

on this aspect is in progress.

### Nomenclature

$a$  = catalyst activity  
 $A_1, A_2, A_D$  = preexponential factors  
 $C$  = concentration, kg-mol/m<sup>3</sup>  
 $E_1, E_2, E_D$  = activation energies, kJ/kg-mol  
 $f$  = rate of catalyst deactivation, 1/h  
 $F$  = negative of yield of B  
 $H$  = Hamiltonian  
 $k_1, k_2, k_D$  = rate constants  
 $k_{10}, k_{20}$  = constants defined in eq 6c  
 $n$  = order of catalyst decay with respect to A  
 $m$  = order of catalyst decay with respect to B  
 $t$  = time, h  
 $T$  = reactor temperature, K

### Greek Symbols

$\beta = E_1/E_D$   
 $\epsilon = E_2/E_D$   
 $\tau$  = reactor space time, h

$\theta$  = run length, h  
 $\lambda$  = adjoint variable in eq 4

### Subscripts

A, B, C, = chemical species  
 0 = initial conditions  
 \* = maximum (\*) or minimum (.) bound

### Literature Cited

Dalcorso, J. P.; Bankoff, S. G. *Chem. Eng. J.* 1972, 3, 62.  
 Ognyne, A. F.; Ray, W. H. *AIChE J.* 1971, 17, 43.  
 Reiff, E. K. *Ind. Eng. Chem. Process Des. Dev.* 1981, 20, 558.  
 Reiff, E. K.; Kittrell, J. R. *Chem. Eng. J.* 1981, 21, 71.

Department of Chemical  
 Engineering  
 Indian Institute of Technology  
 Kanpur, India

Mritunjoy Pramanik  
 Deepak Kunzru\*

Received for review September 27, 1983

Accepted October 17, 1983

## Catalytic Cracking of Heavy Oils in Combination with Pyrolysis for the Production of Light Oils

A two-stage method for catalytic cracking has been developed to process heavy oils. A heavy oil was thermally cracked at about 440 °C in the first stage, and the cracked oil thus produced was carried to the silica-alumina catalyst bed (the second stage). On the basis of the pyrolyzed oil carried to the catalyst bed, yields of C<sub>5</sub>-C<sub>12</sub> gasoline, C<sub>13</sub>+ oil and coke from an atmospheric or a vacuum residue corresponded to those from a direct catalytic cracking of a vacuum gas oil. The asphaltene fraction can be left in the first stage as a pyrolysis residue, so that the formation of coke may be reduced. A tar-sand bitumen, which is disadvantageous for the production of lower olefins by high-temperature pyrolysis, is considered to provide larger amounts of gasoline and kerosene fractions than paraffinic feed stock such as Taching vacuum residue.

### Introduction

Increasing demands for lighter petroleum fractions, motor gasoline in the U.S. and kerosene and gas oil in Japan, have produced occasional market shortages.

To increase the gasoline yield, the use of the heavy end of crude as fluid catalytic cracking (FCC) feed stock has been intensively studied. For the residual oils used as feedstocks for the FCC unit, the most troublesome feature is metallic contaminants and high-molecular-weight condensed aromatic hydrocarbons contained in them, as well as the high sulfur content. To overcome these problem, numerous efforts have been made: catalyst improvement (Ritter et al., 1981), development of a riser cracking (Finneran et al., 1974), of low-conversion operation (Hemler and Vermillion, 1973; Finneran et al., 1974), combination of the hydrodesulfurization and FCC process (Yanik et al., 1977; Murphy and Treese, 1979; Masoslogites and Beckberger, 1973), removal of metals from the catalyst (Edison et al., 1976), and so on.

To treat heavy residues of crudes, coker processes are in operation and coker gas oils will be upgraded to lighter fractions. In the studies on the thermal cracking of residual oils, we have demonstrated that two-stage pyrolysis of heavy oils is an efficient process for the production of lower olefins (Suzuki et al., 1982b; Itoh et al., 1983). In this method, residual oil was first thermally cracked at 440 °C to give pyrolyzed oil and pitch. The pyrolyzed oil was carried to the second, high-temperature stage (750-800 °C) and was further pyrolyzed to lower olefins. A similar process was developed by Kureha Chemical Industry Co. and Chiyoda Engineering and Construction Co. as the Eureka process (Aiba et al., 1981).

In our experiments, it was elucidated that a yield of ethylene was affected significantly by the characteristics of feedstocks. From the structural investigation of heavy oils (Takegami et al., 1980; Suzuki et al., 1981a, Suzuki et al., 1982a), a straight-chain paraffin index (SPI) for heavy oils was proposed (Itoh et al., 1983). The SPI value was well correlated with ethylene yield on the two-stage pyrolysis.

In this communication preliminary experiments on the two-stage process for the catalytic cracking of heavy oils will be carried out, and yields of gasoline and gas oil fractions from various heavy oils are compared.

### Experimental Section

**Materials.** Two tar-sand bitumens, Cold Lake and Orinoco, three fractions from Arabian Light crude, an atmospheric residue, a vacuum residue, and a vacuum gas oil, and Taching vacuum residue have been used as heavy oil feeds. Properties of these oils are shown in Table I. Detailed structural analyses of them have been described previously (Takegami et al., 1980; Suzuki et al., 1981a; Suzuki et al., 1982b). A commercial silica-alumina amorphous catalyst used for the FCC process (Catalyst and Chemicals Ind. Co., No. 2244) was used.

**Apparatus.** The experimental apparatus used in the present study is represented schematically in Figure 1. A quartz reactor tube (3), 150 mm long and 18 mm i.d. at the first section and 150 mm long and 8 mm i.d. at the second section, was used. The temperature of the tow section was controlled independently by the electrical resistance heaters (1). The reactor tube connecting the two sections was also heated electrically. An inner tube (5), 10 mm o.d., on which platinum wire (0.3 mm diameter)

Table I. Properties of Feedstocks

	Cold Lake bitumen	Orinoco bitumen	Taching v.r.	Arabian Light v.r.	Arabian Light a.r.	Arabian Light v.g.o.
wt % crude			41.7	18.5	48.3	8.1
molecular weight <sup>a</sup>	500	630	870	960	420	346
elemental analysis						
C, %	82.8	83.9	87.0	84.0	84.8	85.4
H, %	10.8	10.5	12.7	10.3	11.7	12.4
S, %	4.6	4.5	0.19	5.1	3.2	2.4
N, %	0.30	0.83	0.33	0.45	0.38	0
V, ppm	220	255	1.7 <sup>b</sup>	66 <sup>b</sup>	26 <sup>b</sup>	
Ni, ppm	20.8	29.5	6.6 <sup>b</sup>	24 <sup>b</sup>	10 <sup>b</sup>	
Conradson carbon residue, wt % <sup>b</sup>	n.a. <sup>d</sup>	16.4	7.4	14.2	7.5	1.2
asphaltene, wt %	15.6	24.0	0	11.2	4.4	0
aromaticity <sup>c</sup>	0.30	0.34	0.20	0.36	0.28	0.23

<sup>a</sup> Number-average molecular weight determined by vapor pressure osmometry. <sup>b</sup> Typical values from references.

<sup>c</sup> Determined by <sup>13</sup>C NMR spectra. <sup>d</sup> Not available.

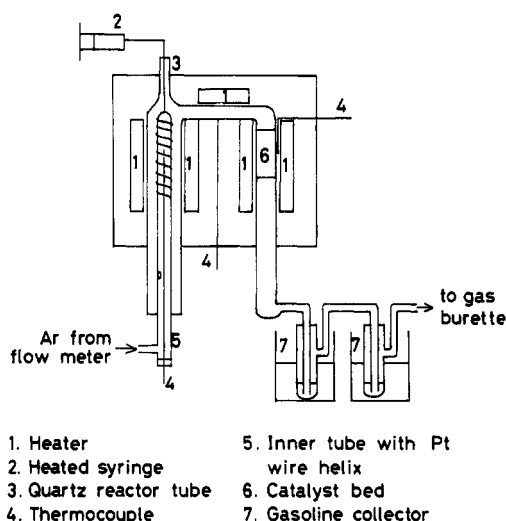


Figure 1. Schematic diagram of the unit.

was wound helically and was inserted in the first section from the bottom. A fixed catalyst bed, 30 mm long, was placed in the second section by packing the catalyst in layers supported by a quartz wool plug.

**Procedure.** The catalyst was dehydrated under an argon flow at 400 °C for 5 h followed by activation at the reaction temperature for 2 h in the reactor tube. After activation, the appropriate reaction conditions were adjusted. In all the experiments, maximum temperatures at the pyrolysis and the catalytic section were set at 450 and 480 °C, respectively, and the flow rate of the carrier gas (argon) was fixed at 20 mL/min at room temperature. Axial temperature gradient in the catalyst bed was fairly small. When the maximum temperature was 480 °C, the average temperature was 472 °C.

A heavy oil was fed from the heated microfeeder (2) through a hypodermic needle (1.0 mm o.d.) to the first stage, at the top of the inner tube. The pyrolyzed oil was carried to the catalyst bed by argon flow to undergo catalytic cracking. In a typical experiment, a charge stock was fed at around 4 mg/min, corresponding to a weight hourly space velocity (WHSV) of around unity against the pyrolyzed oil carried to the catalyst bed. Some of the pyrolyzed oil at the first stage remained on the wall of the reactor tube around the first stage and also on the wall of the glass tube connecting the two reaction zones. The amount of this pyrolyzed oil and the pyrolysis residue was determined by weighing the reactor tube (3) and the inner tube (5) before and after each reaction.

In a direct catalytic cracking experiment, a quartz reactor tube (150 mm long and 8 mm i.d.) was set in the same

place where the catalyst section was set shown in Figure 1, and the catalyst was packed in the same place. A charge stock was fed directly to the catalyst bed.

The effluent from the reactor was cooled by air, and the gasoline fraction was collected by bubbling into *n*-propylbenzene cooled by dry ice in methanol (7), and gases were collected in a gas buret. Analyses of products were made chromatographically with Shimadzu Models GC-4CPF and GC-3BF gas chromatographs (F.I.D.). The gasoline fraction dissolved in *n*-propylbenzene was analyzed by use of a silicone OV-101-coated Golay column (0.25 mm i.d. × 45 m), using phenylcyclohexane as an internal standard. The oil fraction condensed at the outlet of the reactor tube was analyzed in the same manner, with diphenylmethane as an internal standard. The integral of the peak areas was calculated with a Shimadzu Model C-R1A digital integrator. Gas samples were analyzed as described previously (Takegami et al., 1980).

Contents of Ni and V in the oils were measured with a Shimadzu AA-640 Atomic Absorption Spectrometer, equipped with a graphite furnace atomizer.

## Results and Discussion

**Yields of C<sub>5</sub>–C<sub>12</sub> Gasoline, C<sub>13</sub>+ Oil, and Coke.** Typical yields of the catalytic cracking expressed in weight percent basis are shown in Table II. Cracked lighter fractions were divided into three fractions using the gas chromatographic analyses of standard hydrocarbons as follows: C<sub>4</sub> and lighter, C<sub>5</sub>–C<sub>12</sub> gasoline, and C<sub>13</sub>+ oil (kerosene + gas oil).

In all cases, material balance did not reach 100%. This may be explained as follows. Hydrogen sulfide is not analyzed, and certain parts of C<sub>4</sub> and C<sub>5</sub> hydrocarbons escape from the system during the analysis of the gasoline fraction. Because of a micro system, the effect of these losses cannot be ignored. Calibration of the gas chromatograms of the gasoline fractions against the internal standard was carried out on the basis of some known *n*-paraffins. Although aromatic compounds may somehow deviate from this calibration, it could not be corrected because of numerous unidentified peaks in the chromatograms. Despite these errors, however, it is safe to present the following discussions, as the trend of the results is evident.

Runs 1 and 2 show the results from Arabian Light atmospheric and vacuum residues by the two-stage process. For the conventional FCC feedstock, the contents of Conradson carbon residue should be kept below 0.5%, and Ni + V below 2.5 ppm. From the direct catalytic cracking of Arabian Light vacuum gas oil, the conventional FCC feed stock, using this fixed bed apparatus (run 3), the following results were obtained: 37.4% C<sub>5</sub>–C<sub>12</sub> gasoline,

Table II. Results of the Catalytic Cracking of Heavy Oils by the Two-Stage Process<sup>a</sup>

run	1	2	3	4	5	6	7
feedstocks	Arabian Light atm. residue	Arabian Light vac. residue	Arabian Light <sup>c</sup> vac. gas oil	Cold Lake bitumen	Cold Lake <sup>c</sup> bitumen	Orinoco bitumen	Taching vac. residue
amount of feed, mg	196	157	128	155	111	179	161
WHSV	1.2	0.68	0.94	0.85	0.82	0.96	0.76
yield against feed, wt %							
gas C <sub>1</sub> -C <sub>2</sub>	1.3 (1.6) <sup>d</sup>	1.8 (3.2)	1.5	1.7 (2.3)	2.2	1.8 (2.6)	1.2 (1.9)
C <sub>3</sub>	4.4 (5.7)	3.1 (5.4)	7.5	4.1 (5.5)	5.7	2.6 (5.0)	5.4 (8.4)
C <sub>4</sub>	3.3 (4.3)	2.1 (3.6)	7.8	3.7 (4.4)	2.7	3.1 (4.3)	3.1 (4.8)
C <sub>5</sub> -C <sub>12</sub> gasoline	26.8 (34.7)	24.8 (43.0)	37.4	26.5 (35.4)	21.6	22.9 (32.0)	20.3 (32.0)
C <sub>13</sub> + oil	36.5 (40.8)	12.0 (20.8)	33.7	27.0 (36.1)	24.3	22.6 (31.7)	13.1 (20.6)
coke	3.2 (4.2)	6.7 (11.7)	4.9	4.2 (5.6)	29.6	4.5 (6.3)	6.4 (10.0)
pyrolysis residue	10.7	27.2	—	15.8	—	18.5	20.3
pyrolyzed oil <sup>b</sup>	12.1	15.1	—	9.4	—	10.1	16.3
material balance	93.4	93.2	93.0	92.4	86.5	86.1	86.0

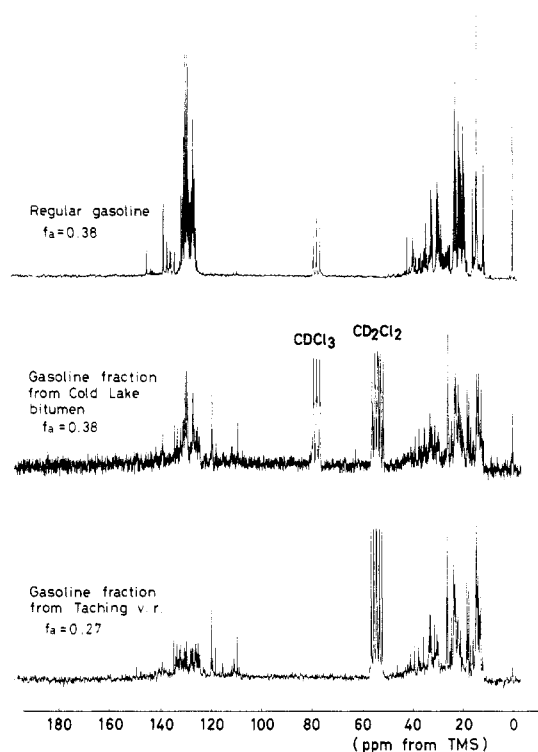
<sup>a</sup> First stage, 450 °C; second stage, 480 °C; reaction time, 40 min; catalyst, 200 mg. <sup>b</sup> Pyrolyzed oil at the first stage, which was not carried to the second stage. <sup>c</sup> Direct catalytic cracking. <sup>d</sup> Parentheses designate corrected yield based on the cracked oil carried to the catalyst bed.

33.7% C<sub>13</sub>+ oil, and 4.9% coke. In order to compare the result from the two-stage process with the direct catalytic cracking, yields were corrected on the basis of the pyrolyzed oil carried to the catalyst bed. The corrected yields were shown in the parentheses in Table II. In the corrected yield, the two-stage cracking of the atmospheric and the vacuum residues provided nearly the same amount of liquid products: 34.7 and 43.0% of C<sub>5</sub>-C<sub>12</sub> gasoline and 40.8 and 20.8% of C<sub>13</sub>+ oil, respectively. Coke formation on the catalyst bed from the atmospheric residue was also the same level as that from the vacuum gas oil.

In runs 4 and 5, the catalytic cracking of Cold Lake bitumen with the two-stage process and the direct process were compared. Although 15.8% of pyrolysis residue and 9.4% of pyrolyzed oil remained in the first stage, yields of C<sub>5</sub>-C<sub>12</sub> gasoline and C<sub>13</sub>+ oil from the two-stage process were superior to those from the direct catalytic cracking. Corrected yields of the liquid products from Cold Lake bitumen, when using the two-stage process, were in the same order of magnitude to those obtained from Arabian Light vacuum gas oil (run 3). As shown in run 5, extremely larger amount of coke, 29.6% was formed in the direct cracking.

The two-stage process for the catalytic cracking of heavy oils evidently reduces the coke formation on the catalyst. As reported previously (Suzuki et al., 1981b), high molecular weight condensed aromatic rings, which will cause severe coke formation, can be left as a pyrolysis residue at the first stage. To ascertain the fractionation effect at the first stage, heavy metal contents of the original oil and the pyrolyzed oil at 440 °C was measured for Cold Lake and Orinoco bitumens. Cold Lake bitumen contains 20.8 ppm of Ni and 220 ppm of V, and Orinoco bitumen contains 29.5 and 255 ppm, respectively. It seems to be difficult to operate the FCC process, using feedstocks containing such large amounts of heavy metals. On the contrary, only 2.5 ppm of nickel and 8.0 ppm of vanadium were contained in the pyrolyzed oil from Cold Lake bitumen. Those from Orinoco bitumen were 2.6 and 8.8 ppm, respectively. The amount of Ni in the pyrolyzed oil is reduced to 1/10 of that in the original oil, and that of V is reduced to 1/30. This level of metal contents is still higher than the required level for FCC feed stock. However, it could be processed by using a current metal passivation catalyst (Ritter et al., 1981).

Thus by the use of the two-stage process, the asphaltene fraction containing large amounts of high molecular weight condensed aromatic rings and heavy metals can be left in the first stage as pyrolysis residue, so that the formation of coke can be reduced, and gasoline and kerosene can be

Figure 2. <sup>13</sup>C NMR spectra of gasoline fractions.

obtained in good yield from heavy oils.

On cracking Orinoco bitumen (run 6), 22.9, 22.6, and 4.5% of C<sub>5</sub>-C<sub>12</sub> gasoline, C<sub>13</sub>+ oil, and coke, were obtained, respectively.

**<sup>13</sup>C NMR Spectra of C<sub>5</sub>-C<sub>12</sub> Gasoline and C<sub>13</sub>+ Oil.** Figure 2 shows the <sup>13</sup>C NMR spectra of the gasoline fractions obtained from the catalytic cracking of Cold Lake bitumen and Taching vacuum residue using the two-stage method, together with the spectrum of commercial regular gasoline. Both in the aromatic and aliphatic regions, a large number of sharp peaks appeared.

In the <sup>13</sup>C NMR spectra of heavy residues (Takegami et al., 1980) peaks of carbon atoms belonging to a long paraffinic straight chain (14.1, 22.7, 29.7, and 32.0 ppm) were prominent, and relative intensity of the peak at 29.7 ppm was the highest. In the spectra of gasoline fractions, however, the peak at 29.7 ppm cannot be seen at all, indicating that content of straight-chain paraffins longer than heptane is very small. Other peaks can be assigned to carbon atoms in branched paraffins (Lindemann, and Adams, 1971), naphthenes, and short alkyl substituents

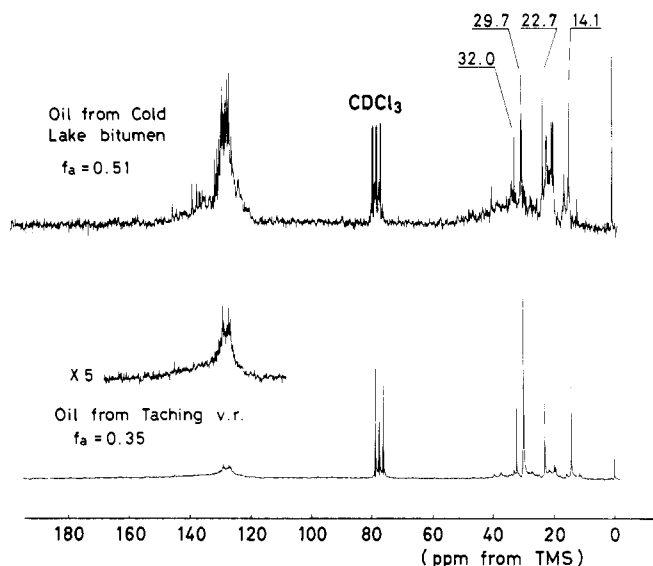


Figure 3.  $^{13}\text{C}$  NMR spectra of gas oil fractions.

on aromatic ring systems (Breitmaier et al., 1975). A peak at 22 ppm can be assigned to a methyl carbon of isopropyl groups. A secondary butyl group can provide peaks at 11, 19, 30, and 35 ppm. Peaks at 40 ppm or downfield can be attributed to quaternary carbon atoms. Judging from the spectral patterns in the aliphatic region, Taching vacuum residue, an extremely paraffinic feedstock, can provide a gasoline fraction which is abundant in isoparaffinic structure via the catalytic cracking.

Aromaticity of the gasoline fraction from Cold Lake bitumen was the same as that of commercial regular gasoline (0.38). That from Taching one was lower (0.27). The peaks in the aromatic region of the spectra of regular gasoline and the gasoline fraction from Cold Lake bitumen appear mainly upfield from 130 ppm. In an aromatic ring system, which is not highly condensed, carbon atoms in the ring junction points or attached to substituents should appear downfield from 130 ppm. The higher relative intensity of the peaks upfield from 130 ppm suggests a limited amount of such carbon atoms.

$^{13}\text{C}$  NMR spectra of gas oil fractions obtained from the catalytic cracking of Cold Lake bitumen and Taching vacuum residue are compared in Figure 3. In contrast to those of gasoline fractions, the patterns of the spectra of the gas oil fractions obtained from the two feedstocks appear quite differently. In the spectrum of the gas oil fraction from Taching residue, peaks assignable to *n*-paraffin are very strong, whereas a large number of other sharp resonances and a broad envelope of overlapped resonances can be seen in the spectrum of that from Cold Lake bitumen. They reveal that a long paraffinic straight chain is abundant in the oil from Taching vacuum residue, and branched or alicyclic hydrocarbons are rich in that from Cold Lake bitumen. Considerable amounts of *n*-paraffins in the gas oil fraction from Taching vacuum residue were suggested by the gas chromatogram.

In a previous paper (Itoh et al., 1983), we have reported the correlation between the pyrolysis products and the structural characteristics of the feedstocks. Ethylene yield increased rectilinearly according to an increase in the SPI value of the feedstock. Using our two-stage pyrolysis method, 24–27 wt % of ethylene, 9–11 wt % of propylene, and 54 wt % of  $\text{C}_1$ – $\text{C}_4$  hydrocarbon gases were obtained from Taching vacuum residue, having the SPI value of 0.410. By contrast, tar sand bitumens (SPI = 0.18) provided only 12–14% ethylene, 6–8 wt % propylene, and 35 wt % of the total hydrocarbon gases.

On the contrary, yields of  $\text{C}_5$ – $\text{C}_{12}$  gasoline and  $\text{C}_{13}+$  oil from Taching vacuum residue are quite small compared with those from Cold Lake bitumen, both against feed and pyrolyzed oil (run 7). In addition a larger amount of coke was formed from the Taching residue. Differences in the yield of gasoline and oil fractions can be interpreted with the differences in the structural feature of the feedstocks. For thermal cracking, pyrolysis products from a normal paraffin (*n*-tetracosane) consist exclusively of lower 1-olefins. For an isoparaffin (6-methyleicosane), however, the reaction mostly develops according to a radical mechanism, but there also occurs an intramolecular cleavage at the branching which favors the liquid formation (Blouri et al., 1981). For catalytic cracking, White (1968) reported how cracker feed influences yield. He concluded that polycycloparaffins and monocyclic aromatics make the best feedstock for the production of  $\text{C}_5$  to 200 °C gasoline, followed by monocyclo paraffins, normal paraffins, and dicyclic aromatics. As we have reported previously (Takegami et al., 1980; Suzuki et al., 1982a), Taching vacuum residue consists mostly of long paraffinic straight chains, whereas tar-sand bitumens are abundant in alicyclic and branched structures. Thus, it should be reasonable that Cold Lake bitumen provides more gasoline and oil fractions than Taching vacuum residue.

It should also be noticeable that the  $\text{C}_{13}+$  oil from Cold Lake bitumen consists mainly of lower boiling point hydrocarbons up to  $\text{C}_{17}$ , while that from Taching vacuum residue consists of broad boiling point ranges. Although these fractions must be hydrotreated to upgrade as kerosene or gas oil, Cold Lake bitumen seems to provide a larger amount of kerosene fraction than Taching residue.

#### Acknowledgment

The authors are grateful to Shimadzu Corp. for the measurement of atomic absorption spectra.

Registry No. Silica, 7631-86-9; alumina, 1344-28-1.

#### Literature Cited

- Alba, T.; Kaji, H.; Suzuki, T.; Wakamatsu, T. *Chem. Eng. Prog.* **1981**, (2), 37–44.
- Blouri, B.; Giraud, J.; Nouri, S.; Herault, D. *Ind. Eng. Chem. Process Des. Dev.* **1981**, 20, 307–313.
- Breitmaier, E.; Haas, G.; Voelter, W., "Atlas of Carbon-13 NMR Data"; vol. I and II, Heyden & Son Ltd.; London, 1975.
- Edison, R. R.; Slemssen, J. O.; Maslogites, G. P. *Hydrocarbon Process.* **1976**, 55(5), 133–138.
- Finneran, J. A.; Murphy, J. R.; Whittington, E. L. *Oil Gas J.* **1974**, 72(2), 52–55.
- Hemler, C. L.; Vermillion, W. L. *Oil Gas J.* **1973**, 71(45), 88–92.
- Itoh, M.; Suzuki, T.; Tsujimoto, Y.; Yoshii, K.; Takegami, Y.; Watanabe, Y. *Fuel* **1983**, 62, 98–102.
- Lindemann, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, 43, 1245–1252.
- Maslogites, G. P.; Beckberger, L. H. *Oil Gas J.* **1973**, 71(47), 49–53.
- Murphy, J. R.; Treese, S. A. *Oil Gas J.* **1979**, 77(26), 135–142.
- Ritter, R. E.; Rheau, L.; Welsh, W. A.; Magee, J. S. *Oil Gas J.* **1981**, 79(27), 103–110.
- Suzuki, T.; Itoh, M.; Watanabe, Y.; Mitsudo, T.; Takegami, Y. *Jpn. Pet. Inst.* **1981a**, 24, 151–159.
- Suzuki, T.; Itoh, M.; Mishima, M.; Watanabe, Y.; Takegami, Y. *Fuel* **1981b**, 60, 961–966.
- Suzuki, T.; Itoh, M.; Takegami, Y.; Watanabe, Y. *Fuel* **1982a**, 61, 402–410.
- Suzuki, T.; Itoh, M.; Mishima, M.; Takegami, Y.; Watanabe, Y. *Ind. Eng. Chem. Process Des. Dev.* **1982b**, 21, 149–154.
- Takegami, Y.; Watanabe, Y.; Suzuki, T.; Mitsudo, T.; Itoh, M. *Fuel* **1980**, 59, 253–259.
- White, P. J. *Hydrocarbon Process.* **1968**, 47(5), 103–108.
- Yanik, S. J.; Frayer, J. A.; Hulting, G. P.; Somers, A. E. *Oil Gas J.* **1977**, 75(20), 139–145.

Department of Hydrocarbon Chemistry

Faculty of Engineering

Kyoto University

Kyoto 606, Japan

Maki Itoh

Toshimitsu Suzuki\*

Yoshihiko Tsujimoto

Yoshinobu Takegami

Yoshihisa Watanabe

Received for review April 14, 1983

Revised manuscript received August 26, 1983

Accepted September 13, 1983