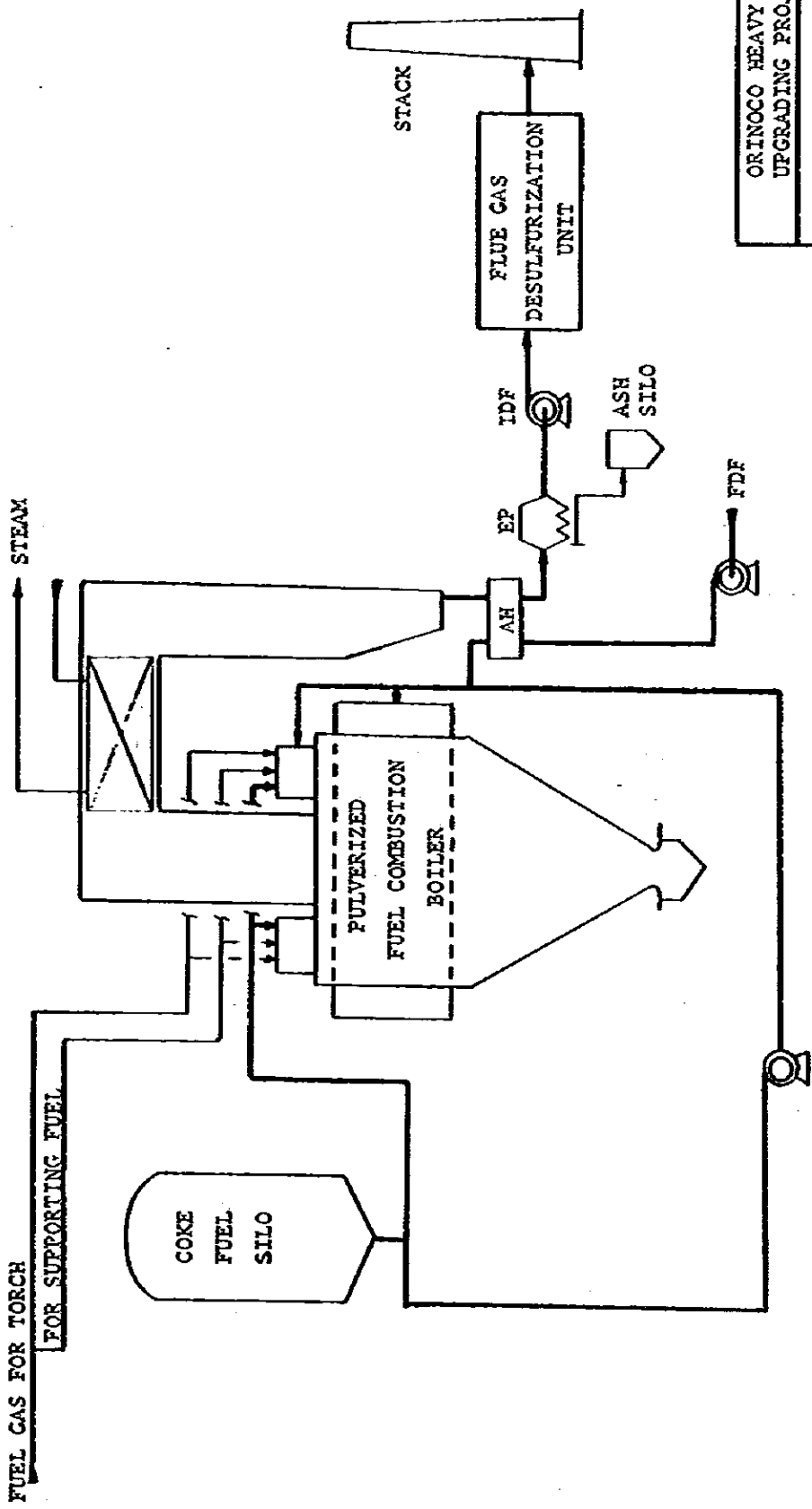
##### (a) Stable ignition and combustion

- The boilers are of the vertical U-frame combustion type.
- A supplementary fuel is used in an amount corresponding to 10% of the total heat requirements of boilers.
- An air temperature as high as possible is used (such as 350°C).
- Primary air is restricted to a level as little as possible, and instead, tertiary air is used for major combustion, so that combustion control can be improved.





ORINOCO HEAVY OIL  
UPGRADING PROJECT  
SIMPLIFIED FLOW DIAGRAM  
OF  
COKE HANDLING SYSTEM  
FIG. I.5



ORINOCO HEAVY OIL  
UPGRADING PROJECT

SIMPLIFIED FLOW DIAGRAM  
OF  
COKE BOILER SYSTEM

FIG. 1.6

(b) Furnaces

- The furnaces are of a water jacketed wall structure. Burner zones are lined with a refractory material to help ignite and burn the coke feed.
- The furnace is equipped with a hopper. When molten ash is deposited on the furnace bottom, it is withdrawn through the bottom and received by the hopper.

(c) Dust collection

A dust collector is installed to catch dust and soot entrained by flue gas.

(d) Measures against corrosion at high temperatures

An additive, magnesium hydroxide, is injected into boilers. This additive is generally known to be effective in raising the melting point of ash, and thereby in reducing high-temperature corrosion of metallic materials. It is further expected that this additive serves also to suppress the emission of  $SO_3$ , thus making this additive effective as a measure against low-temperature corrosion. The quantity to be added is usually set, using Mg/V as the indicator. Preferably it is injected at a level about 1/2,000 to 1/6,000 as much as the fuel quantity.

(e) Measures against corrosion at low temperature

The fuel has a sulfur content of 5.8% and an estimated  $SO_x$  content of about 3,500 ppm. If about 5% of  $SO_2$  is converted to  $SO_3$ , the  $SO_3$  level may reach 170 to 180 ppm at the boiler outlet. In that case, the dew point of sulfuric acid rises. Therefore, temperatures are controlled, as follows:

Feedwater temperature at the inlet of economizer:	$\geq 190^\circ\text{C}$
Flue gas temperature at the outlet of air preheater:	$\geq 180^\circ\text{C}$

### 1.3.3 Economics

(1) Boiler data:

Steam production	500 tons/hr.
Steam pressure	100 kg/cm <sup>2</sup> G
Steam temperature	500°C
Fuel consumption	40,100 kg/hr.
Consumption of supporting fuel	4,460 kg/hr.
Rate of combustion air flow	682,000 kg/hr.
Gas flow rate at combustion chamber outlet	726,560 kg/hr.
Gas temperature at air preheater outlet	190°C
Auxiliary power	8,300 kw
Cooling water flow rate	Approx. 80 m <sup>3</sup> /hr.
Control air	Approx. 5 Nm <sup>3</sup> /min.

**(2) Construction cost:**

With two boilers each having a capacity of 500 tons/hr. and related equipment listed below, the cost of a boiler plant is estimated at 14,000 million Japanese Yen. The cost is calculated for middle 1980 on the present price basis, assuming that the plant is erected in the Chiba area, Japan. The related equipment includes;

- Coke transport and storage facilities.
- Burning facilities, including mills, coke feeders, and burners.
- Boilers.
- Blowers.
- Electric dust collector.
- Water supply system
- Steam- and water-pipes.
- Instrumentation and control devices.

The cost also includes the costs for design and construction work.

**(3) Area requirement for the fluid coker process:**

An area of 130 m x 150 m is required to accommodate fluid coker units and coke handling equipment. Major storage silos have the following sizes:

A coke silo for the startup/shutdown use:	15 m $\phi$ x 22 mH
Fluid coke silos:	22 m $\phi$ x 33 mH x 5
A fine coke silo:	13 m $\phi$ x 20 mH

The 500-ton-per-hour boiler of the pulverized coke combustion type has a size of about 11.5 m x 14 m x 36 mH.

## CHAPTER 2 DETAILED DESCRIPTION OF EUREKA PROCESS (Prepared by Kureha Chemical Industry Co., Ltd.)

### 2.1 TECHNOLOGY OF PROCESS

#### 2.1.1 Introduction

The most important factors required in an upgrading process of heavy crude oil are:

- (1) High oil yield
- (2) Oil properties which can afford the conversion of the oil to the widest range of useful petroleum products through ordinary treating processes, and
- (3) Effective utilization of residues.

Besides meeting the above requirements, the produced synthetic crude oil must be able to compete costwise with crude oil from conventional oil fields.

Upgrading processes of heavy crude oil can be classified as follows:

- (1) Physical removal of impurities (solvent extraction).
- (2) Hydrogenation (hydrogen addition), and
- (3) Removal of surplus carbon by thermal energy application (carbon rejection).

The EUREKA Process is a thermal cracking process belonging to the classification (3).

Generally no catalyst is used in thermal cracking, which gives the characteristics that it does not specify the kinds of impurities contained in treated heavy oil, and that it is not necessary to settle the problem of catalyst exchange caused by heavy metal and heavy component poisoning or coking.

The EUREKA Process, which is a thermal cracking process achieved by the use of steam, differs remarkably from other processes in that it is characterized by its unique properties of pitch. As to the oil properties, the yield of heavy gas oil fraction is relatively high, which shows that further treatments can convert it to a petroleum product pattern which fits into the specific refinery requirement.

The remnant is a highly stabilized and homogeneous pitch, a polycondensation material of an aromatic nature.

This kind of pitch, besides being used as an additive in coke manufacturing for the iron and steel industry, may be utilized for a wide variety of applications.

Another of its merit is that, though it is in a solid state similar to coal at normal temperatures, it can be handled in a fluid state through the EUREKA Process and the plant can be kept clean without the need for handling solid bodies.

Since the first EUREKA Process commercial plant (with an approximate capacity of 20,000 BPSD) commenced operation in February 1976, it has been successfully operated for over four years.

More than thirty kinds of crude oil have been treated, most of which are of Middle East origin with the recent inclusion of Venezuelan heavy crude oil.

Generally speaking, one of the difficulties of heavy oil upgrading may be coking problems. In the EUREKA Process thorough and careful countermeasures against coking have been applied and their effectiveness have been confirmed through actual operation during the last four years.

Because of the characteristic high cracked oil yield and the capacity for producing valuable pitch, the EUREKA Process has attracted public attention.

Tests are being carried out with various kinds of feedstock. It has been proved that Canadian oil sand bitumen and other kinds of heavy oil can also be used as feedstocks.

The Shengji vacuum residue of the People's Republic of China will be used as a feedstock to the second commercial plant of EUREKA Process at the Nanjing Petrochemical Complex. It is expected to commence operation in 1982, and the cracked oil is supposed to become a feedstock to an ethylene plant.

In view of the long-term experience and confirmation in the actual plants, it is clear that the EUREKA Process is the most suitable of the heavy oil upgrading processes.

### 2.1.2 Background & History of Process Development

The EUREKA Process, a thermal cracking technique achieved by means of high temperature steam, was established by the Kureha Chemical Industry Co., Ltd. as a result of a series of developments in thermal cracking technology for acetylene and ethylene manufacture.

First, KUREHA achieved the manufacture of vinyl chloride by a new technology including naphtha thermal cracking, and started the operation of the first commercial plant in 1964.

Know-how was subsequently exported to foreign countries, and five plants have so far been constructed worldwide. The above development was followed by the study of thermal cracking of crude oil when KUREHA anticipated the necessity for treating heavier materials for petrochemicals in the future. In 1970, KUREHA started its commercial plant operation for thermal cracking of crude oil to produce acetylene and ethylene by means of high temperature steam.

With its accumulated thermal cracking technology, KUREHA set about the technical development of the EUREKA PROCESS in 1970 with a view to producing cracked oil which can be easily desulfurized, and pitch of highly aromatic nature by means of the thermal cracking of vacuum residue. In 1972, KUREHA constructed a 45 BPSD pilot plant with the co-operation of Chiyoda Chemical Engineering & Construction Co., Ltd.

In those days, there were two social backgrounds in Japan.

On the one hand, low sulfur fuel oil was required to meet the demands of pollution

problems and the surplus vacuum residue had to be utilized effectively as the import of heavier crude oil was on the increase.

On the other hand, the iron industry was confronted with the scarcity and price rise problems of high-grade coal as a raw material.

To solve the latter, Sumitomo Metal Industries, Ltd., in co-operation with KUREHA, developed a technique for producing coke of superior quality by using a large quantity of cheap non-coking coal instead of expensive coking coal, with the aid of the special additive of a highly aromatic pitch, produced by the EUREKA Process, and put the techniques to practical use.

In the meantime, Arabian Oil Co., Ltd. which produces high sulfur heavy crude oil at Khafji in the Middle East, and Fuji Oil Co., Ltd. which purchases the Khafji crude as one of its importing crude oils showed a keen interest in the EUREKA Process.

As a result, a joint venture company, the Eureka Industry Co., Ltd. was established by the four concerned companies, KUREHA, SUMITOMO, ARABIAN OIL, and FUJI OIL.

In February 1976, the first commercial plant with a capacity of some 20,000 BPSD of vacuum residue was completed on the FUJI OIL site at Sodegaura on the coast of Tokyo Bay. It has been operating successfully up to the present.

The second commercial plant to be constructed in Nanjing, China is now being engineered by CHIYODA. This plant, with a capacity of 20,000 BPSD is expected to start operation in summer in 1982 and will dispose of the vacuum residue of Shengli crude.

The following is a summary of the KUREHA's historical events related to the KUREHA thermal cracking technique:

- 1964 Mixed gas process commercial plant for the production of vinyl chloride by naphtha cracking started operation.
- 1967 Pilot plant for crude oil cracking.
- 1968 Pilot plant for carbon fiber production.
- 1970 Crude oil cracking commercial plant started operation.  
Carbon fiber production plant started operation. Pilot plant for activated carbon production.
- 1971 Pilot plant for vacuum residue cracking.  
Eureka Industry Co., Ltd., a joint venture of FUJI OIL, ARABIAN OIL, SUMITOMO, and KUREHA was established.
- 1972 Commercial plant for activated carbon production started operation.
- 1973 Co-development study was started with the Union Carbide Corporation and CHIYODA on the crude oil cracking process for olefin production.
- 1976 20,000 BPSD commercial plant for vacuum residue cracking started operation.

### 2.1.3 Process Description

Fig. 2.1 shows a brief process flow chart. The EUREKA Process consists of the following.

- (1) Heater Section
- (2) Cracking Reaction Section
- (3) Cracked Oil and Gas Fractionating Section
- (4) Cracked Gas Desulfurizing Section
- (5) Pitch Flaker Section
- (6) Waste Water Treatment Section

Petroleum residual oils are mostly complex mixture of hydrocarbons and their molecular structures are not known very well.

The above makes it difficult to grasp and explain the exact reacting process of thermal cracking reactions. The fundamental chemical reactions, however, are considered to be as follows:

- (a) Thermal cracking reaction of paraffinic and naphthenic portions of large molecules forms paraffinic oil of lower molecular weights with a small amount of gaseous hydrocarbons.
- (b) Radical condensation reaction between dealkylated asphaltenes forms higher molecular weight aromatic pitch.

These reactions take place simultaneously in the reactor.

The feedstock is fed to the preheater, where it is heated to about 340°C. It then enters the bottom of the fractionator to be mixed with recycled oil. The mixing ratio of the feedstock and the recycled oil, namely the recycle ratio, is determined by the properties of the feedstock as well as by the selection of the end point of the cracked oil. The effluent sent out of the fractionator is charged to the reactor through the switch valve after being heated up to cracking temperature by the charge heater.

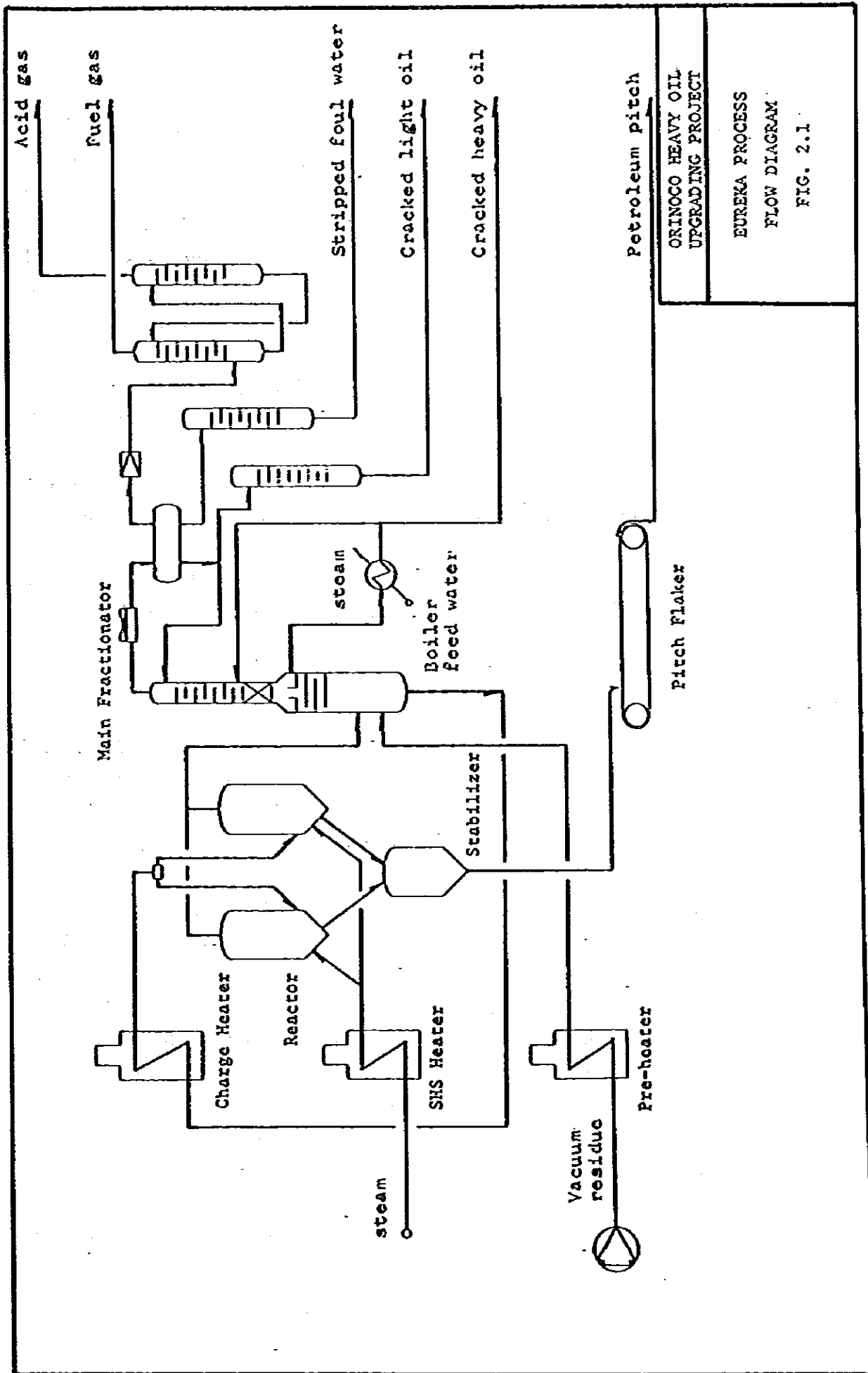
There are two paired reactors so that the feed may be done alternately, acting similarly to coke drums in delayed cokers.

Both cracking and polycondensation in a fluid state take place in the reactors. The heat required for the cracking reaction is provided by the charge heater effluent and the superheated steam (SHS) blown into the reactors.

At the same time, the SHS plays a part in stripping the cracked oil immediately out of the reaction system. The thermal cracking reaction is carried out semibatchwise, and the standard cycle time is four hours. The procedures on the above basis are:

- |                                    |        |
|------------------------------------|--------|
| (a) Feed charge                    | 2 hrs. |
| (b) Soaking                        | 1 hr.  |
| (c) Quench, Blow down and Stand-by | 1 hr.  |





ORINOCO HEAVY OIL  
UPGRADING PROJECT

EUREKA PROCESS  
FLOW DIAGRAM

FIG. 2.1

The cracked products – oil and gas – are introduced into the fractionator from the top of the reactor, together with steam.

A very small amount of entrained pitch is washed at the lower part of the fractionator. The upper of the fractionator is an ordinary distilling column.

The viscosity of the reactor bottom material gradually increases as a result of a polycondensation reaction. The extent of the reaction is conveniently measured in terms of the softening point (SP) of the bottom material. This bottom material is called “pitch.”

When the SP reaches a predetermined point, the pitch is quenched and blown down into a vessel called “a stabilizer”.

Pitch is in a fluid state in the vessel, and continuously pumped to the flaker.

In the flaker, pitch is uniformly and thinly spread on the surface of the steel belt, and solidifies into flake pitch as it is cooled.

The cracked gas is used as a fuel in the process after hydrogen sulfide and others have been removed. The cracked oil is separated into two fractions – cracked light oil (CLO) and cracked heavy oil (CHO).

The heat carried by the CHO is effectively recovered as steam. The recovered steam almost compensates for the consumption of steam within the reaction section of this process.

#### 2.1.4 Process Features

The reaction condition of the EUREKA Process is milder than that of a delayed coker, and the reaction temperature in the reactor is 410–430°C under atmospheric pressure.

The reactor system consists of a pair of equivalent units, and though the reaction is carried out semibatchwise, the feed is continuous.

If the heavy oil is kept at the cracking temperature for some time, there occur two completely opposite simultaneous reactions – cracking and polycondensation. It is generally impossible to thermally convert heavy oils into light oils without forming such polycondensation products as tar, pitch, coke, and so on.

Herein lies the problem of the polycondensed products of the thermal cracking process. The residue thermal cracking processes are classified into the following three categories according to the state of the products:

- (1) Solid . . . . . Coker (Delayed coking, Fluid coking process)
- (2) Liquid . . . . Homogeneous pitch (Eureka process)
- (3) Gas . . . . . Fuel gas (Flexicoking process)

The third process is essentially the same as fluid coking if coke gasification is excluded.

If the reaction is stopped on its way to coke formation in category (1), a liquid product might be obtained, but homogeneous pitch will not be obtained in this case.

As a result, the reactor will suffer from severe coking, and stable and continuous operation will be practically impossible.

It is clear, therefore, that the second case is unique and differs remarkably from the other two.

The outstanding characteristics of the EUREKA Process are as follows:

- (a) A high yield of cracked oil is obtained.
- (b) As the reactor bottom material – pitch – can be handled in a fluid state, the plant itself is operated easily and the plant yard can be kept clean and hygienic since it is not necessary to perform the cutting off of coke and the like.
- (c) The produced pitch is a highly stable and homogeneous material, and it may be utilized effectively in many ways. One of them is its use as a special additive for manufacturing high-grade coke from low-grade coking coal, and the method has already been put to practical use.

The utilization as a gasifier feedstock and as a fuel is also drawing attention.

- (d) The cracked gas yield is low at only 4 to 5%. Yet the production rate almost satisfies the amount of fuel required by the unit.

The typical product yields and properties of the EUREKA Process are shown in Table 2.1.

#### 2.1.5 Feedstock Variation

The yields and product properties from the commercial plant and pilot operation are summarized in Table 2.1. While the product yields are somewhat influenced by the feedstock properties, the product properties, with the exclusion of sulfur content are almost independent of the feedstock in the case of the Middle Eastern crude oils such as Khafji, Kuwait, Arabian Light, Iranian Heavy, and Murban.

Table 2.2 shows the crude oil sources processed at a commercial plant or test plant.

**Table 2.1 Feed & Product Properties and Product Yields**

Crude Source		Arabian Light	Arabian Heavy	Iranian Heavy	North Slope	Shengli
<b>Feed</b>						
Nominal Cut Point	(°F)	1,000+	930+	1,020+	1,000+	950+
Gravity	(°API)	8.0	5.9	6.3	8.5	14.3
CCR	(WT%)	20.5	21.2	20.9	15.1	13.5
Sulfur	(WT%)	4.2	5.19	3.37	1.93	1.32
Metals V/Ni	(PPM)	66/24	131/45	429/121	63/33	3.5/50
<b>Product Yield</b>						
Cracked Gas (C1-C4)	(WT%)	5.2	4.9	4.9	5.3	5.5
CLO	(WT%)	11.3	14.1	14.2	12.9	12.3
CHO	(WT%)	53.4	50.3	50.6	58.9	57.2
Pitch	(WT%)	30.1	30.7	30.3	22.9	25.0
Total	(WT%)	100.0	100.0	100.0	100.0	100.0
<b>Product Properties</b>						
<b>CLO</b>						
Nominal Cut Point	(°F)	C5-460	C5-460	C5-460	C5-450	C5-450
Gravity	(°API)	51.8	51.8	51.8	52.0	54.2
Sulfur	(WT%)	1.5	1.6	1.1	0.8	1.23
Bromine No.		89	89	89	89	66
<b>CHO</b>						
Nominal Cut Point	(°F)	460-1,000	460-1,000	460-1,000	460-990	450-930
Gravity	(°API)	21.5	21.5	21.5	20.7	28.4
Sulfur	(WT%)	2.7	3.7	2.6	1.5	0.99
Bromine No.	(WT%)	35	35	35	35	30
<b>Pitch</b>						
Softening Point*	(°F)	360	360	360	420	270
Sulfur	(WT%)	6.9	7.95	4.7	2.9	1.3

\* By Kureka Testing Method

**Table 2.2 Vacuum Residue Experienced in Eureka Test Plant**

Oil sand bitumen	Arabian light	
Lloydminster	Iranian light	
Bow river	Kuwait	
Orinoco heavy oil (Cerro Negro)	Ummshaif	
Bachaquero		
Arabian Heavy	Murban	
Khafji	Oman	
Iranian Heavy	Zakum	
Gach Saran		
Hout		
Basrah Heavy	Shengli	Others

#### 2.1.6 Process Application & Utilization of Cracked Oil

Fig. 2.2 shows the application of the EUREKA Process. The Figure is based upon actual operation in Japan, and the cracked oil is used for low sulfur fuel oil after hydro-treating.

In addition, the heavy gas oil yield of the EUREKA Process is relatively high, and it is possible to manufacture various petroleum products to meet the demand of the market by the combined application of other treatment equipment.

Some examples of these schemes are shown in Figs. 2.3, 2.4 and 2.5. A proper combination could be selected depending on the specific requirement to meet the market demand by the refinery.

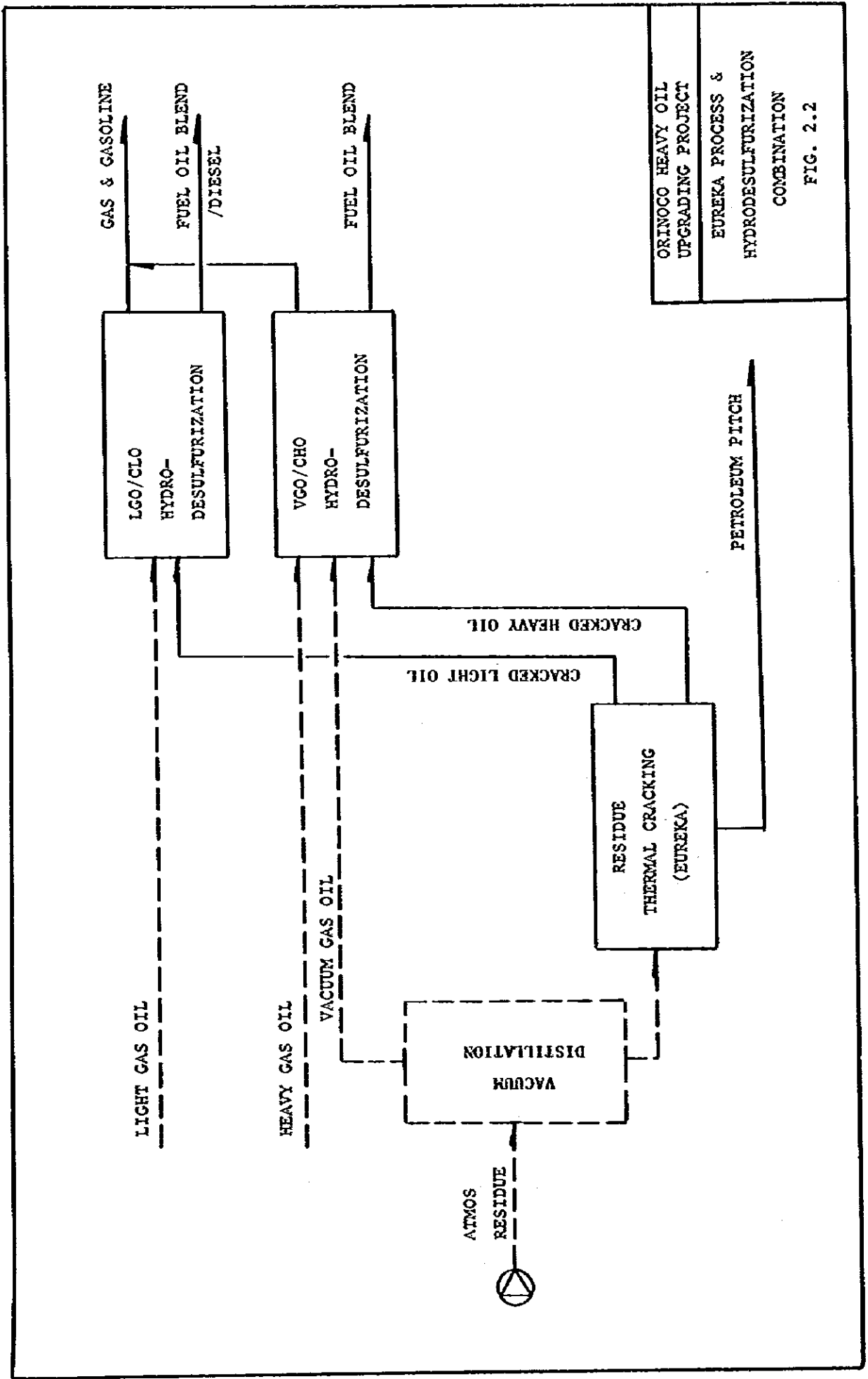
Fig. 2.5 shows an example in which the cracked oil is used as feedstock for an ethylene plant.

The following features of the further processing of the EUREKA Process cracked oil may be mentioned.

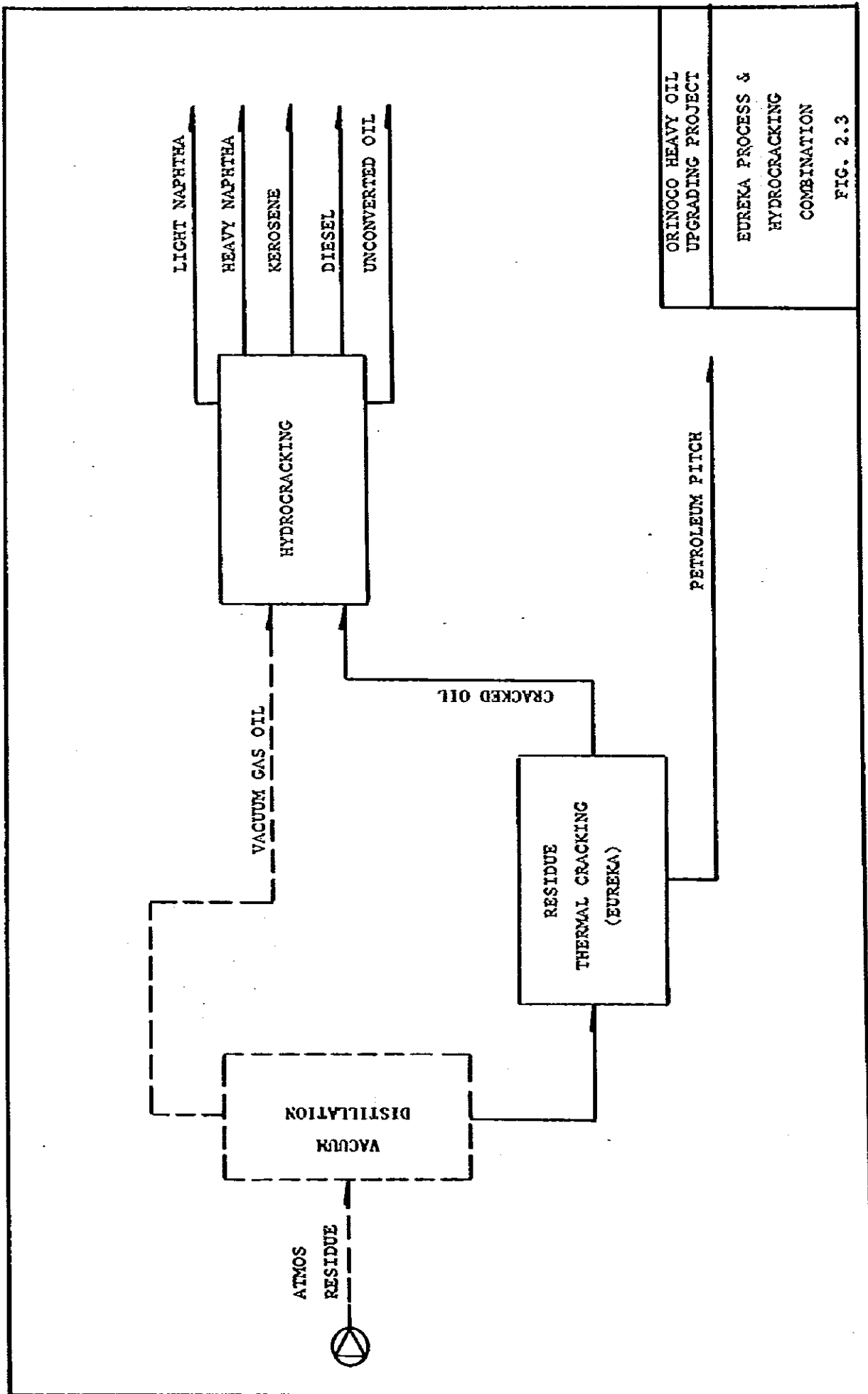
(1) Since the octane number of  $C_5/180^\circ\text{C}$  portion naphtha is relatively low and the sulfur content is high, it may not be used as a gasoline blendstock as it is. It can be converted to a high octane gasoline blendstock, if it is treated in the pretreater and/or the catalytic reformer. In this case, the sulfur compounds in  $C_5/180^\circ\text{C}$  portion can be reduced to almost zero in the pretreater.

(2) Diesel Oil for  $180/360^\circ\text{C}$  Fraction

The  $180/360^\circ\text{C}$  portion has a good specific gravity, distillation properties, and



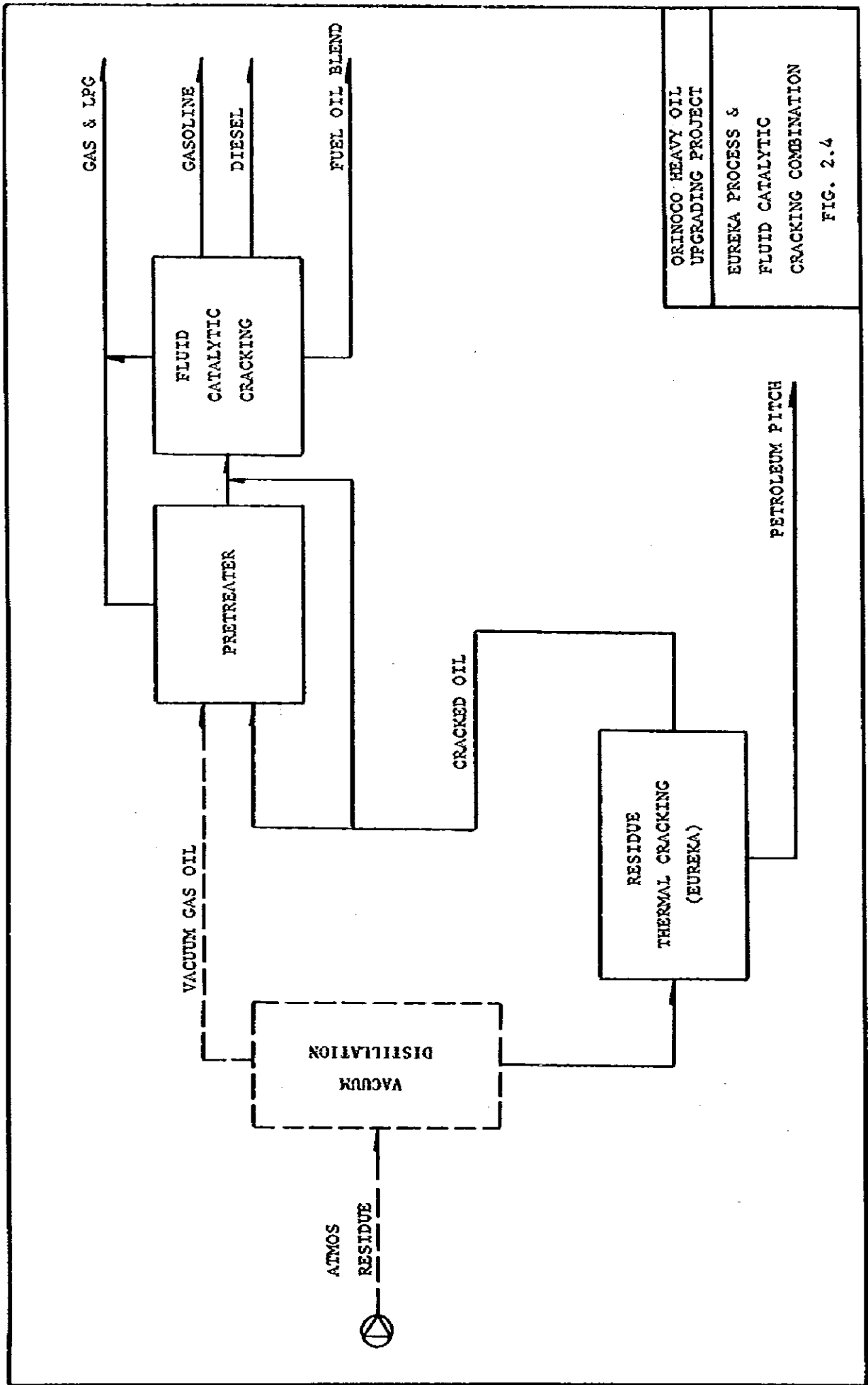
ORINOCO HEAVY OIL UPGRADING PROJECT  
 EUREKA PROCESS & HYDRODESULFURIZATION COMBINATION  
 FIG. 2.2



ORINOCO HEAVY OIL  
UPGRADING PROJECT

EUREKA PROCESS &  
HYDROCRACKING  
COMBINATION

FIG. 2.3

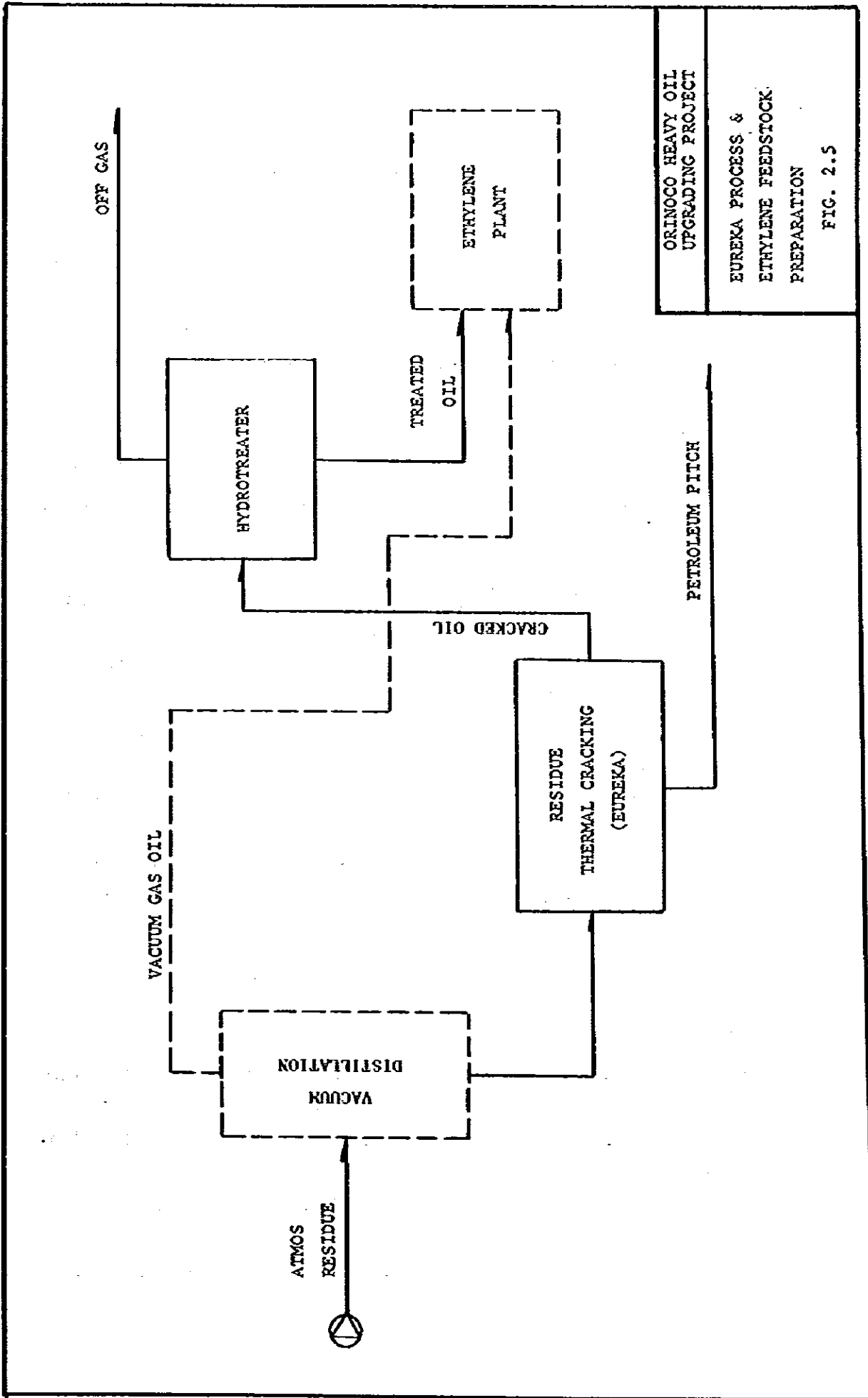


ORINOCO HEAVY OIL  
UPGRADING PROJECT

EUREKA PROCESS &  
FLUID CATALYTIC  
CRACKING COMBINATION

FIG. 2.4





ORINOCO HEAVY OIL  
UPGRADING PROJECT

EUREKA PROCESS &  
ETHYLENE FEEDSTOCK  
PREPARATION

FIG. 2.5

cetane number for diesel oil. However, its sulfur and olefin contents are rather high. This portion can be used as a diesel oil blendstock after it is hydrotreated.

### (3) FCC, Hydrocracker Feedstock for 360/500°C Fraction

The 360/500°C portion can be converted to various petroleum products through FCC or Hydrocracker treatment.

If fed to the FCC unit after being pretreated in the hydrotreater to remove sulfur and carbon residue, it makes the FCC unit operate at milder conditions with higher gasoline yield.

## 2.2 PROCESS SCHEME FOR IMPROVED CRUDE OIL PRODUCTION

### 2.2.1 Introduction

The EUREKA Process thermal cracking tests on the samples sent from Venezuela through Japan International Cooperation Agency (JICA) were carried out on a laboratory and bench scale at KUREHA Laboratory in Iwaki City, Fukushima Pref. from March 1 to March 31, 1980.

The Venezuelan Orinoco heavy crude (CERRO NEGRO) was pretreated by JICA, and about 100kg vacuum residue was supplied as the test sample.

The cut point of this sample was markedly lower than the cut point fixed up as the condition of this study (995°F) because the sample was relatively susceptible to thermal cracking and there were also some technical restrictions on the pretreatment equipment.

It was thought that the tested sample might be a little different from what it is supposed to be, since the tested sample showed a somewhat larger Conradson Carbon Residue value than that of LAGOVEN crude assay, the study basis.

For the above reasons, all the data given in this report were prepared by making a correction to the test results to fit in with 995°F + vacuum residue of LAGOVEN's crude assay.

### 2.2.2 Cracking Tests and Test Facilities

#### (1) Outline of test facilities and method

The test was performed by the combination of the fundamental study by the flask scale apparatus and the more quantitative study by the bench scale. Fig. 2.6 shows the rough design of the Bench Scale. Table 2.3 shows an example of typical experimental conditions.

The properties of the sample used for the cracking test and the study basis data from LAGOVEN's crude assay are given in Table 2.4.

The results of the thermal cracking test revealed the following characteristics of the

Orinoco heavy crude vacuum residue, as compared with the vacuum residue from the Middle Eastern crudes actually used at the present commercial plant.

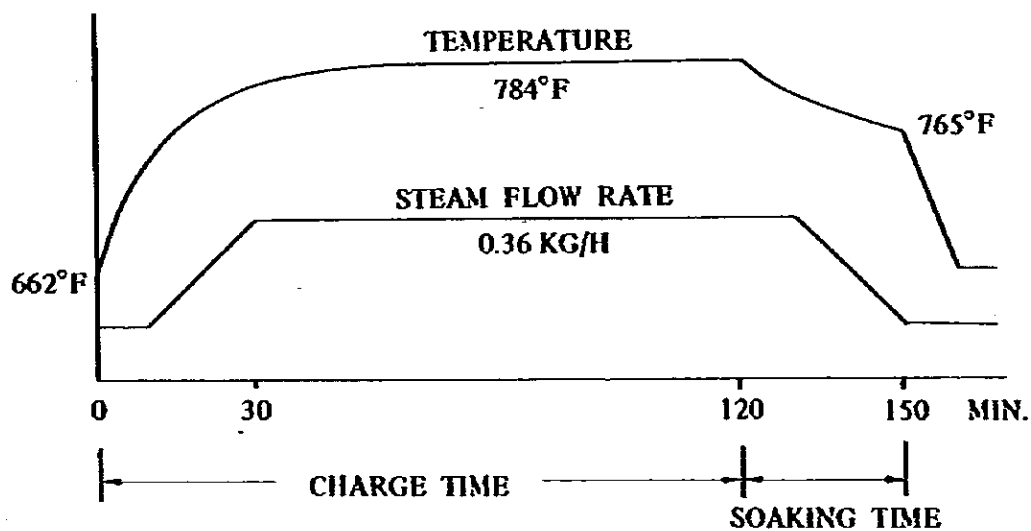
- (a) Reaction rate is faster, so the reaction temperature can be lowered.
- (b) Coking in the reactor is smaller.

From these characteristics, this material is regarded to be treated easily by EUREKA Process more than the vacuum residue from the Middle East crude, and it may be said that this material is suitable as feedstock for the EUREKA Process.

**Table 2.3 Experimental Conditions**

Feed Rate	Kg/H	2.4
Recycle Ratio	—	0.21
Tube Heater Cond'ns		
Outlet Temperature	°F	842
Outlet Pressure	PSIG	286

Reactor cond'ns are shown below.



Reactor Pressure : Atmospheric

**Table 2.4 Properties of Cogollar IX/Cerro Negro Vac. Residue**

	(A)	(B)	Reference
Nominal Cut Point, °F	830	995	932
API Gravity	3.9	1.8	7.4
Sulfur, wt%	4.1	4.3	3.9
Nitrogen, "	0.83	0.82	0.51
C.C.R., "	22.8	25.7	20.0
Vanadium, ppm	559	654	202
Nickel, "	148	162	136

(A): The sample for the test, prepared by JICA

(B): The study basis, taken from the Crude Assay

Reference – Typical feedstock of Sodegaura Plant  
(Mid. – East mixtures)

### 2.2.3 Yield & Properties of Cracking Products

#### (1) Yield

Fig. 2.7 shows the overall material balance based on the study basis feedstock, that is to say, a necessary correction was made to the experimental results. Though the pitch softening point was fixed at the same level as applied to present commercial plant production, it is considered, from the properties of the pitch obtained from the experiment, that the softening point can be further raised. In that case, it will be possible to lower the pitch yield and to raise the cracked oil yield respectively, as compared with the values given in Fig. 2.7.

#### (2) Properties

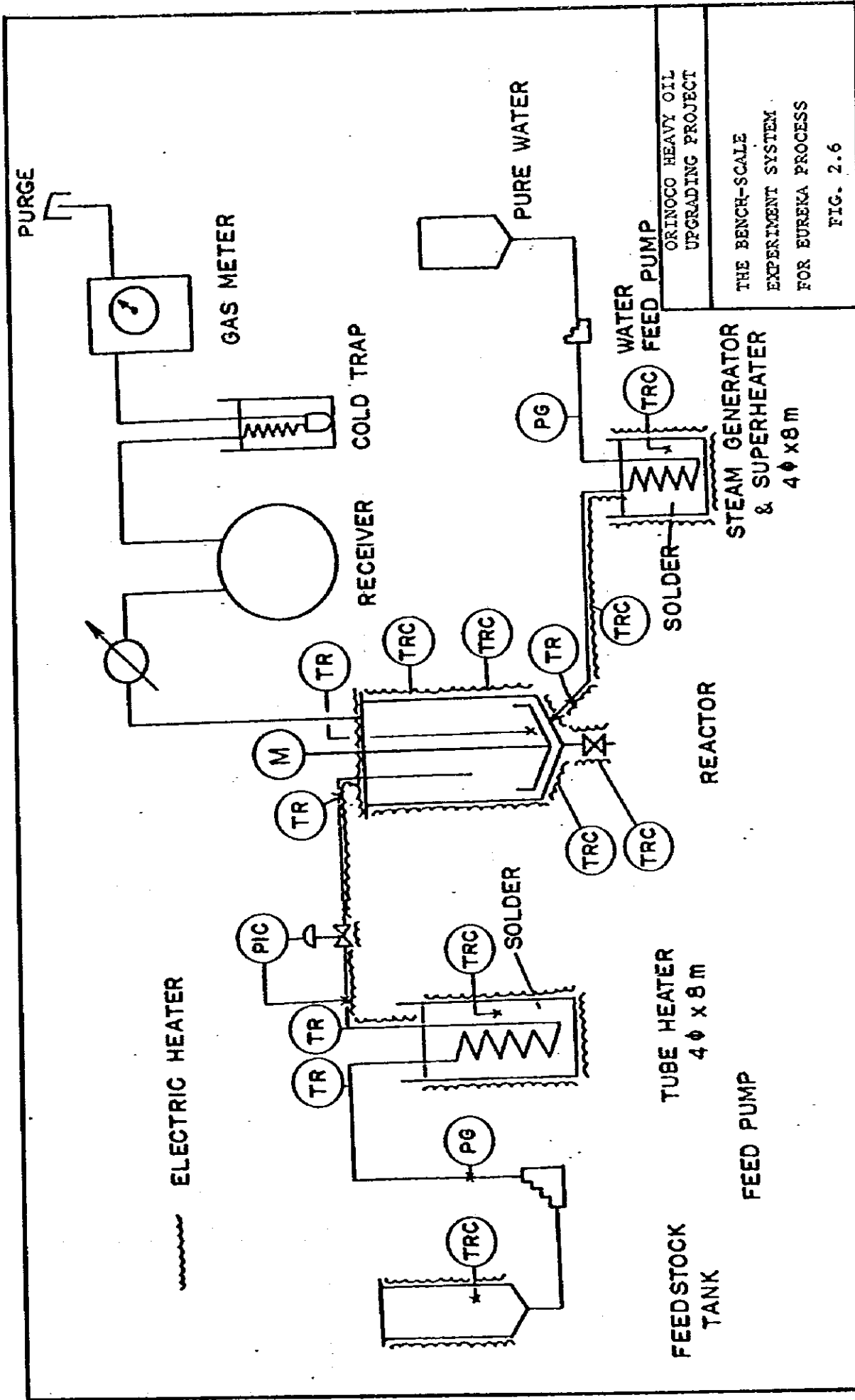
##### (a) Cracked gas composition

Table 2.5 shows the gas composition obtained from the corrected data of the experiment.

CO and CO<sub>2</sub> values are somewhat larger than those of the vacuum residue of the Middle Eastern crude oils. It is supposed that the difference comes from the oxygen compounds in them.

##### (b) Cracked oil properties

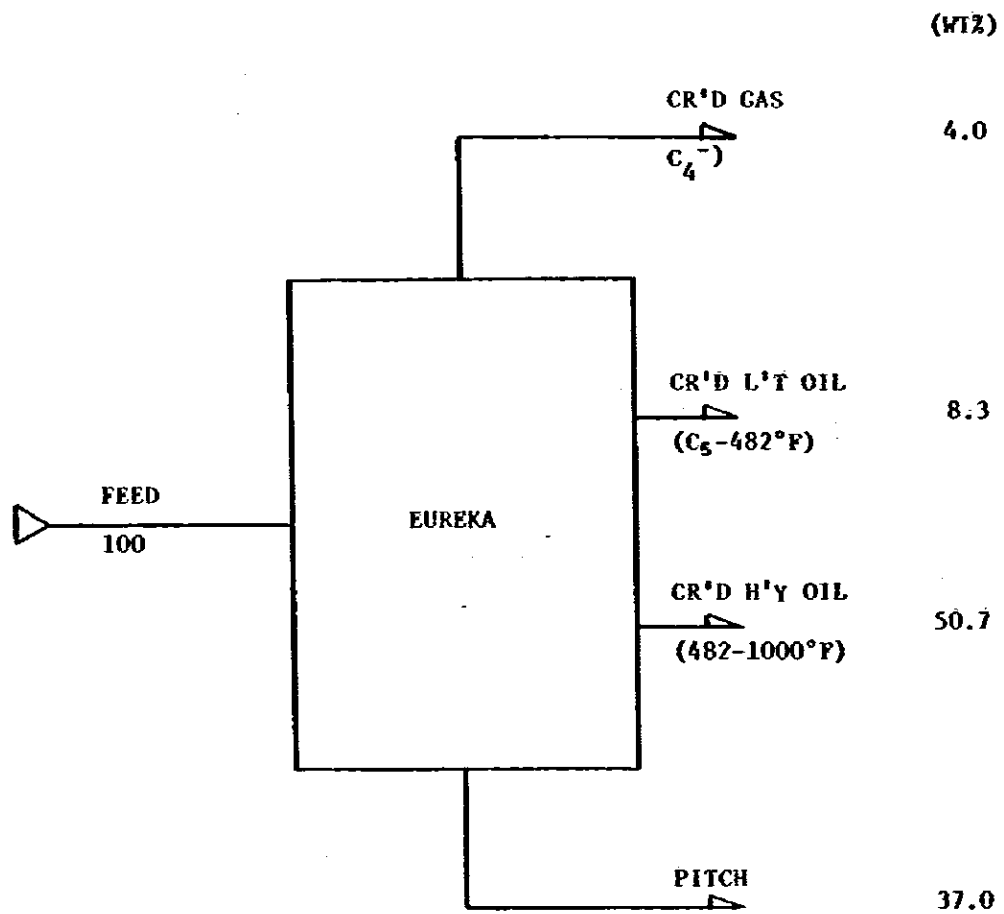
Table 2.6 shows the properties of the cracked oil obtained from the corrected data of the experiment. In spite of the high rate of heavy metals contained in the material, their transfer into the cracked oil is very small, and the heavy



ORINOCO HEAVY OIL  
UPGRADING PROJECT

THE BENCH-SCALE  
EXPERIMENT SYSTEM  
FOR EUREKA PROCESS

FIG. 2.6



ORINOCO HEAVY OIL  
UPGRADING PROJECT

OVERALL  
MATERIAL BALANCE

FIG. 2.7

**Table 2.5 Cracked Gas Composition**

	vol. %
H <sub>2</sub>	3.54
CH <sub>4</sub>	35.42
CO	1.73
CO <sub>2</sub>	1.39
C <sub>2</sub> H <sub>4</sub>	2.07
C <sub>2</sub> H <sub>6</sub>	15.16
C <sub>3</sub> H <sub>8</sub>	8.75
C <sub>3</sub> H <sub>6</sub>	4.62
C <sub>4</sub> H <sub>10</sub>	4.87
C <sub>4</sub> H <sub>8</sub>	4.82
1,3-C <sub>4</sub> H <sub>6</sub>	0.01
H <sub>2</sub> S	17.59
Mercaptanes	0.3

**Table 2.6 Cracked Oil Properties**

		CLO	CHO
Nominal Cut Point	°F	C <sub>5</sub> – 482	482 – 1,000
API Gravity	–	50.6	16.8
Sulfur	wt%	0.6	3.6
Nitrogen	"	–	0.3
Vanadium	ppm	–	<0.1
Nickel	"	–	<0.1
Bromine No.	–	84.9	42.3
Diene Value	–	4.9	4.5
Total Acidity	–	<0.1	1.46
<b>ASTM Distill</b>			
IBP	°F	109	426
10 vol%	"	205	576
50 "	"	324	788
90 "	"	442	928
97 "	"	486	995

metal compound in the cracked oil is the same as that in Middle East raw materials.

(c) Pitch properties

Table 2.7 shows the pitch properties obtained from the corrected data of the experiment.

In comparison with the Middle East materials, the sulfur content in the pitch is lower because the sulfur content in the raw material tends to be transferred uniformly into the cracked products (gas and oil).

The produced pitch is also very homogeneous, and the quinoline insolubles are low.

At the same time, it is supposed that the homogeneity of this pitch will make it easier to treat it in a fluid state at high temperatures than to treat the pitch of the Middle East crude origin. This will be an advantage in the operation of the EUREKA Process unit as well as in the effective utilization of the produced pitch.

Taking account of the ash content in the pitch was excluded from this study because the ash quantity after the desalting treatment of the raw crude oil could not be confirmed.

**Table 2.7 Pitch Properties**

			Reference
Softening Point	°F	428	439
Volatile Matter	wt%	45.3	39.7
C	"	86.1	85.8
H	"	6.1	6.0
S	"	4.4	5.7
N	"	1.7	1.2
H/C	—	0.85	0.83
Vanadium	ppm	1,598	688
Nickel	"	400	487
Heptane Insol.	wt%	72.1	80.4
Benzene Insol.	"	49.5	51.5
Quinoline Insol.	"	10.5	17.8

Reference — Typical pitch properties of Sodegaura Plant (Mid.—East mixture)



## 2.2.4 Investigation of Improved Crude Oil Production System

### (1) Flow Scheme

On the basis of the results of the foregoing cracking test, the upgrading scheme to produce improved crude oil with the fixed properties (25–30°API, sulfur content max. 1 wt%) was investigated. (See Fig. 2.8) This scheme consists of the following process units:

- Atmospheric Distillation Unit
- Vacuum Flashing Unit
- EUREKA Thermal Cracking Unit
- #1 Hydrotreating Unit
- #2 Hydrotreating Unit
- Hydrogen Generation Unit
- Acid Gas Removal Unit
- Sulfur Recovery Unit

In addition to the above units, the scheme is equipped with a Blending System and a Boiler system for which the pitch from the EUREKA Unit is used as a fuel.

This process configuration was selected as it is suitable for producing 125,000 BPSD improved crude oil to meet the specified properties, from as little raw crude oil as possible.

The improved crude oil produced here almost satisfies the target properties except the distillation yield of each fractions.

The selection is based upon the following considerations:

- (a) Though it is possible to use raw crude or reduced crude directly as a feedstock for the EUREKA unit, it was considered valuable from the economic viewpoint of the whole system to equip it with both an atmospheric distillation unit and a vacuum flashing unit so as to separate the light distillates first by the ordinary method and to use the vacuum bottoms as feedstocks for the EUREKA unit.
- (b) The kind of desulfurization unit and the operating conditions (pressure, temperature, kind and quantity of catalysts, H<sub>2</sub> consumption, etc.) are largely influenced by the properties of the crude oil and the target properties of the produced oil. However, as regards the specific gravity (25 – 32°API) and sulfur content (max. 1 wt%) of the improved crude as whole fraction, these properties may be satisfied even by blending the other desulfurized distillates (VGO, Cracked Oils) without desulfurizing the light distillates (Naphtha, straight run Gas Oil).

With a view to attaining the target yield of each distillate, the desulfurization

process unit for light oils (Straight run Gas Oil, CLO) and heavy oils (VGO, CHO) are to be prepared separately in this study in consideration of desulfurization conditions.

As to the virgin naphtha, the specifications of the improved crude oil are sufficiently satisfied without the need for desulfurizing itself, by blending it with the desulfurized oil, since the produced quantity and the sulfur content are both small.

Among the target properties of the improved crude oil, the distillate yields at  $C_4-375^\circ\text{F}$  and  $650-1,000^\circ\text{F}$  have not been achieved by this proposed scheme and under each operating condition.

These target can be achieved by changing the desulfurizing unit of the scheme a little to hydrocracking type.

With regard to distillates of  $650-1,000^\circ\text{F}$ , however, if the user of the improved crude oil desire to convert it to the appropriate petroleum product pattern according to the changes of market demand, he can easily attain it by treating that fraction with such process as FCC and the like.

For these reasons, the hydrocracking process has not been adopted in the proposed scheme.

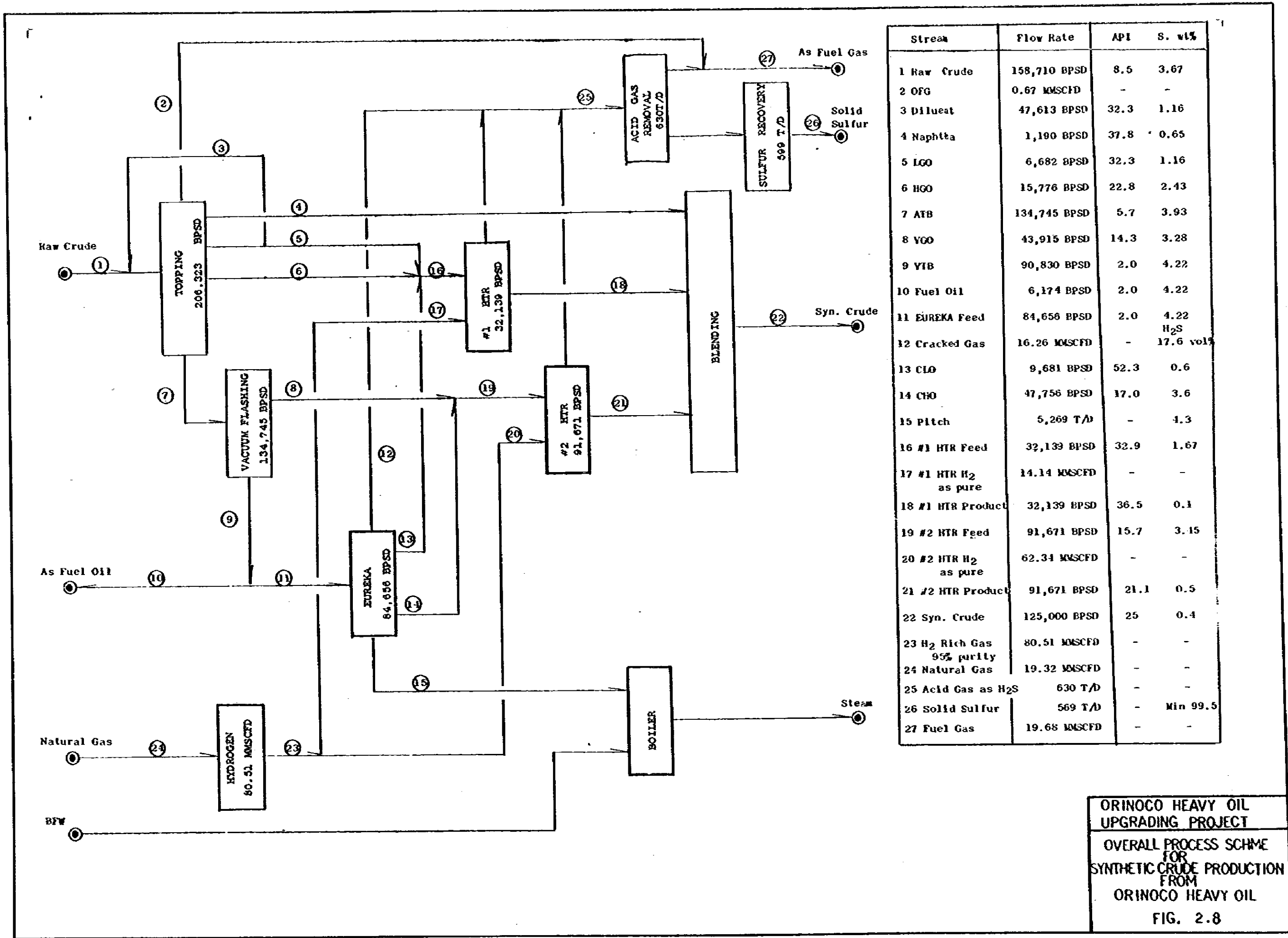
(c) With regard to the fuel system in the upgrading system, the following selection has been made to utilize all the process gas generated in the system for its fuel, since the amount of the process gas is small and it is suitable for the fuel of the  $\text{H}_2$  generating unit, and to use a part of the vacuum bottoms for fuel oil to supplement the insufficiency.

- As a rule, the fuel required by the EUREKA unit can be fully supplied by the cracked gas generated in the Process. In this system, however, part of the cracked gas is used for the  $\text{H}_2$  generating unit, and the insufficiency of the EUREKA unit is supplemented by fuel oil.
- Though the kind of fuel used for the steam reforming  $\text{H}_2$  generation unit differs according to the types of reformer, gas or naphtha is generally utilized. All the gas generated in the system is therefore supplied for this purpose.
- Fuel oil is used for all of the required fuels in the atmospheric distillation, vacuum flashing and desulfurization units.

(d) All of the pitch produced by the EUREKA unit is used as fuel for the boilers to generate the steam for the power plant.

## (2) Material balance

The material balance is given in the flow scheme of Fig. 2.8. The API gravity and the sulfur content are also shown.



Stream	Flow Rate	API	S. wt%
1 Raw Crude	158,710 BPSD	8.5	3.67
2 OFG	0.67 MMSCFD	-	-
3 Diluent	47,613 BPSD	32.3	1.16
4 Naphta	1,190 BPSD	37.8	0.65
5 LGO	6,682 BPSD	32.3	1.16
6 HGO	15,776 BPSD	22.8	2.43
7 ATB	134,745 BPSD	5.7	3.93
8 VGO	43,915 BPSD	14.3	3.28
9 VTB	90,830 BPSD	2.0	4.22
10 Fuel Oil	6,174 BPSD	2.0	4.22
11 EUREKA Feed	84,656 BPSD	2.0	4.22
12 Cracked Gas	16.26 MMSCFD	-	17.6 vol%
13 CLO	9,681 BPSD	52.3	0.6
14 CHO	47,756 BPSD	17.0	3.6
15 Pitch	5,269 T/D	-	4.3
16 #1 HTR Feed	32,139 BPSD	32.9	1.67
17 #1 HTR H <sub>2</sub> as pure	14.14 MMSCFD	-	-
18 #1 HTR Product	32,139 BPSD	36.5	0.1
19 #2 HTR Feed	91,671 BPSD	15.7	3.15
20 #2 HTR H <sub>2</sub> as pure	62.34 MMSCFD	-	-
21 #2 HTR Product	91,671 BPSD	21.1	0.5
22 Syn. Crude	125,000 BPSD	25	0.4
23 H <sub>2</sub> Rich Gas 95% purity	80.51 MMSCFD	-	-
24 Natural Gas	19.32 MMSCFD	-	-
25 Acid Gas as H <sub>2</sub> S	630 T/D	-	-
26 Solid Sulfur	569 T/D	-	Min 99.5
27 Fuel Gas	19.68 MMSCFD	-	-

ORINOCO HEAVY OIL UPGRADING PROJECT  
 OVERALL PROCESS SCHEME FOR SYNTHETIC CRUDE PRODUCTION FROM ORINOCO HEAVY OIL  
 FIG. 2.8

### (3) Properties of improved crude oil

The estimated properties of improved crude oil are shown in Table 2.8.

**Table 2.8 Properties of Improved Crude Oil**

Fraction	Yield (vol %)	Gravity (°API)	Sulfur Content (wt%)
Whole	100	25	0.41
C <sub>5</sub> – 375°F	7.3	49.8	0.09 (max.)
375 – 650°F	32.4	31.4	0.1 (max.)
650 – 1,000°F	60.3	19.3	0.6 (max.)
1,000°F+	0	—	—

### (4) Economic factors

#### (a) Plant cost

The plant cost of each process unit constituting the whole process scheme is summarized on the following:

**Table 2.9 Construction Costs of Process Units**

Process Unit	Capacity	No.s	Construction Cost (10 <sup>6</sup> Japanese Yen)
Atm. Distillation	103,162 BPSD	2	9,292
Vacuum Flashing	67,373 BPSD	2	6,640
No. 1 Hydrotreating	16,070 BPSD	2	3,607
No. 2 Hydrotreating	45,836 BPSD	2	14,599
Eureka	42,328 BPSD	2	24,944
Hydrogen Plant	1.08 MM Nm <sup>3</sup> /SD as H <sub>2</sub>	2	9,508
Acid Gas Removal	315 Ton/SD as H <sub>2</sub> S	2	2,384
Sulfur Recovery and Solidification	285 Ton/SD as S	2	3,265
<b>Total</b>			<b>74,239</b>

Note:

- (1) Location: Chiba, Japan
- (2) As of mid. 1980 and no escalation included.

**(b) Utilities Consumption**

The utilities consumption of each process unit is summarized in Table 2.10 and 2.11.

**(c) Catalyst and Chemical**

The initial catalyst and chemical inventory and operating catalyst and chemical requirement are shown in Table 2.12.

**(d) Plant Area**

The plant area of each process unit constituting the whole process scheme is as follows:

Process Unit	Capacity	Plot Area
EUREKA Process	84,656 BPSD	50,000 m <sup>2</sup>
#1 HTR	32,139 BPSD	12,000 m <sup>2</sup>
#2 HTR	91,671 BPSD	24,000 m <sup>2</sup>

Table 2.10 Estimated Utility Requirements (1/2)

(Eureka Case)

Process Unit	Capacity BPSD	Elec. KW	Steam Ton/H			Water Ton/H				Fuel x10 <sup>6</sup> kcal/H				
			49KG 400°C	15KG 270°C	3.5KG sat.	BFW	Cond.	Process water	Foul water	Loss water	Cooling water	Gas	Oil	
Atm. Distillation	206,323	1,734	21.2	20.7	-21.2		68.4		-89.1		(4) 27 727			109.4
Vacuum Flashing	134,745	1,644	6.9		-6.9	50.3			-50.3		(4) 22 4,266			109.3
Eureka	84,656	10,000		73.0		177.8			-250.8		(5) 8,466	135.3		69.9
No. 1 Hydrotreating	32,139	3,105		7.8	-3.4	19.6			-9.5		(5) 555			23.1
No. 2 Hydrotreating	91,671	11,049		30.6	-4.6	105.6			-55.0		(5) 2,437			95.6
Hydrogen Plant	(1) 2,160	2,149		-22.5		138.7		4.3	-73.4		(4) 22 571	171.3		
Acid Gas Removal	(2) 630	644		5.6	95.2			-100.8			(4) 8 1,637			
Sulfur Recovery	(3) 599	2,246		-59.9		83.9					(4) 24			
<b>Total</b>		<b>32,571</b>	<b>28.1</b>	<b>115.2</b>	<b>-0.8</b>	<b>575.9</b>	<b>68.4</b>	<b>-187.6</b>	<b>-528.1</b>	<b>-71.1</b>	<b>18,762</b>	<b>306.6</b>	<b>407.3</b>	

Note: Negative figures indicate quantity made.

(1) x10<sup>3</sup> Nm<sup>3</sup>/D as H<sub>2</sub>

(2) Ton/D as H<sub>2</sub>S

(3) Ton/D as sulfur

(4) Mechanical cooling

(5) Including mechanical cooling

**Table 2.11 Estimated Utility Requirement (2/2)**

	Unit	Instrument Air	N <sub>2</sub>
EUREKA	84,656 BPSD	180	–
#1 HTR	32,139 BPSD	600	–
#2 HTR	91,671 BPSD	800	1620

(Nm<sup>3</sup>/H)**Table 2.12 Catalyst and Chemical Costs**

Process Unit	Total Capacity	Initial Cost (10 <sup>6</sup> ¥)	Operating Cost (10 <sup>6</sup> ¥/Y)
No. 1 Hydrotreating	32,140 BPSD	128	32.0
No. 2 Hydrotreating	91,672 BPSD	627	313.5
Eureka	84,656 BPSD	6.9	67.6
Hydrogen Plant	2.16 MM Nm <sup>3</sup> /SD as H <sub>2</sub>	297.2	97.6
Acid Gas Removal	630 Ton/SD as H <sub>2</sub> S	22.5	–
Sulfur Recovery	570 Ton/SD as S	36.8	8.8
<b>Total</b>		<b>1,118.4</b>	<b>519.5</b>

(e) Operating personnel

The operating personnel required for each process unit is as follows:

Process Unit	Capacity	No. of Operator (per shift)
EUREKA Process	84,656 BPSD	13 persons
#1 HTR	32,139 BPSD	7 persons
#2 HTR	91,671 BPSD	10 persons

(5) Intermediate tank list

The intermediate tanks required by EUREKA Process, #1, #2 HTR plants are as follows:

Name of Tank	Capacity	No. of Requirement
EUREKA Feed	1 day 13,500 kl	2 units
CLO	2 days 3,400 kl	1 unit
CHO	2 days 15,500 kl	1 unit
VGO	2 days 14,000 kl	1 unit
LGO	2 days 3,000 kl	1 unit
HGC	2 days 6,000 kl	1 unit

(6) Process waste

The quantity and properties of the waste water from each process unit are given in Table 2.13.

## 2.3 UTILIZATION OF BY-PRODUCT

### 2.3.1 Utilization for Boiler Fuel

(1) General

Pitch produced by the EUREKA Process is similar to coal in appearance, and can be handled in almost the same way as coal, but in their properties as fuels, pitch has larger calorific value (9,000 Kcal/kg), and less ash content than coal in their properties as fuels. And the pitch is more easily crushed because of a higher Hardgrove index. In addition, though pitch is solid under normal temperature, it can be handled as liquid if it is kept above the softening point.

As pitch has the above properties, it can be used as fuel in the following two ways:

(a) Atomized liquid pitch firing method.



Table 2.13 Process Waste Water

Plant Name	Atm. Crude Distillation	Vac. Flashing	H <sub>2</sub> Plant	#1		#2	
				Eureka Process	#1 HTR	#2 HTR	#2 HTR
Plant Capacity (BPSD)	206,323	134,745	80.51 MMSCFD	84,656	32,139	91,671	
Waste Water	Desalt. Water	O.H. Cond.					
Quantity	68.4	20.7	73.4	250.8	9.5	55	
Property							
pH							
COD	200	200		342			
Oil	100	100					
H <sub>2</sub> S	400	1,100		9			80,000
NH <sub>3</sub>	100	350		46			40,000
Phenol	4	30					

Note: \*1 with Foul Water Stripping section.  
 \*2 without Foul Water Stripping section.

**(b) Pulverized solid pitch firing method.**

As to these firing methods, the fundamental firing tests have already been performed by a boiler manufacturer, and they have obtained satisfactory results. Although the above two methods are both practical from a technical viewpoint, the pulverized pitch firing method is considered more favorable in this study due to the convenience of pitch transfer and storage.

The boiler system with the pulverized pitch firing is almost the same as the ordinary boiler system with pulverized coal firing.

Steam user's requests and local conditions should be considered carefully before boiler system will be decided. Typical case is as follows:

**(2) Outline of boiler plant**

**(a) Specification of boiler plant**

In the first place, the boiler plant must be met with the following established conditions.

— **Fuel**

All the pitch produced by the EUREKA process unit in the refinery.

EUREKA pitch output: 5,269T/SD = 220T/H (7,080H/Y)

2,635T/SD = 110T/H (1,680H/Y)

Fuel for boiler: 220T/H (7,080H/Y)

110T/H (1,680H/Y)

— **Evaporation**

2,640T/H (7,080H/Y) at 100kg/cm<sup>2</sup>G, 500°C

1,320T/H (1,680H/Y) at 100kg/cm<sup>2</sup>G, 500°C

— **Number of boilers and its each capacity**

Number of boiler ..... 4

Capacity ..... 660T/H (each)

— **Plant availability**

On the basis of 330 day/year operation, refinery plant has been designed as 2-Train system.

Since the required electric power and steam supply have not as yet been confirmed, all pitch produced is to be temporarily used as boiler fuel.

During the refinery maintenance period, the availability of the boiler system is also lowered to 50%.

The operating scheme of boiler plant and refinery is as follows:

Refinery	Boiler Plant
Two trains operation	100% Availability 295 days/y (7,080H/Y)
One train operation	50% Availability 70 days/y (1,680H/Y)

The boiler plant consists of the following system:

- Pitch transfer system
- Pitch storage yard
- Pulverizing and feeding system
- Boiler

(b) Outline of each system of boiler plant

- Pitch transfer system

The EUREKA pitch in coarse grain form is transferred to the pitch bunker of each boiler from EUREKA process unit by conveyer belt.

The capacity of the conveyer is 220T/H and can transfer all the pitch produced through EUREKA plant unit.

- Pitch storage yard

The pitch storage yard should be determined on the basis considering the condition of the field, refinery, boiler load change, and emergency stops, and it is difficult to determine it correctly with the given information. For the time being, about 40,000t storage yard has been established to meet the requirements for emergency stops or load change of the boiler and refinery. At the time of partial load or emergency stop of the boiler, the pitch from the EUREKA plant unit is transferred by conveyer to the storage yard.

The softening point of the pitch is high and it does not oxidize so easily as coal, so there is little danger of spontaneous explosion. The belt conveyer, tripper, and bulldozer are used for storage of the pitch. The storage work is done during daytime duty.

The pitch is collected at the bulk pit by bucket loader and conveyed to the boiler bunker.

- Pulverizing and feeding system

The pitch pulverizing and feeding system is set up separately for each boiler and, on the supposition that the load change of the boiler is small, the adopted system is a direct combustion type that is to send the pulverized pitch directly to the burner so that the mechanism may be kept as simple as possible. Pulverizing and drying equipment are included in

the direct combustion system.

The pulverizing and feeding system is as follows:

**Pitch bunker:**

The capacity of the bunker, which stores temporarily the pitch sent from EUREKA process unit, is enough to cover the load change of the boiler.

**Feeding equipment:**

Feeding equipment assures accurate metering of pitch feed and removing of impurities in pitch. Also it has some features to facilitate interfacing with combustion control equipment

**Pulverizer:**

It pulverizes the pitch suitable for boiler fuel and exposes the increased surface area to primary air which flash dries moisture of the pitch. The pulverized pitch is transferred to the burner.

— **Boiler**

The boiler is of the single drum water tube type without a convection evaporating tube bank.

Four units of 660 T/H boiler are planning to be installed and divided into two groups.

Maintenance is carried out parallel with the periodical over-haul of the refinery. In the design of the boilers, combustion technology should be adopted, taking pitch characteristics into account.

— **Firing system**

A pulverized pitch firing system shall be set up separately at each boiler unit.

The pulverized pitch is sent to burner directly. As to the auxiliary combustion systems for using fuel oil, gas oil, and so on, the equipment shall be minimized on the supposition that the load factor will be kept almost constant.

— **Feed water system**

A 50% of the feed water pumps are driven by electric motor, another 50% by the condensing steam turbine.

— **Draft system**

The draft system is of the balance draft type with FDF and IDF.

— **Air heater**

The air heaters (AH) system consists of regenerative AH and steam AH, and the required steam for steam AH shall be got from the low pressure turbine bleed. The temperature of the flue gas shall be kept about 150°C at the AH outlet.

- **Electric precipitator (EP)**  
An electric precipitator shall be attached to each boiler unit.
- **NH<sub>3</sub> gas is poured in it to raise the efficiency of dust collect.**
- **Control system**  
Control system such as the automatic combustion control, the automatic control for the belt conveyer, the pitch storage yard, and so on are all monitored at the central control room.
- **Ash treatment**  
The ash discharged from the dust hoppers for ECO, AH, EP, and so on is sent to the ash silo by compressed air and periodically taken away by dump trucks.

### **(3) Economic Factors**

#### **(a) Plant cost**

- **Scope of the estimate**  
Transportation and storage of pitch  
(Include belt conveyer to the bunker 800m x 2 belt conveyer in the storage yard 500m x 2)  
Pitch bunker  
Pulverizing and feeding system  
Boiler  
Ash treatment  
Accessory equipment for boiler plant  
(FDF, IDF, EP)  
Design cost of the above items  
Local construction cost of the above items
- **Excluded from the estimate**  
Water treatment system  
Flue gas treatment system  
Chimneys  
Turbines  
Condensor  
Power transmission system  
Turbine housing  
Other common facilities
- **Plant cost**  
Boiler plant (600 T/H x 4 units): 35 billion yen  
On the condition that the plant location is along Tokyo Bay, and the engineering is to have started in January 1980.

(b) Consumption of utilities

Boiler feed water	15 T/HR
Cooling water	40 T/HR
Electric power	40,000 KW

(50% of BFP is driven by steam turbine.)

(c) Plant operating personnel

The number of personnel required for the boiler plant operation is as follows:

Boiler unit	}	Day workers
Monitoring and control		15 men
Transportation & storage of pitch		Shift operators
Ash treatment		4 men/shift
Other engineering work		

(d) Plant area

The following spaces are included in the boiler plant area, but those of flue gas treatment and chimney are not included.

- Bunker room
- Boiler room
- Electric precipitator
- IDF

The required area:

$$\text{Boiler yard} = 200\text{m} \times 80\text{m} = 16,000\text{m}^2$$

$$\text{Storage yard} = 100\text{m} \times 150\text{m} = 15,000\text{m}^2$$

### 2.3.2 Utilization Other than for Boiler Fuel

Besides the fuel for boilers as stated above, EUREKA process pitch can be utilized for various purposes such as special additives, gasification material, and so on. A typical example is utilization as special additives for metallurgical coke production.

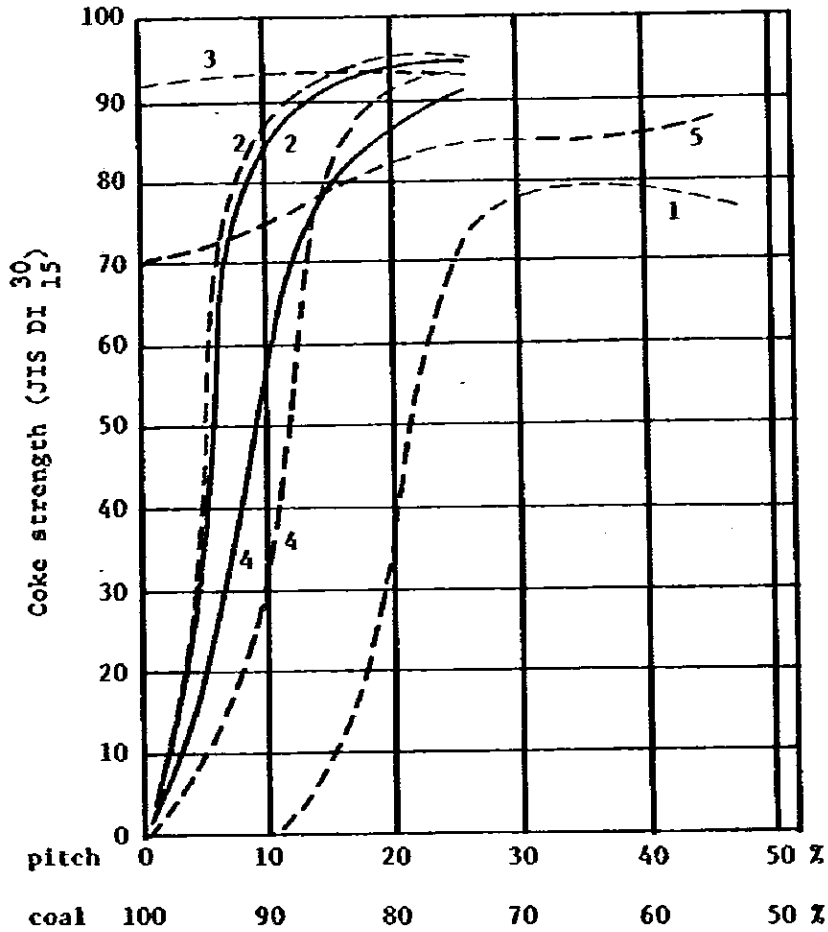
In this case, pitch is evaluated as a material of higher value than fuel, and the utilization of EUREKA process pitch in this field will make the process more economically advantageous than other heavy oil cracking processes. The pitch produced by the thermal cracking tests of Orinoco Heavy Oil is particular, is characterized by its lower sulfur content and Quinoline insolubles as compared with the pitch acquired from Middle East crude vacuum residue.

Table 2.14 shows the comparison of the quality of the pitch with that of the caking component in caking coal.

For the above reasons, the pitch produced in upgrading Orinoco Heavy Oil is suited for use as the additives, and utilization of pitch in this field will be promoted.

The following is an outline of the utilization for metallurgical coke production.

No	Coal
1	Anthracite
2	Semi-anthracite
3	Medium high-volatile coaking coal
4	High-Volatile non-coking coal
5	High-volatile coaking coal



———— pitch from vacuum residue cracking  
 - - - - - pitch from crude oil cracking

ORINOCO HEAVY OIL  
 UPGRADING PROJECT

BLENDING EFFECT  
 OF  
 PITCH TO VARIOUS COALS

FIG. 2.9

Table 2.14 Comparison of the Quality of the Pitch with that of Caking Component in Caking Coal

Sample	Vitrinite of Caking Coal				Pitch		
	A	B	C	C*	A	B	C*
Proximate	1.7	1.7	2.1	-	-	-	-
Inherent Moisture							
Analysis (%)							
Ash	3.6	1.4	2.3	0.1	0.1	0.1	
Volatle Matter	42.7	36.1	28.1	42.8	43.8	43.8	45.3
Fixed Carbon	52.0	60.8	67.5	57.1	56.1	56.1	53.4
Ultimate							
C	84.5	86.6	87.6	85.3	84.0	84.0	86.1
Analysis (%)							
H	6.1	5.8	5.3	6.1	6.1	6.1	6.1
N	1.2	1.6	1.7	1.8	1.0	1.0	1.7
S	1.1	0.7	0.3	4.5	7.3	7.3	4.4
O	7.1	5.3	5.1	1.7	1.6	1.6	
H/C	0.864	0.799	0.720	0.852	0.866	0.866	0.85
Softening Temperature (°C)	355	374	391	200	180	180	180
Fusion Temperature (°C)	403	402	421				
Temperature of Maximum Fluidity (°C)	438	438	449				
Solidification Temperature (°C)	473	472	478	Approx.	500	500	
Maximum Fluidity (D.D.P.M.)	22,000	13,000	427	5 x 10 <sup>4</sup>	5 x 10 <sup>4</sup>	5 x 10 <sup>4</sup>	
Plastic Temperature Range (°C)	118	98	87				
Aromatic Factor	0.74	0.79	0.85	0.79	0.78	0.78	
Specific Gravity	1.26	1.25-1.30	1.30	1.22	1.21	1.21	

C\* is the pitch produced from Cogollar IX / Cerro Negro



**(1) Characteristics and utilization of EUREKA pitch**

The pitch produced by the EUREKA process is far more aromatic in comparison with the residue of the SDA process, and is also characterized by its higher softening point and lower contents of volatile matter as compared with ordinary coal pitch.

EUREKA pitch with these characteristics can be used as a special additive in manufacturing metallurgical coke for blast furnaces by the following methods:

- (a) It can raise the produced coke properties when added to ordinary blended coal.
- (b) It allows the use of cheap non-coking coal for the manufacture of coke and/or saves the use of expensive coking coal.

SUMITOMO METAL IND. CO., LTD. and KUREHA are proceeding with joint development to utilize the pitch as a special additive for manufacturing metallurgical coke, and the pitch has been put to practical use as an important part of the Sumi Coal System.

The characteristics of the system for utilization of EUREKA pitch may be summarized as follows:

- By utilizing the pitch as a special additive, expensive coking coal can be substituted by cheap non-coking or poor-coking coal.
- It enlarges the scope of selection of coal resources which can be used for the manufacture of coke for the iron and steel industry.
- By adding some pitch blending apparatus to the conventional coke oven system, the system can utilize EUREKA pitch.

Fig. 2.9 shows the blending effects of the pitch.

**(2) Actual results**

The first commercial plant of the EUREKA process completed in February, 1976 at Sodegaura, Chiba Pref. has been operating successfully since then, and all pitch produced there (about 250,000t annually) has been used at the Wakayama and Kashima coke plants of SUMITOMO METAL IND.

At the same time some 1,000,000t of non-coking coal is being used annually for the manufacture of coke for the iron and steel industry.

Table 2.15 shows the typical operation data of the actual coke plants by simple blending method.

**Table 2.15 Operation Data of Coke Plant by Simple Blending Method**

	Standard	Operation A	Operation B	Operation C
<b>Coal blend (wt%)</b>				
Low volatile coking coal	6	0	6	0
Medium-volatile coking coal	10	10	0	10
Medium, high-volatile coking coal	63	63	63	53
High-volatile coking coal	21	21	21	21
Semi-anthracite (311)	0	4	0	0
High-volatile non-coking coal (711)	0	0	7	7
Pitch	0	2	3	3
<b>Coal charge analysis (wt%)</b>				
Total moisture	8.5	8.4	8.8	8.7
Ash	9.2	9.3	9.5	9.5
Volatile matter	26.7	27.6	28.5	28.1
Fixed carbon	64.1	63.1	62.3	62.8
Total sulfur	0.57	0.59	0.70	0.70
<b>Coke analysis (wt%)</b>				
Ash	12.4	12.6	12.5	12.4
Total sulfur	0.55	0.58	0.59	0.59
<b>Coke strength</b>				
DI <sub>15</sub> <sup>20</sup> *	92.2	92.3	92.2	92.6

\* JIS K 2151

## CHAPTER 3. DETAILED DESCRIPTION OF M-DS PROCESS

(Prepared by Maruzen Oil Co., Ltd.)

### 3.1 TECHNOLOGY OF PROCESS

#### 3.1.1 Introduction

Solvent deasphalting process has been occupying an important position in the petroleum industry as one of fundamental refining processes for more than 50 years. This process is mainly used for lube refining, but it is also attracting much attention as a process for preparing from residues the feed to such steps as catalytic cracking, hydrocracking and hydrodesulfurization. The solvent deasphalting process selectively removes polar polycondensed aromatic compounds as asphalt, and produces asphaltene-free oils having less content of heavy metals. The more harmful substances the feed contains, the more markedly the economics of catalytic processing would become worse, and operation may ultimately become impracticable. Even under these circumstances, if a feedstock like Orinoco heavy crude residue is pretreated by solvent deasphalting, the pretreated feed can be successfully upgraded by subsequent catalytic processing.

From technical and economic points of view, breakthroughs have to be made in two points, for adopting a solvent deasphalting scheme is acceptable for severe crude upgrading. Firstly, it is necessary to find the use of asphalt and to develop the technologies for its effective utilization. Generation of steam for the production of Orinoco heavy crude can be fully adequate as a major use of asphalt. A technology has been developed, by which to handle and burn effectively the asphalt having a high softening point. As a result, it has become possible to generate steam by using the those asphalt-burning boilers. Secondly, the deasphalting cost, which has been rather expensive, will have to be reduced. The solvent ratio could have been lowered to a minimum level by using a specially designed deasphalter and selecting optimum operating conditions. Use of the new model of deasphalter can lead to a reduction in the direct deasphalting cost. The new deasphalter can be run stably even when it is used to remove high softening asphalt. The above mentioned two breakthroughs make our solvent deasphalting scheme promising for Orinoco heavy crude upgrading. As stated above, the solvent deasphalting process can be used to upgrade heavy crude oils to a given level by combining it with other processes, such as desulfurization, hydrocracking, FCC, etc. However, the development of an economic solvent deasphalting technology itself is a key factor in the practice of an upgrading scheme involving solvent deasphalting. In this Section, therefore, we will confine ourselves to describe the solvent deasphalting process as an independent technology.

### 3.1.2 Process Features

The M-DS process has the following advantages over other similar processes:

**(1) A higher yield of upgraded oil.**

A high yield of deasphalted oil can be expected, owing to successful development of an improved extractor which shows excellent performance under the well-controlled conditions of a low solvent ratio, a low deasphalting temperature, and a relatively high molecular weight solvent.

**(2) Lower plant construction and operating costs.**

The operating cost could have been minimized by successful development of an improved extractor and plant optimization.

**(3) Superior selectivity in demetalization.**

A long period of tests with a pilot plant have proven that the M-DS process gives superior selectivity in demetalization, and in addition, no entrainment of asphalt particles occurs in an operation using an extremely low solvent ratio.

**(4) Higher performance and reliability.**

It has been confirmed from a long period of pilot plant tests that the operation can be easy and steady. This indicates that a high onstream factor can be expected in a commercial plant operation.

### 3.1.3 Process Development

MARUZEN launched a research and development program for M-DS Process in early 1970s. In 1972, a large-scale pilot plant was constructed on the basis of about two years of basic research work. Since then, the pilot test runs have been under way to investigate all the process variables.

In the basic research work on solvent deasphalting, the utmost efforts have been made to get the correlation data from among process variables such as feedstock properties, deasphalted oil properties, type of solvent, solvent ratio, deasphalting temperature, and other operating conditions. The greatest aim in the pilot test runs on solvent deasphalting was to develop an extractor adequate to operate at a lower solvent ratio. The test runs were also aimed at confirming the results of basic research work.

In 1974, Maruzen was successful in the development of a specially designed extractor, after several times of design modifications and subsequent performance test.

In the meantime, concurrently with the solvent deasphalting pilot test runs, company was carrying out a series of pilot test runs on the hydrodesulfurization of deasphalted oils. Thus, the technical correlation data required to optimize the design of M-DS process were increasing as these pilot test runs went on. Following the successful

accomplishment of development work, MARUZEN has completed in 1976 the basic design work for the first commercial plant which was planned to be installed at its Chiba Refinery, located on the outskirts of Tokyo. However, the plan has been put off for the time being, due to the sluggish demand for fuel oils at home and the drastic change in international crude market situation since the oil crisis.

#### 3.1.4 Patent Holder

A basic patent for the M-DS process is under application (Japanese preliminary publication of patent No.30802/1977.)

#### 3.1.5 Feedstock

Any crude oil of heavy quality containing a residue fraction can be upgraded by solvent deasphalting to obtain deasphalted oil. Solvent deasphalting is particularly effective in pretreating those residues containing high levels of heavy metals and asphaltene. Ordinary solvent deasphalting uses, as a feed, those vacuum residues which are as short as possible.

In the case of M-DS process, either atmospheric residue or vacuum residue is used as the feed, depending upon the extent to which the feed is upgraded. Various types of Middle East Crudes were closely analyzed with a view to using them for the pretreatment by the M-DS process. As for Venezuelan crudes, both of Boscan and Orinoco PAO crude residues have been put to test. The tests on these residues have revealed the effectiveness of this process.

#### 3.1.6 Principles

Solvent deasphalting is in principle one of the pretreating technologies used to upgrade the feedstocks by rejecting asphalt. It has been widely used as a process for pretreating feedstocks of lubricating oil refining, hydrocracking and catalytic cracking processes. In addition, this technology has been highly appraised as a pretreater in the hydrodesulfurization of tough feedstocks (residual oils) such as represented by Khafji crude. This is because the desulfurization of atmospheric residual oil is becoming an urgent problem for refiners of the world, especially of Japan. In this feasibility study, the solvent deasphalting process is adopted as a pretreater for hydrodesulfurization of heavy end so that it plays major role in the heavy crude upgrading scheme.

In general, the highly condensed hydrocarbons and/or metallic compounds, which are very poisonous to the hydrodesulfurization catalyst, are mostly distributed in the so-called asphalt. It is generally known that most of sulfur and nitrogen atoms originally existing in a crude oil go into the entire range of its heavier fractions, but that vanadium and nickel atoms mostly go into porphyrin complexes and high molecular weight

asphaltene. This means that vanadium and nickel are easily removed from a feedstock by solvent deasphalting, whereas sulfur and nitrogen remain in deasphalted oil still at relatively high levels.

An objective of solvent deasphalting is therefore to remove these poisonous substances from feedstocks along with the rejected asphalt. The solvent deasphalting is based on the principle that different solvent power of a solvent over asphaltene and oil fraction makes it possible to separate asphaltene from oil. The catalyst-poisoning substances have, by chance, a range of molecular weights and relative volatility similar to those of oil fraction, so it is difficult to separate them by means of distillation.

Most of low molecular weight paraffinic hydrocarbons can be used as a solvent for solvent deasphalting; however, those light paraffinic hydrocarbons ranging from propane to pentane are preferably employed in commercial operation of this process. Ethane or hexane and higher paraffinic hydrocarbons are not used for solvent deasphalting, because oil is very poorly soluble in ethane and excessively soluble in hexane and higher hydrocarbons.

Butane and heptane, for example, are compared with each other for the solubility of poisonous substances in these solvents. Butane allows porphyrins, heavy metals and polycondensed aromatics to be dissolved therein only to less extents, so that the deasphalted oil obtained contains relatively small amounts of poisonous substances. On the other hand, n-heptane selectively removes asphaltene, but it allows much of heavy metals and aromatics to be dissolved well therein. N-Heptane therefore is not suitable to remove poisonous substances, particularly in the solvent deasphalting of Orinoco heavy crude.

As the factors which affect the performance of solvent deasphalting in a practical operation, there may be mentioned the type of solvent, solvent to oil ratio, operating temperature and pressure, properties of feedstock and so on. This means in other words that the equilibrium of a mixed phase of feedstock and solvent is governed by the aforementioned factors. When atmospheric residue is deasphalted by a solvent, layer formation begins to take place at the point of a solvent-to-oil ratio of 1:1 and the two layers, oil rich layer and asphalt rich layer, come to be clearly formed as the solvent is further added beyond this ratio. The influence of solvent ratio on the properties and yield of asphalt depends greatly on the type of solvent, feedstock properties and operating conditions.

If propane is used for vacuum residue deasphalting, it is customary to use a temperature 15 to 20°C below the critical temperature. In that case, the quality of deasphalted oil is slightly apt to deteriorate and the yield of asphalt decreases, concurrently with the increase in solvent ratio.

On the contrary, if pentane is used to deasphalt the same feedstock, the quality of deasphalted oil deteriorates with the decrease in solvent ratio, and at the same time, the asphalt yield decreases. However, in the region of fairly high solvent ratios, the asphalt

yield converges into a constant level or forms a slow declining curve. The quality of deasphalted oil is in general improved with the increase in solvent ratio, but when the operating temperature is elevated upto critical temperature, the relationship between the solvent ratio and yield of asphalt becomes similar to that in case of propane deasphalting. Thus, the influence of solvent ratio in solvent deasphalting is of a very sophisticated nature, as the ratio is interrelated with other factors such as temperature, the type of solvent and the physical properties and chemical composition of feedstock.

As mentioned above, the general quality of deasphalted oil is improved concurrently with the increase in the solvent ratio; however, it is always important to set an optimum solvent ratio, taking into consideration the overall economics of both the solvent deasphalting and the hydrodesulfurization operations.

### 3.1.7 Process Description

Fig. 3.1 shows a simplified flow diagram of a solvent deasphalting scheme consisting of such sections as deasphalting, deasphalted oil recovery, asphalt recovery, and solvent recovery. The process uses a variety of feedstocks including both of atmospheric and vacuum residues derived from various crude oils. The solvent recovery section is subject to some modifications, because different solvents are used, depending on the type of crude oil used and the purpose of refining. The process flow shown in Fig. 3.1 is based on an atmospheric residue derived from a Middle East crude oil.

#### (1) Deasphalting section

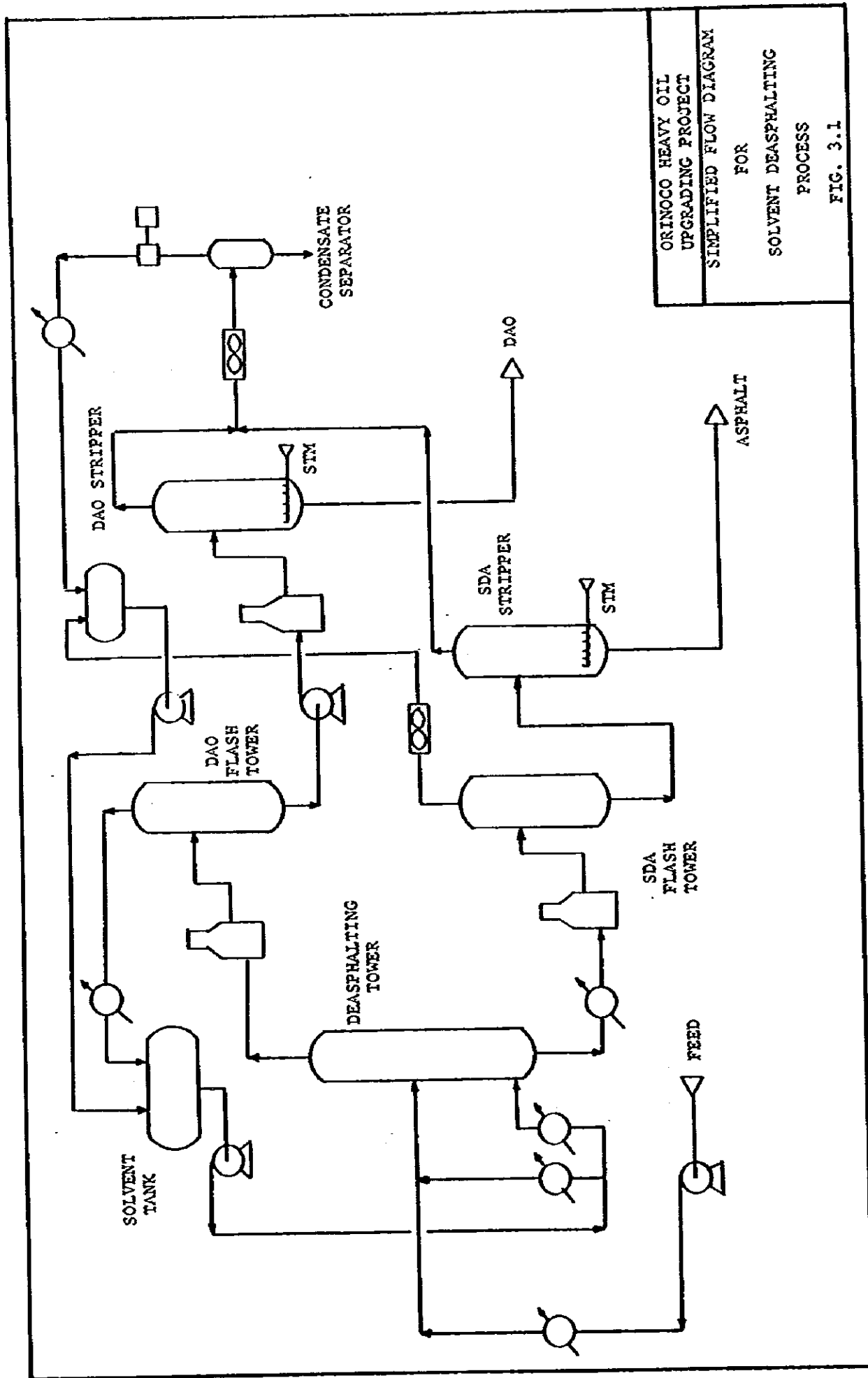
The feed and the solvent are respectively adjusted to a given temperature, and mixed with each other. The mixture is fed to the extractor. The deasphalting extraction proceeds in the upper half of the extractor. After having gotten rid of asphalt, the mixture of deasphalted oil and solvent flows out of the extractor through the lower top. Asphalt, while going down the extractor, comes in contact with a counter-current of rising solvent which is fed to the extractor through the bottom. The contact eliminates oil from asphalt, which is then accumulated on the bottom and withdrawn therethrough.

#### (2) Deasphalted oil recovery section

Deasphalted oil containing the solvent is heated by a heating furnace, and fed to the DAO flash tower, where most of solvent is separated under pressure. DAO still containing a small amount of solvent is again heated and fed to the stripper, where the remaining portion of solvent is completely removed by blowing steam into the reaction zone to strip the feed, whereby DAO product is obtained.

#### (3) Asphalt recovery section

Asphalt is withdrawn from the extractor through the bottom. Since this asphalt



ORINOCO HEAVY OIL  
 UPGRADING PROJECT  
 SIMPLIFIED FLOW DIAGRAM  
 FOR  
 SOLVENT DEASPHALTING  
 PROCESS  
 FIG. 3.1



Table 3.1 Typical Yield and Product Properties of Low Solvent Ratio  
Deasphalting (Reduced Crude Feed)

Crude	Iranian Heavy				Kuwait				Khafji			
	Yield	Vol.%	wt%	wt%	Yield	Vol.%	wt%	wt%	Yield	Vol.%	wt%	wt%
DAO	93.4		92.0		93.8		92.6		85.0		82.6	
SDA	6.6		8.0		6.2		7.4		15.0		17.4	
Properties	FEED	DAO	SDA	SDA	FEED	DAO	SDA	SDA	FEED	DAO	SDA	SDA
Sp. Gr. 15/4°C	0.953	0.940	1.147	1.147	0.957	0.945	1.135	1.135	0.986	0.956	1.140	1.140
Vis.@°C, cst	195	119	-	-	114	139	-	-	1190	297	-	-
R & B Soft. pt, °C	-	-	153	153	-	-	137	137	-	-	139	139
Sulfur wt%	2.66	2.44	5.37	5.37	3.71	3.50	7.2	7.2	4.27	3.72	7.21	7.21
Con. C.R. wt%	9.1	5.9	-	-	9.4	6.9	-	-	13	7.0	-	-
V ppm	130	53	1010	1010	48	18	425	425	96	27	425	425
Ni ppm	40	18	320	320	14	6.1	113	113	28	7.8	124	124

contains a small amount of solvent, it is heated by a furnace and fed to a flash tower to remove most of solvent. Asphalt is then sent to asphalt stripper, where the remaining portion of solvent is completely removed by blowing steam into the stripper, whereby asphalt product is obtained.

#### **(4) Solvent recovery section**

Solvent is recovered from the DAO- and asphalt-flash towers, cooled and condensed into the liquid state, and is sent to a solvent tank. The solvent vapor leaving both strippers contains stripping steam. Such vapor is cooled to remove water, and is compressed by compressors for condensation. The condensed solvent is then sent to the solvent tank for further recycling.

### **3.1.8 Process Yield and Product Properties**

Table 3.1 gives typical yields and properties of some products obtained by operating a large-scale solvent deasphalting pilot plant at a low solvent ratio, using atmospheric residues of Middle East Crudes as the feeds. In all of these runs, solvent deasphalting was used as pretreatment for hydrodesulfurization. Priority is put on economic production of low-sulfur heavy oil having a sulfur content in the range of 0.1 to 0.3% by means of a direct hydrodesulfurization unit of a 1% class (the unit capable of desulfurizing Kuwait reduced crude down to a sulfur content of 1%). For this reason, the solvent ratio was set at a level as low as about 2.

As found in Table 3.1, the asphalt yield is as low as below 10% of feed weight (or less than 3% of crude oils) in the two cases of Iranian Heavy and Khafji. Nevertheless, the rate of metal removal achieved by solvent deasphalting is as high as about 60% and the rate of desulfurization reaction (not shown in the table) is about 2.5 times as fast as the rate attained when the residue is directly desulfurized. Thus, the solvent deasphalting pretreatment has been proven to be remarkable effective.

### **3.1.9 Catalyst and Chemicals**

Solvent loss is the only item which falls into this category in the case of the solvent deasphalting process. The loss is estimated at about 0.2 wt.% based on the weight of the feed.

### **3.1.10 Utilities Consumption and Economic Data**

Table 3.2 gives an illustrative example of utilities consumption required when an atmospheric residue of a Middle East crude is deasphalted at a low solvent ratio.

Table 3.2 Utilities Requirements

Basis: 33,000 BPSD Middle East Reduced Crude feed.

Utilities:

Electricity	kW/hr.	3,600
Steam, HP	tons/hr.	3.08
"    MP	tons/hr.	18.15
Cooling water	tons/hr.	900
Fuel	MMKcal/hr.	14.6
Solvent	tons/hr.	0.37

The cost of construction is estimated at ¥5,000 x 10<sup>6</sup> (as of July 1980, at a Chiba, Japan site) for a 33,000-BPSD low-solvent deasphalting unit using a Middle East atmospheric residue.

### 3.1.11 Operating Conditions

A key section for the M-DS process is the deasphalting section where solvent is used to remove asphalt from the residue feed. Solvent used include low molecular weight paraffines, such as butane and pentane, which is used alone or as a mixture. The solvent is contacted in a liquid phase with the feed in the extractor. Operating conditions are selected in such a manner that they are most suitably fit to the purpose of operation. They depend on the types of feed and solvent. In principle, the operating conditions are mainly determined by the temperature/pressure relation of a hydrocarbon solvent in its liquid phase, as shown in the diagram of gas/liquid equilibrium. As regards the operating temperature, it is necessary to maintain the temperature at or above a minimum allowable temperature, depending upon the properties of asphalt, so that the asphalt/solvent mixture can always be kept at the free flowable state in the extractor.

Therefore, the operating conditions for the extractor can be roughly set within the following ranges:

Temperature:	100 – 180°C
Pressure:	15-28 kg/cm <sup>2</sup> (2 kg/cm <sup>2</sup> higher than a saturated vapor of solvent)

The quantity of solvent recycled is also an important operating condition which has a direct impact on the costs of construction and operation of a deasphalting unit. This quantity is kept at a lower level in the M-DS process than in other similar processes. In general, the solvent ratio used for atmospheric residue deasphalting is set at a lower level than for vacuum residue deasphalting.

### 3.1.12 Commercial Experience

Propane deasphalting has been in worldwide use as a basic process for refining lube oil for about 50 years. The M-DS process is a technical improvement of the propane deasphalting process. A major objective of this improvement was to fit this old process into the upgrading of heavy crude oils. As a variation of solvent deasphalting, the M-DS process may well be regarded as the process that has been endorsed by the longest period of accumulated experiences in commercial operation among all the oil refining processes. Large differences between M-SD and other solvent deasphalting processes lie in the deasphalting operation at a low solvent ratio and the design of an extractor that allows such operation to go on stably. As described above in the sub-section of Process Development, priority of R & D was given to extractor design and performance tests with a pilot plant. The M-DS process has thus been technically established through long years' R & D efforts including long and continuous test operations. As already mentioned, commercialization of this process has been put off, but we have completed basic design of a 33,000-BPSD unit based on this process, assuming the pretreatment of Middle East crude residues.

### 3.1.13 Process Application

Solvent deasphalting has been used, and its future use is being studied, for such purposes as the production of a heavy lube base, the preparation, from residues, of the feed to FCC and hydrocracking steps, and as in the case of the M-DS process, the pretreatment in the production of a low-sulfur fuel oil from residues of tough crude oils. When solvent deasphalting processes are studied on the extent to which deasphalted oil is refined, it is found that the production of lube oil requires the highest level of refining; hence, it requires a solvent of a relatively low molecular weight in the range of  $C_3$  to  $C_4$  and the highest solvent ratio. If solvent deasphalting is used for the preparation of the feed to FCC and hydrocracking unit, a  $C_4$ - $C_5$  solvent and a high solvent ratio are used because heavy metals have to be removed to large extents. On the other hand, the M-DS process utilizes a  $C_3$ - $C_5$  solvent at a low solvent ratio. It is intended here to reduce the cost of deasphalting, and at the same time, to lighten the burden imposed on the treatment of a low-quality crude residue, so that the process may offer excellent overall economics. The deasphalted oil available from the M-DS process is not necessarily suitable for the use as a feed to FCC and hydrocracking steps, because it has relatively high contents of metals and carbon residue. This defect can be surmounted mostly by hydrodesulfurization. If, therefore, deasphalting at a low solvent ratio is combined with hydrodesulfurization, the M-DS process is fully applicable to the feed preparation for FCC and hydrocracking, as well as to the production of a heavy lube base. A combination of solvent deasphalting and DAO desulfurization can play an important role in a refining

scheme converting even residues to light oil and low-sulfur fuel oil.

In the meantime, asphalt, another product of solvent deasphalting, finds its major use in such fields as hydrogen production by means of partial oxidation, and the generation of power and steam. Steam is produced for power generation by burning asphalt in the boiler equipped with a flue gas treatment unit. Dependent upon the type of crude oil to be refined and the required degree of upgrading, an independent system can be organized, wherein all the utilities requirements of the refinery, especially of the hydrocracking and hydrodesulfurizing steps, are met by producing hydrogen, steam and power from asphalt combustion.

### 3.1.14 Merits/Demerits of the Process

The following are considered as currently available processes which would be applicable to the demetalization and upgrading of Orinoco heavy crude, from a technoeconomical point of view.

- Solvent deasphalting
- Coking
- Hydrocracking

Although the quality and yield of demetalized oil varies inevitably with the processes, it is common to all cases that a residual material is by-produced from the operation in varying degrees. Unfortunately at this time, there seems to be no other way of utilizing residual materials than gasification or combustion in boiler on a commercial scale.

In this respect, the evaluation of demetalization processes should take into account how to handle the residual material which is rejected asphalt in case of this study. There is little difference among the aforementioned upgrading processes in the fact that a residual or another is by-produced from such a process.

#### (1) Solvent desphalting

Although it has been a generally accepted fact that deasphalting is too expensive to use it for pretreating the feedstock of hydrodesulfurization process, a recent solvent deasphalting process, such as the one integrated in the M-DS Process, has been greatly improved in various aspects.

For example, conventional SDA processes use a C<sub>4</sub> or C<sub>5</sub> solvent or a mixture thereof in quantity 5 to 8 folds as much as the feed quantity. The M-DS process, on the other hand, is characterized by using a solvent in a quantity far less (1/2 to 1/3) than in conventional SDA processes, to attain at the same level of SDA asphalt as in conventional ones. Naturally, the M-DS process requires less costs of SDA process construction and operation than do conventional SDA processes. When a M-DS utilities cost was calculated, using unit costs of utilities set in Japan as of the 2nd quarter of 1979 as the standards, there was even an extreme case where the

M-DS utilities cost was half as low as the corresponding cost for conventional SDA processes. (In this feasibility study, however, any extremely low solvent ratio has not been adopted in the light of the properties of asphalt and DAO.) On the other hands, when DAO properties were compared on the basis of the same asphalt yield, the M-DS process tends to give a higher metal content, although there is little difference in specific gravity and the sulfur content.

In general, most of solvent deasphalting processes are trying to reduce the utilities consumption, as in the case of the M-DS process. Among these processes, Rose Process (developed by Kerr McGee) has attracted attention when this process could have reduced the energy requirement for solvent recovery to a great extent by operating the solvent recovery section under super-critical conditions.

M-DS, as well as other solvent deasphalting processes, depends on evaporation and condensation to recover the solvent. Because conventional SDA processes require a large amount of solvent which is several times as much as the feed quantity, their solvent recovery sections occupy quite a large proportion in the total cost of process. It is no exaggeration to say that the cost reduction of a SDA process depends on how the solvent recovery section can be rationalized.

The M-DS process was successful in rationalizing its solvent recovery section by managing to use quite a small amount of solvent for extraction. The Rose process, on the other hand, has achieved the same goal by eliminating the step of solvent evaporation for the recovery. Kerr McGee already reported (at the 1976 NPRA annual meeting held in Texas, U.S.A.) that the utilities consumption by the Rose process accounted for about 40% of those of conventional SDA processes when calculated in terms of utilities cost. M-DS and Rose Process cannot be exactly compared with each other under the same conditions for their utilities consumption. But if they are compared in terms of their utilities cost, it is found that M-DS may happen to have a utilities cost less than the figure given for the Rose process.

As described above, M-DS is the most economic process and affords the most flexible operation, among all other competitive solvent deasphalting processes. On the other hand, it has a disadvantage that deasphalted oil still has a higher metals content than that of coker distillate. This disadvantage, however, can be offset by less hydrogen consumption in the subsequent hydrodesulfurization process, if the sulfur content of product is set at the same level as in coking. Therefore, solvent deasphalting is no doubt a promising demetalization route for Orinoco heavy crude.

## (2) Coking

Coking process may be one of the most attractive demetalization processes for Orinoco heavy crude. The commercialized coking process can be, in general, divided into delayed coking process and fluid coking process.

Since the fluid coking process is considered more economical than delayed coking in upgrading Orinoco heavy crude, we made a further detailed analysis. Yield of coke plus gas in each coking process can be given by the following equations.

$$W_o = 5.5 + 1.76 K \quad \text{(Delayed coking)}$$

$$W_f = 5.0 + 1.30 K \quad \text{(Fluid coking)}$$

where  $W_o$  = yield of delayed coke plus gas, wt%;  $W_f$  = yield of fluid coke plus gas, wt%; and  $K$  = Conradson carbon residue of feedstock.  $W_o$  and  $W_f$ , in the case of Orinoco Cerro Negro Crude having a Conradson carbon residue of 13.3% is calculated to be 28.9 wt% and 22.3 wt%, respectively.

Consequently, the yield of coke plus gas in delayed coking and fluid coking is estimated to be about the same or higher than the yield of rejected asphalt by produced from M-DS deasphalting process. Both the delayed coking and the fluid coking involve problems to be solved on how to handle the reject coke. In this sense, flexicoking, consisting of fluidcoker and gasifier, developed by ER & E, poses no problem in coke handling. The first commercial plant based on flexicoking was erected in Japan.

The delayed coking process combined with a coke burning plant was compared with that combined with a gasifier. The comparison revealed that the latter is more economic from an overall point of view.

Orinoco heavy crude can be upgraded up to the level of typical Middle-East Crude Oil by a combination of coking and hydrodesulfurization processes. However, the plant investment and operating costs of a coking route are, in general, more expensive than those of a solvent deasphalting route, although a more detailed comparison on economics of both routes is essential prior to reaching a conclusion.

### (3) Hydrocracking

H-Oil process can be considered at this time as a sole process in this category applicable for upgrading Orinoco heavy crude. Even in this process, addition of a considerable amount of diluent like gas oil to the feedstock will be needed to keep steady plant operation and catalyst activity. This requires a larger-size plant, which in turn, deteriorates process economics. Taking account of the properties of Orinoco heavy crude, especially heavy metals and asphaltene contents, the hydrocracking route is likely to involve many technical difficulties.

It is worthy to note, too, that a very viscous residue is byproduced from the hydrocracking route in an amount of around 20% to 30% of the feed. In addition, the hydrocracking of high-metals and high-sulfur feedstock like Orinoco heavy crude is inherently uneconomical because of its high costs of plant construction and operation.

In conclusion, promising as a demetalization process is either process of solvent

deasphalting or coking, from the points of view of economics, flexibility and reliability. Among others, the improved solvent deasphalting process, represented by M-DS Process, promises to be most economical as a demetalization process for Orinoco heavy crude.

### 3.1.15 By-product Utilization

It is always impossible to consider the development of a variety of products used in small amounts, in order to effectively utilize the asphalt by-produced from solvent deasphalting. In this section, however, problems in the fields of its major uses will be outlined, with emphasis put on a quantitative aspect.

#### (1) Boiler fuel

The boiler fuel use is regarded as the most realistic and important means of asphalt by-product utilization. It is a key subject of this study. The manner of use as fuel and its underlying problems are discussed elsewhere in this report, and are not dealt with here in this sub-section.

#### (2) Raw material for hydrogen production

Industry people have a growing interest in hydrogen production by partial oxidation of the asphalt by-product, because complete utilization of heavy crude oil can be achieved by combining hydrogen production with DAO hydrocracking and hydrodesulfurization. If a crude oil has a high content of asphalt, as is the case of Orinoco heavy crude, another interesting application is to use asphalt to produce a gas from partial oxidation and use the synthetic gas for the production of methanol and ammonia.

The partial oxidation process is commercially experienced in treating various feedstocks including heavy crude oils and pulverized coal. Thus, asphalt, having a softening point at least sufficient to handle it in the liquid form, can be used as a gasification feed. In treating a crude oil containing high levels metals, such as Orinoco heavy crude, the partial oxidation process can economically recover even V and Ni. We are ready to offer the technologies of partial oxidation whenever it is required.

#### (3) Road paving use

It is a common practice to incorporate SDA asphalt into road-paving asphalt. The asphalt by-produced from M-DS can be used also for this purpose. It should be noted, however, that a mixing base of a relatively low viscosity must be prepared for this use. In that case, solvent deasphalting may become less effective.

#### (4) Coke binder use in steelmaking

When steelmaking coke is produced, the volume of high-coking coal used can be