[Technical Paper]

A Fundamental Study on Vietnamese Crude Oil Refining
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Vietnamese crude oil such as Bach Ho has a high paraffin content, and it must be processed in a different manner from ordinary crudes to obtain maximum fuel products. In this paper, we discuss the following: characteristics of Vietnamese crudes and distillates; experimental data on normal paraffin removal from distillates (mainly gas-oil fraction) to meet product specifications; and the applications of recovered normal paraffins. Design analysis and economics study are also conducted to illustrate the feasibility of the projects. In order to produce on-spec gas-oil from Bach Ho crude, normal paraffin extraction process using molecular sieve has been selected, and LAB (Linear Alkyl Benzene) and SAS (Sodium Alkane Sulfonate) productions from the recovered normal paraffins are discussed.

1. Introduction

The need for establishing oil refineries and petrochemical complex in Vietnam has long been recognized by the Vietnamese Government. PetroVietnam intends to set up the first oil refinery with a processing capacity of 120,000 BSD of Vietnamese crude oil per year, and to start up its operation from the beginning of next century. Vietnamese crude oils, such as Bach Ho (White Tiger) and Dai Hung (Big Bear) crudes, have high paraffin contents, so they must be processed in a different manner from ordinary Middle Eastern crudes to obtain maximum fuel products. Because of the high normal paraffin contents in the crude oil fractions, paraffin separation processes and processes to convert the paraffin to petrochemical feedstocks must be considered for future Vietnamese petroleum and petrochemical industries. In this paper we discuss the following topics: (1) characteristics of Vietnamese crudes and distillates; (2) normal paraffin removal from distillates (mainly gas-oil fraction) to meet the product specifications; and (3) applications of recovered normal paraffins.

2. Characteristics and Refining of Vietnamese Crude Oils

Vietnamese crudes, according to the samples from the Bach Ho and other fields show high paraffin contents (greater than 17 wt% paraffins)^{1),2)}. All the sam-

ples are low in sulfur, nitrogen, vanadium, nickel, and asphaltene resin constituent elements (*cf.* Table 1)³⁾. Because of high paraffin contents, pour points of Vietnamese crudes are about 30°C causing much difficulties in production, transportation and storage. The high pour point suggests that some technical methods of pour-point reduction are required to minimize the above difficulties.

In Table 2 the basic assays and some general refining properties of Vietnam Bach Ho crude distillates are shown^{1)–3)}. For example, the kerosene fraction has properties suitable for light kerosene. However, if intended to produce jet fuel, some technical characteristics, such as freezing point, must be considered further.

The gas-oil fraction has high-quality characteristics for diesel fuel. The cetane index, for instance, is 61.3–69.8. However, its pour point, 7.5°C, is rather high. From the 240–360°C fraction, the normal paraffin yield can be as high as 51.7 wt% of the fraction, or about 23.2 wt% of the whole crude. Liquid normal paraffins are particularly valuable feeds for downstream chemicals production.

The heavy fuel oil fraction, approximately 55 wt% yield, has a low sulfur content 0.12–0.20 wt%, making it a good fuel from environmental standpoint and a suitable feed for residual catalytic cracking. However, its high pour point, 48–51°C, creates difficulties in storage and handling.

Because of the high normal paraffin content of the gas-oil fraction, and the high wax content of the fuel oil, paraffin separation processes and the processes to convert the paraffin wax to petrochemical feedstocks must be considered.

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Table 1 The Properties of Vietnamese Crude Oils

No.	Property		Bach Ho	Dai Hung	Rong
1.	Density	[API°]	39.85	29.06	38.15
		[60/60°F]	0.8258	0.8822	0.844
	Sp. Gr.	[15°C]	0.8254	0.8813	0.8436
2.	Gas in oil	[wt%]	0.08	Nil	0.15
3.	Sulfur	[wt%]	0.03	0.1	0.07
4.	Pour point	[°C]	35	25	34
5.	Typical constant	[UOP-K]	12.58	11.9	12.59
6.	Kinematic viscosity	[50°C, cSt]	5.34	8.76	8.4
		[70°C, cSt]	3.44	5.6	4.79
7.	Molecular weight	[—]	254	270	274
8.	Paraffin content	[wt%]	29	17.8	28.9
9.	Ash content	[wt%]	0.013	0.03	0.02
10.	Carbon content	[wt%]	84.4	87.08	85.19
	H ₂ content	[wt%]	14.5	12.76	13.72
11.	N ₂ content	[wt%]	0.04	0.036	0.05
12.	Reid vapor pressure	[psi]	3.36	2.86	2.38
13.	Sediment	[wt%]	0.01	0.017	0.013
14.	Acid index	[mgKOH/g]	0.06	0.59	0.06
15.	Conradson content	[wt%]	0.86	4.1	2.78
16.	Salt content	[mg/kg]	37.53	215.19	35.7
17.	Resin content	[wt%]	1.97	7.55	4.54
18.	Asphaltene content	[wt%]	0.77	2.5	2.42
19.	Vanadium content	[ppm]	0.09	0.15	0.15
20.	Ni content	[ppm]	2.64	2.54	1.72

Refining sweet Vietnamese crudes requires neither high quality anti-corrosive plant materials nor deep desulfurization processes. However, their high pour points cause more difficulties in the use of the product oil fractions. As stated before, this means that other methods for pour-point reduction are required. Examples of such methods are summarized in **Table 3**. Of the methods, normal paraffin removal was chosen because it best meets the objectives of maximum production and cost effectiveness.

The basis of the following study on normal paraffin distribution in the Bach Ho crude was our gas-chromatographic analysis (**Fig. 1**)⁴. It shows smooth distribution, compared with the previously reported data which had clearly shown a minimum at carbon number around 10².

3. Effects of Normal Paraffin Removal

3.1. Experimental

Normal paraffin removal experiments have been carried out using the urea adduction method⁵) to investigate the relationship between freeze/cloud points of kerosene fraction and normal paraffin content. The relationship between the pour point of gas-oil and normal paraffin content was also investigated. The properties of feedstocks for the experiments are shown in **Table 4**. Experimental procedure is shown in **Fig. 2**.

Normal paraffin free oil thus obtained is re-mixed with the virgin distillate fraction to obtain changeable paraffin contents in the sample fractions.

A 1000 cc flask with a rotating mixer is used for kerosene (100 g) and urea (200 g) reaction. After 4 hours of agitation at room temperature, solid urea adduct produced is separated by filtration and washed thoroughly by solvent and then dried. The dried urea adduct is then decomposed with hot water into normal paraffins and urea. Dewaxed oil is recovered by eliminating the solvent using an evaporator. For the gas-oil fraction, separation is carried out in the same manner but on a double scale.

Normal paraffin distributions in feedstock kerosene and gas-oil and the distribution in the recovered normal paraffin are shown in **Fig. 3**.

The properties of the sample fractions are then measured using an authorized method.

3.2. Effects of Normal Paraffin Contents

3.2.1. On Freeze/Cloud Points of Kerosene Fraction

The relationship between freezing and cloud points of kerosene fraction and normal paraffin contents are shown in **Table 5** and **Fig. 4**.

The freezing point of virgin kerosene is -40°C . In order to produce on-spec jet fuel, certain amount of normal paraffin should be removed to meet the specification, which is below -47°C .

3.2.2. On Pour/Cloud Points of Gas-Oil Fraction

The relationship between pour point and cloud point with respect to the normal paraffin content in gas-oil is shown in **Table 6** and **Fig. 5**.

For gas-oil fraction when its normal paraffin content decreases, its pour point also decreases, as shown in

Table 2 The Properties of Bach Ho Crude Distillates

			Elf ^{a)}	JE(1) ^{c)}	JE(2) ^{c)}	JE(3) ^{c)}	Dr. Du ^{b)}	Dr. Du ^{a)}
			Analysis	Analysis	Analysis	Analysis		
Kerosene	Boiling range	[°C]	(145-240)	(210-240)	(210-240)		(149-232)	(150-280)
	Density	[kg/m ³]	792	792	797		779	805
	Pour point	[°C]		-32.5	-33			
	<i>n</i> -Paraffin	[wt%]		Est. 42 (180-270)	37.9			
	Freezing point	[°C]	-50				-49	
	Smoke point	[mm]	25	28 (210-240)	31		35	22
Gas oil	Boiling range	[°C]	(145-375)	(270-300)	(240-270)	(240-360)	(232-342)	(180-350)
	Density	[kg/m ³]	820	819	810	822	818	829
	Pour point	[°C]	1	-2.5 10 (300-330)	-14	7.5	-3	
	<i>n</i> -Paraffin	[wt%]			39.6	51.7 23.7 (on crude)	WAX 9.5 (on crude)	40 (200-350)
	Cetane index				61.3	69.8	47.6	67
	Cetane number		58.2					
	Cloud point	[°C]	4			7	-3	
VGO	Boiling range	[°C]	(375-550)					
	Density	[kg/m ³]	878	839 (360-400) 865 (400-566)				
	Pour point	[°C]	53	22.5 (330-360) 35 (360-400) 52.5 (400-566)				
Residue	Boiling range	[°C]	(375+)				(342+)	
	Density	[kg/m ³]	914				868	
	Pour point	[°C]	48				51	
	<i>n</i> -Paraffin	[wt%]					WAX 49	
	Density	[kg/m ³]					872 (369+)	
	Pour point	[°C]					54	
Residue	WAX	[wt%]					50	
	Boiling range	[°C]					(509+)	
	Density	[kg/cm ³]					905	
	WAX	[wt%]					47	

a) OGI 1989. b) OGI 1990. c) PEC Report.

Table 3 Pour Point Reduction Methods

Method	Merit	Demerit or problem to be solved
(1) Mixing with Middle Eastern crudes	• No processing unit necessary	• Importing crudes
(2) Addition of P.P. improver (G.O., F.O.)	• No processing unit	• Much improver required
(3) Adjusting cutting range (F.O.)	• No processing unit	• Reduction of gas-oil yield
(4) Cracking (by RFCC)	• More white oil available	• Processing unit (high investment) required
	• Reduction of F.O.	• Less effective on RFCC bottom oil
(5) Normal paraffin removal (dewaxing)	• Normal paraffin (or wax) available	• Processing unit required

Fig. 5. However, the degree of the effect is not as dramatic in the range of normal paraffin content above 20%.

In order to meet the specification of diesel oil pour

point (below 0°C), normal paraffins in the fraction should be kept less than 35 wt%. Also shown in **Fig. 5** is the relationship between normal paraffins content and pour point obtained by mixing with Dubai crude

Fig. 1 Normal Paraffin Distribution of Bach Ho Crude Oil

Table 4 The Properties of Kerosene and Gas-Oil Used for the Study

		Kerosene	Gas-oil	Crude
Cut range	[°C]	160-240	240-360	—
Yield on crude	[wt%]	13.0	23.3	100
Density (15°C)	[g/cm ³]	0.7830	0.8218	0.8187
Sulfur	[wt%]	0.001	0.02	0.03
Pour point	[°C]	—	+7.5	+35
Cloud point	[°C]	-50	+7	—
Freezing point	[°C]	-40	+9	—

distillate³⁾. The difference between the slopes of two curves suggests that Dubai gas-oil contains normal paraffins of higher solubility.

4. Evaluation and Selection of Normal Paraffin Removal Technology

A study has been carried out for processes to separate and recover normal paraffins from a wide range gas-oil fraction of Bach Ho crude oil. The reason as to why gas-oil fraction, not kerosene, has been taken up for this study is that gas oil pour point improvement is much more crucial than that of the freeze point of kerosene. Processes evaluated are those of Molex and Nurex. The former is a liquid phase separation of *n*-paraffins from iso-paraffins using molecular sieve and the latter is that based on urea adduction about which has already been mentioned. The Molex process has been selected mainly because of its cost advantage (Table 7)⁴⁾. Sources of the data are published information and consultant's data files.

5. Normal Paraffin Application

Normal paraffins are widely used in various chemical industries as basic raw materials, and their major application is the production of detergents.

Their application depends on normal paraffin carbon

Experimental Procedure

Fig. 2 Separation of Normal Paraffins from Bach Ho Distillate by Adduction of Urea

Fig. 3 The Result of Separation by Adduction of Urea: Normal Paraffin from Kerosene and Diesel Fraction of Bach Ho Crude Oil

numbers, in which carbon numbers 10 to 15 (contained in kerosene and gas-oil fraction) are important raw materials for production of linear alkylbenzene detergents (LABs). As shown in Fig. 1, substantial amounts of normal paraffins are found in this carbon range. According to the forecast of demand on normal paraffins in the world, some shortage is expected now and in the near future⁴⁾.

As stated before, it is better to consider a normal paraffin application in the refinery to make the project more profitable, taking the future domestic market of normal paraffins into consideration.

Table 5 Relationship between NP Contents and Freeze/Cloud Pts in Kerosene

No.	Mixing ratio [wt%]		NP content [wt%]	Measured [°C]	
	Virgin distillate	NP free oil		Cloud pt.	Freezing pt.
1	100	0	43.9	-50	-40
2	50	50	22.0	-54	—
3	0	100	0.0	-69	-69 ↓

NP: Normal paraffin.

Table 6 Relationship between NP Contents and Pour/Cloud Pts in Gas-Oil

No.	Mixing ratio [wt%]		NP content [wt%]	Measured [°C]	
	Virgin distillate	NP free oil		Pour pt.	Cloud pt.
1	100	0	51.7	7.5	7
2	75	25	39.1	2.5	3
3	50	50	26.4	-5.0	-3
4	25	75	13.8	-12.5	-12
5	0	100	1.1	-62.5	-68

NP: Normal paraffin.

Fig. 4 Relationship between NP Contents and Freeze/Cloud Pts in Kerosene

Fig. 5 Relationship between NP Contents and Pour Point in Gas-Oil

Table 7 Normal Paraffin Separation Process Comparison

		UOP Molex	Japan Energy-Nurex
Investment cost (for 20,000 BPSD)		85 MM US\$	105 MM US\$
Facilities included		Molex, HDS	Nurex, NP hydrotreater
		Post fractionation	Post fractionation
Utilities			
Electricity	[MW]	5.2	11
Steam	[ton/h]	5	7
Cooling water	[1000 m³/h]	2.2	9
Fuel	[Gcal/h]	70	135
Industrial water	[ton/h]	3	—

Linear alkylbenzene sulfonate (LAS) production has already been started in Vietnam. There are four factories as of 1998 producing LAS using around 50,000 tons/year of LAB, and their expansion will be considered.

The demand for normal paraffins with carbon numbers larger than 16 is rather limited. SAS (Sodium Alkane Sulfonate) production is, however, recommended and realized because of its high biodegradability^{3),4)}.

Fig. 6 Material Balance for Normal Paraffin Separation from 120,000 BSD Refinery

6. Process Design and Economics

In a Bach Ho fed 120,000 BSD refinery, conditions to produce the maximum amount of on-spec diesel oil (pour point 0°C) and normal paraffin feedstocks for LAB and SAS are being studied. The properties of feedstock gas-oil are shown in Table 4.

The resulting material balance is shown in Figs. 6 and 7. The Molex feed capacity is ca. 14,000 BSD, and on-spec diesel oil of 20,145 BSD can be produced as shown in the scheme, while the feedstocks for LAB and SAS are 100,890 and 115,745 tons/year, respectively. In LAB production, Pacol plus HF Alkylation and Pacol plus Detal processes are considered. Pacol is a catalytic dehydrogenation process using a platinum catalyst, and Detal process is a direct alkylation of benzene with olefins using a solid heterogeneous catalyst. Both processes were developed by UOP.

Using the material balance, production costs of normal paraffins for LAB and SAS are estimated. The results shown in Table 8 indicate that commercial production of LAB and SAS at current market prices is feasible.

7. Conclusions

As a result of this investigation, the following conclusions have been obtained.

(1) Vietnamese crude oil such as Bach Ho crude contains a low content of sulfur, but a high content of

Fig. 7 Material Balance for LAB and SAS Production

normal paraffins that results in better kerosene smoke point, better diesel cetane number, and higher freezing point in jet fuel and higher pour point in the gas-oil fraction. Normal paraffin distribution of Bach Ho crude has also been investigated.

- (2) In order to reduce the pour point of the above fraction, several methods are reviewed. Of the methods normal paraffin removal from the fraction is found effective and is recommended.
- (3) Experiments on normal paraffin separation using urea are carried out to establish a relationship between normal paraffin content and pour point of gas-oil (or freezing point of kerosene).

Table 8 Summary of Economic Results

	Case-1		Case-2	
	Molex	60.4 MM US\$	Molex	60.4 MM US\$
Estimated	Pacol+HF Alk	82.8 MM US\$	Pacol+Detal	72.3 MM US\$
erected cost	SAS	173.0 MM US\$	SAS	173.0 MM US\$
	Total	316.2 MM US\$	Total	305.7 MM US\$
Cost of production				
NP		236.6 US\$/ton		236.6 US\$/ton
LAB		656.0 US\$/ton		667.1 US\$/ton
SAS		1496.8 US\$/ton		1496.8 US\$/ton
Production				
LAB		114,600 ton/yr.		109,300 ton/yr.
SAS		154,700 ton/yr.		154,700 ton/yr.
Reference (market price)	NP: 400 US\$/ton, LAB: 800 US\$/ton, SAS: 2500 US\$/ton			

Basis

Bach Ho crude price 17.0 US\$/BBL.

Price of utilities: Fuel 10 US\$/MMkcal, Electricity 0.1 US\$/kWh, Steam 16.5 US\$/ton, Water 2 US\$/ton.

Depreciation period: 15 year. As of March 1998 in Japan.

- (4) Normal paraffin removal processes are reviewed. Molex is found to be suitable for gas-oil fraction.
- (5) For normal paraffin application, in which the degree of pour point reduction of gas oil and that of carbon distribution are both taken into consideration, LAB and SAS are selected. Economic studies suggest that their commercial production is feasible.

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要 旨

ベトナム原油の精製に関する基礎的研究
—ノルマルパラフィンの分離と有効利用—加藤 恒一^{†1)}, Pham Quang Du^{†2)}^{†1)} 日鉱エンジニアリング(株), 105-0001 東京都港区虎ノ門 4-1-40^{†2)} Research & Development Center for Petroleum Processing, PetroVietnam, 4 Nguyen Thong St. Dist. 3, Ho Chi Minh City, Vietnam

ベトナムにおいては国産原油を主として処理する製油所計画が進んでいる。バックホー等のベトナム原油は高濃度のノルマルパラフィンを含むため、留分をも含めて流動点が高く、規格に合致する製品を効率的に得るためには中東原油と異なった精製法が必要となる。

バックホー原油およびその留分の性質を検討し、軽油の流動点を規格(0℃)に合わせるため同留分から抽出すべきノルマ

ルパラフィンの量を分離実験により求めた。同時に得られるノルマルパラフィンの用途について検討し LAB (Linear Alkyl Benzene) と SAS (Sodium Alkane Sulfonate) を選定した。120,000 BSD の製油所に対する本スキームのプロセス設計, 設備検討を行い LAB および SAS 生産の経済的可能性を確認した。

Keywords

Crude oil, Normal paraffin, Dewaxing, Linear alkylbenzene, Pour point, Separation