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A new hydrodealkylation process with fluid-beds to produce high purity naphthalene and methylnaphthalenes from heavy aromatic oils

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Abstract

By use of fluid-bed technology, direct hydrodealkylation of heavy oils was studied and a new process to produce high purity naphthalene and 2-methylnaphthalene was developed. As a basic research, catalyst activity, selectivity and stability for hydrodealkylation of heavy oil, hydrodealkylation reaction scheme and kinetics and coke formation kinetics and mechanism were investigated. Reaction rate constants were theoretically analyzed with fluid-bed consecutive reaction model. These research and analyses were utilized for optimization and design of the process. Pilot operation provided high yield and quality of the products which were suitable for synthesis of monomers for high performance polymers. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodealkylation; Naphthalene; Methylnaphthalene; Fluidized bed; Light cycle oil

1. Introduction

As the significance of FCC process has been increasing for heavy oil cracking, it is desirable to effectively utilize light cycle oil (LCO) which contains heavy aromatic, i.e. polycyclic compounds in large quantities. On the other hand, the polycyclic compounds are expected to be utilized as base materials for high performance polymers such as polyethylene naphthalate (PEN).

The polycyclic compound has been mainly supplied from coal tar distillation, but it seems the role of coking oven is decreasing due to the rationalization of steel industry. Petroleum heavy aromatic oils such as LCO will be considered an important source of the polycyclic compounds, especially naphthalene or alkylnaphthalene as raw materials for chemical synthesis. Since the content of each naphthalene compound in LCO is very small due to the presence of many species and isomers of alkylnaphthalene, separation of a specific alkylnaphthalene has less industrial meaning. Therefore, dealkylation would be an important processing method to produce base material such as high purity naphthalene or 1- and/or 2-methylnaphthalene at a high yield.

In this paper, a new process of heavy oil hydrodealkylation with fluid-beds [1] and some results of the basic research for the process are reported and discussed.

2. Concept of new hydrodealkylation process for heavy aromatic oils

Heavy feed oil such as LCO includes components likely to form coke, saturate fraction liable to hydro-

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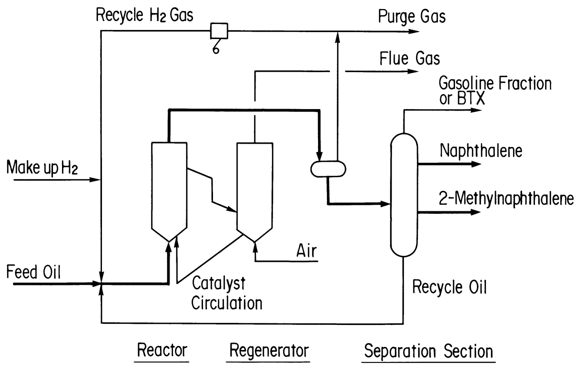

Fig. 1. New hydrodealkylation process with fluid-beds.

crack and release a large amount of heat, and sulfur and nitrogen compounds to be excluded from the products. New processes should have features to deal with such feed oil properties, compared with the conventional processes mainly used to produce benzene from clean feed oil like toluene.

Fig. 1 illustrates the new hydrodealkylation process with two fluid-beds, one for hydrodealkylation reaction and the other for catalyst regeneration. In the fluid-bed reactor, highly exothermic hydrodealkylation reaction can be conducted at a uniform temperature in the bed, and the catalyst is transferred to the regenerator to burn or gasify the coke deposited on the catalyst in the reactor.

The fluid-bed reactor is operated at pressures between 1.0 and 1.6 MPa to maintain hydrogen partial pressure necessary for promoting the hydrodealkylation and preventing excess coke formation. Depending on the main product required, the process is operated either in naphthalene mode or in methylnaphthalene mode. Operational differences between the two modes are the reaction temperature, separation and recycling of the product oil.

Catalyst used in the process should have characteristics as follows: high dealkylation activity, substantially no activity of naphthalene-ring hydrocracking, sufficient hydro-desulfurization and -denitrogenation activity, resistance against high concentrations of sulfur and basic nitrogen in the feed, resistance against high amount of coke deposit on the catalyst, and thermal stability in the repeated reaction and regeneration.

3. Research for hydrodealkylation of alkylnaphthalenes

3.1. Experimental

Two types of apparatus were used for fundamental research of hydrodealkylation: an isothermal fixed-bed microreactor with catalyst volume of 4 ml to investigate the catalyst activity, and a fluid-bed reactor of 1 inch in diameter with catalyst inventory of 500 ml to mainly analyze the reaction scheme and kinetics. As feed materials for this purpose, pure compounds such as methylnaphthalene, dimethylnaphthalene and ethylnaphthalene as model feed, and actual heavy oils such as LCO and coal tar were used.

As pilot unit, an equipment which consisted of two fluid-bed columns, one for hydrodealkylation and the other for catalyst regeneration, was used for continuous reaction for the period of 1 to 4 weeks. Catalyst inventory of the reactor and regenerator were about 8 and 10 l, respectively. Many kinds of LCO with various boiling range were used as feed oil and hydrodealkylated in both naphthalene and methylnaphthalene modes. The product oil was separated from the reactor effluent gas in a cooling section and introduced to distillation columns to obtain and analyze the products.

The reaction conditions for the experiments were varied within a wide range: total pressure up to 2.0 MPa, reaction temperature between 773 and 923 K, contact time between 3 and 30 s.

3.2. Results and discussion

3.2.1. Catalyst activity and selectivity

Various kinds of catalysts were tested to evaluate the activity and selectivity using the isothermal fixed-bed reactor and 1 in fluid-bed reactor. Such catalysts as Ni/alumina, molybdenum oxide/alumina, chromia/alumina, vanadium oxide/alumina, alumina, FCC catalyst, activated carbon were tested.

High activity of hydrodealkylation was observed with molybdenum oxide/alumina, chromia/alumina, vanadium oxide/alumina, and FCC catalyst. Ni/alumina had relatively lower activity compared with these catalysts. Alumina itself did not show catalytic activity. Activated carbon had high hydrodealkylation activity but coke yield was extremely high.

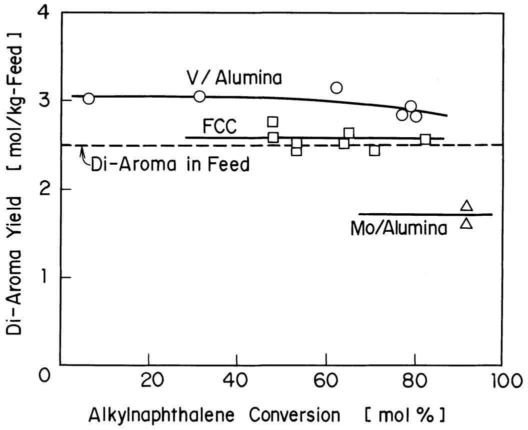

Fig. 2. Di-aromatics molar balance for hydrodealkylation with various catalysts.

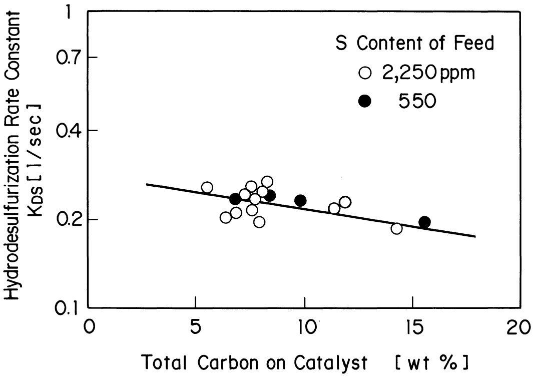

Fig. 3. Hydrodesulfurization activity of vanadium oxide/alumina with deposit coke during LCO hydrodealkylation. Reaction temperature: 873 K.

Fig. 2 shows the typical effect of catalyst on the molar balance of di-aromatics, i.e. naphthalene plus all the alkylnaphthalenes, between that in the product oil and in the feed LCO over the boiling point range 200–270°C. When molybdenum oxide/alumina was used as the catalyst, the amount of di-aromatics was decreased, and excessive yields of gas and mono-aromatics were observed. Nickel/alumina showed the same tendency at high conversion conditions. It can be considered that naphthalene ring is hydrocracked due to strong hydrocracking activity of these catalysts.

To the contrary, vanadium oxide/alumina showed remarkable increase in di-aromatics with relatively low yields of gas and mono-aromatics. In order to investigate this catalytic phenomenon, *n*-tridecane, a typical non-aromatic compound in LCO, was used as testing material and fed to the vanadium oxide/alumina catalyst under the hydrodealkylation conditions. As a result, a rather high yield of the aromatic product was obtained from *n*-tridecane; mono-aromatics plus di-aromatics yield was about 30% and di-aromatics yield was about 10%. This result indicated that the vanadium oxide/alumina possessed considerable cyclization activity. On the other hand, when methylnaphthalene was used as the feed material to the catalyst, molar yield of naphthalene and methane was found nearly equal to the molar conversion of methylnaphthalene. It may be understood from this result that the vanadium oxide/alumina has very little activity of aromatic ring hydrocracking. From these experimental results, it may be presumed that vanadium oxide/alumina had mild hydrogenation/dehydrogenation activity, which is followed by high hydrodealkylation and considerable cyclization activity without causing aromatic ring cracking.

With FCC catalyst, no remarkable increase or decrease of di-aromatics was observed.

Concerning the hydrodesulfurization, vanadium oxide exhibited high activity which was rather stable even at high concentration of deposited coke on the catalyst, as seen in Fig. 3. Molybdenum oxide/alumina also showed high desulfurization activity. FCC catalyst did not show sufficient desulfurization activity.

Among the catalysts tested, vanadium oxide/alumina was found to have all the characteristics necessary for heavy oil dealkylation and furthermore, it showed excellent resistance to coke deposit on the catalyst; hydrodealkylation activity was not influenced by coke deposition as shown in Fig. 4.

Extensive investigation of reaction analysis and kinetics was further conducted using vanadium oxide/alumina as one of the typical catalysts for the process.

3.2.2. *Hydrodealkylation reaction scheme and reaction analysis*

Fig. 5 illustrates the effect of contact time on the alkylnaphthalene composition obtained from the experiments in the fluid-bed reactor with LCO. Consecutive reaction scheme of alkylnaphthalene

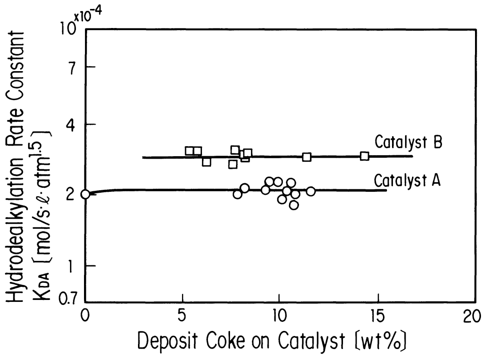

Fig. 4. Stability of LCO hydrodealkylation activity of vanadium oxide/alumina catalysts agaist coke deposit on the catalysts. Average pore radius of alumina: 16.8 nm (catalyst A), 11.6 nm (catalyst B). Reaction temperature: 873 K.

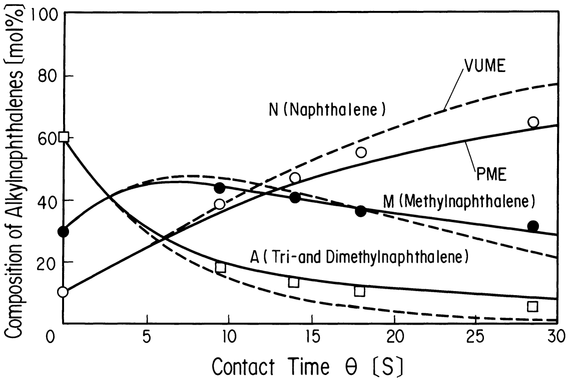

Fig. 5. Effect of contact time on alkylnaphthalene composition and prediction from the fluid-bed reaction model developed (873 K, Feed: LCO). PME: Perfect mixing emulsion model. VUME: Vertically unmixed emulsion model.

dealkylation is understood from the graph as trimethyl-naphthalene(TMN) ⇒ dimethylnaphthalene(DMN) ⇒ methylnaphthalene(MN) ⇒ naphthalene(N)

From the rate analysis for the hydrodealkylation of 2-methylnaphthalene and LCO under various conditions, the rate of hydrodealkylation was found to be proportional to feed oil partial pressure (1st order) and to the square root of hydrogen partial pressure[2] as

$$r_{\mathrm{DA}} = K_{\mathrm{DA}} \times P_{\mathrm{F}} \times P_{\mathrm{H_2}}^{0.5} \qquad (1)$$

The consecutive dealkylation reaction of alkylnaphthalenes in a fluid-bed was analysed based on the two phase theory for fluid-bed reaction considering back-mixing in the emulsion phase in the bed.

For the consecutive 1st order reaction in a fluid-bed with back-mixing in the emulsion phase:

$$\mathrm{A} \rightarrow \mathrm{M} \rightarrow \mathrm{N} \qquad (2)$$

yields of intermediate product M and end product N is expressed (Eq. (3)) as

$$\frac{C_{\mathrm{bA}}^{1}}{C_{\mathrm{bA}}^{0}} = \mathrm{e}^{-N_{\mathrm{b}}} + \left(1 - \mathrm{e}^{-N_{\mathrm{b}}}\right)\left(1 + \frac{\epsilon_e N_{\mathrm{rA}}}{1 - \mathrm{e}^{-N_{\mathrm{b}}}}\right)^{-1} \qquad (3)$$

$$\begin{aligned}\frac{C_{\mathrm{bM}}^{1}}{C_{\mathrm{bA}}^{0}} = \frac{C_{\mathrm{bM}}^{0}}{C_{\mathrm{bA}}^{0}} &\left[\mathrm{e}^{-N_{\mathrm{b}}} + (1 - \mathrm{e}^{-N_{\mathrm{b}}})\left(1 + \frac{\epsilon_e N_{\mathrm{rM}}}{1 - \mathrm{e}^{-N_{\mathrm{b}}}}\right)^{-1}\right] \\ &+ (1 + \mathrm{e}^{-N_{\mathrm{b}}})\left(1 + \frac{\epsilon_e N_{\mathrm{rM}}}{1 - \mathrm{e}^{-N_{\mathrm{b}}}}\right)^{-1} \\ &\times \left[1 - \left(1 + \frac{\epsilon_e N_{\mathrm{rA}}}{1 - \mathrm{e}^{-N_{\mathrm{b}}}}\right)^{-1}\right] \qquad (4)\end{aligned}$$

$$\frac{C_{\mathrm{bN}}^{1}}{C_{\mathrm{bA}}^{0}} = \frac{C_{\mathrm{bN}}^{0}}{C_{\mathrm{bA}}^{0}} + \left(1 - \frac{C_{\mathrm{bA}}^{1}}{C_{\mathrm{bA}}^{0}}\right) + \left(\frac{C_{\mathrm{bM}}^{0}}{C_{\mathrm{bA}}^{0}} - \frac{C_{\mathrm{bM}}^{1}}{C_{\mathrm{bA}}^{0}}\right) \qquad (5)$$

where, $N_{\mathrm{b}} = k_{\mathrm{ob}} a_{\mathrm{b}} \theta_{\mathrm{f}}$, $N_{\mathrm{rA}} = K_{\mathrm{rA}} \theta_{\mathrm{f}}$, $N_{\mathrm{rM}} = K_{\mathrm{rM}} \theta_{\mathrm{f}}$

The predicted line, shown in Fig. 5, based on the fluid-bed reaction model considering back-mixing (Eqs. (3) and (5)) agrees well with the experimental data, compared with the dotted line indicating the case in which back-mixing can be neglected.

Fig. 6 shows the relationship between overall reaction rate coefficient and contact time in the bed where gas back-mixing in the catalyst emulsion phase exists.

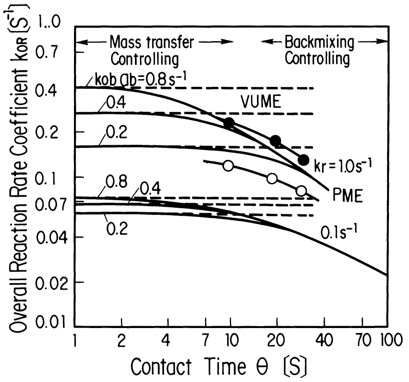

Fig. 6. Relationship between overall reaction rate coefficient K_{OR} and reaction parameters K_{r}: catalyst activity, $K_{\mathrm{ob}}a_{\mathrm{b}}$: mass transfer capacitance coefficient, θ: contact time, K_{OR}: obtained from LCO hydrodealkylation at 873 K. (● for trimethylnaphthalene, ○ for tri- and di-methylnaphthalene).

Dotted line in the same figure indicates the case of no gas back-mixing in the emulsion, which is calculated from a fluid-bed model neglecting back-mixing [3]. By comparing these two cases, it can be understood that there are two regions; mass transfer controlling region in which back-mixing does not affect the overall reaction rate constant, and back-mixing controlling region in which the back-mixing affects and lowers the overall reaction rate constant. The data obtained from the LCO hydrodealkylation reaction agrees with the model considering back-mixing and indicates that the effect of back-mixing on reaction performance should be considered if the contact time is too large and the operation condition falls within the back-mixing controlling region. Therefore, the hydrodealkylation reaction condition was taken outside the region where back-mixing is seriously predominant.

3.2.3. Rate of coke formation

The rate of coke formation was investigated by using 2-methylnaphthalene as a model feed compound and the rate equation Eq. (6)) was obtained based on experimental data shown in Fig. 7.

$$r_{C_{\mathrm{MN}}} = k_{C_{\mathrm{MN}}}(P_{\mathrm{F}}/P_{\mathrm{H_2}})^2 \tag{6}$$

This equation implies that an intermediate substance, which is in hydrogenation dehydrogenation equilibrium with the feed compound, may exist on the catalyst surface, and the dimer formation of the intermediate substance may be the determining step for the rate of coke formation.

From the analysis for LCO dealkylation, the rate of coke formation was obtained as:

$$r_C = k_C P_{\mathrm{F}}^{1.4}/P_{\mathrm{H_2}}^2 \tag{7}$$

The mechanism of coke formation of LCO may be similar to that of 2-methylnaphthalene, but the complexity of the multi-components may make the effect of feed partial pressure slightly different.

Fig. 8 shows the rate of coke formation obtained by experiments and that predicted by Eq. (7) for LCO dealkylation. Good agreement is seen between them.

4. Pilot operation and results of lco hydrodealkylation

Pilot unit was operated for continuous LCO hydrodealkylation for a month in order to confirm the process performance, to obtain engineering data, and to investigate the properties of products. LCO feed rate was 2–4 kg/h, which corresponded to WHSV

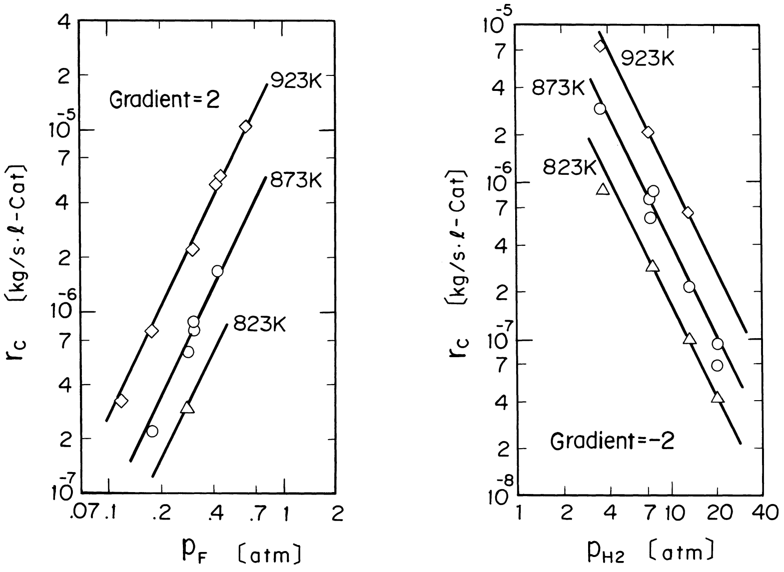

Fig. 7. Effect of feed and hydrogen partial pressure on rate of coke formation (Feed oil: Methylnaphthalene).

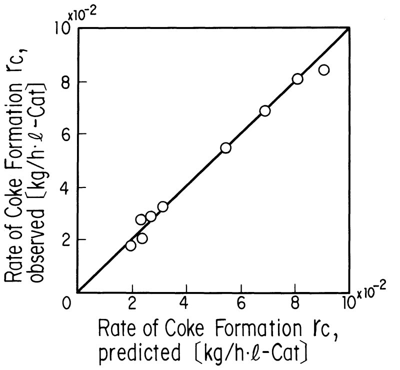

Fig. 8. Comparison of rate of coke formation predicted by Eq. (7) with experimental data.

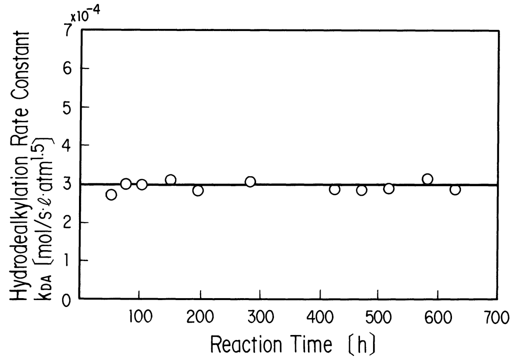

Fig. 9. Stability of hydrodealkylation catalyst activity during 1 month pilot operation Vanadium oxide/alumina catalyst with deposit coke 3–15wt%, Reaction temperature 873 K.

about 0.5–1 kg/kgh, and catalyst circulating rate was about 5–10 kg/h at normal operation condition. As the feed LCO, various fractions with wide and narrow range of boiling point were used.

From six continuous runs, stability of the operation and catalyst activity was confirmed as shown in Fig. 9, and expected yield and properties of the products were obtained.

Table 1 shows typical results of LCO hydrodealkylation in one pass reaction with vanadium oxide/alumina catalyst in naphthalene mode and methylnaphthalene mode operation. The boiling point range of the feed LCO was 200–270°C (wide range), and 230–270°C (narrow range). At molar balance, more than 115 mol% of the di-aroma (naphthalene plus all the alkylnaphthalenes) was obtained with wide range LCO due to the cyclization activity of the catalyst. When narrow range LCO was used, the di-aromatics molar balance remained at about 100% but the di-aromatics yield was high because of higher content of di-aromatics and lower content of other components in the feed. It was thus confirmed that alkylnaphthalene

Table 1
Results of pilot unit operation (1 pass reaction)

Operation mode		NA	MN		NA	MN		NA	MN
Feed LCO	LCO-1			LCO-2			LCO-3		
Reaction temperature (°C)		630	580		650	600		630	580
H_2 partial pressure (atm)		7.6	7.4		8.5	9.2		9.2	9.3
Contact time (s)		13.3	14.4		8.7	11.0		9.5	9.1
Boiling point of feed (°C)	200–270			230–270			230–270		
Feed composition or yield (wt.%)									
Naphthalene	2.1	21.5	12.5	1.7	33.5	21.5	1.7	28.2	11.9
2-methylnaphthalene	6.4	4.9	10.1	13.8	4.7	12.4	11.2	8.6	16.7
1-methylnaphthalene	3.3	2.2	4.7	6.8	1.7	5.1	5.7	3.3	7.1
C2-naphthalene+	18.3	1.7	7.4	24.4	1.5	5.3	32.6	2.5	13.7
Di-aromatics total	30.1	30.3	34.7	46.7	41.4	44.3	51.2	42.5	49.4
Other fraction	69.9	21.4	27.4	53.3	14.9	19.3	48.8	16.7	20.9
Oil total	100.0	51.7	62.1	100.0	56.3	63.6	100.0	59.2	70.2
Gas		33.0	26.2		34.8	25.4		27.8	19.7
Coke (gasified)		15.9	10.7		12.4	9.0		11.7	7.6
All total, recovered		100.6	99.0		103.5	98.0		98.7	97.5
Di-aroma mol balance (mol%)		115.1	125.1		101.1	103.9		94.3	102.6

Operation mode: NA, naphthalene mode; MN, methylnaphthalene mode.
Catalyst: vanadium oxide/alumina.

Table 2
Yield simulation for LCO hydrodealkylation process (recycle feed operation)

Operation mode	Naphthalene	Methylnaphthalane	
Feed LCO (wt.%)	100.0	100.0	
H_2	2.3	1.2	
Total	102.3	101.2	
Naphthalene	43.2	29.8	48.8
2-methylnaphthalene	–	19.0	
Light Oil (BTX rich)	12.4	14.5	
Fuel gas	33.3	25.8	
Coke (gasified)	13.4	12.0	
Total	102.3	101.2	

contained in the feed could be effectively converted to naphthalene and/or methylnaphthalene.

Based on the precise analysis of feed oil, product oil and gas, and regenerator gas of the pilot operation, material balance in reaction section of this process was obtained and utilized for simulation of recycle operation. As the recycle system, the oil fraction heavier than 2-methylnaphthalene and impurity of naphthalene fraction are separated by distillation and recycled as shown in Fig. 1 schematically.

Simulated yield of naphthalene and/or 2-methylnaphthalene in the recycle operation was estimated nearly 50 wt.% of feed LCO which contains 51.2 wt.% di-aromatics fraction as shown in Table 2.

Table 3 shows the properties of naphthalene and 2-methylnaphthalene obtained from the distillation column. The purity of the products agreed well with the design value obtained by engineering study. It is noticed that the purity and sulfur and nitrogen content are sufficient for being used as raw material for chemical synthesis, especially as base material for synthesis of PEN precursor such as methylation to 2,6-dimethylnaphthalene, the technology of which has progressed recently [4].

Table 3
Properties of naphthalene and 2-methylnaphthalene obtained in pilot operation

	Naphthalene	2-Methylnaphthalene
Purity (wt.%)	99.5+	99+
Sulfur (ppm)	<10	<30
Nitrogen (ppm)	<2	<3

5. Conclusion

By use of fluid-bed, direct hydrodealkylation of heavy oils was studied. Parallel to the selective hydrodealkylation without ring cracking, sufficient hydrodesulfurization and denitrogenation proceeded by selected catalysts even in the presence of high amount of coke deposited on it. Based on the reaction analysis, rate equations for hydrodealkylation and coke formation were obtained to design the new hydrodealkylation process. This process produces not only high purity naphthalene but also methylnaphthalene, especially 2-methylnaphthalene which is expected to be used for alkylation to provide monomers for high performance polymers.

6. Nomenclature

a_b	Interface area between the bubble and emulsion phases per unit bed volume(cm^{-1})
C_{bi}^0	Concentration of component i at bed inlet (mol/cc)
C_{bi}^1	Concentration of component i at bed outlet (mol/cc)
k_{ob}	Mass transfer coefficient between bubble and emulsion phases (cm/s)
K_{DA}	Hydrodealkylation rate constant of catalyst per unit bed volume (mol/s/cc/$atm^{1.5}$)
K_{OR}	Overall reaction rate coefficient for 1st order reaction in fluid-bed (1/s)
K_{ri}	Reaction rate constant of catalyst particles for component i (1/s)
r_C	Rate of coke formation for LCO (g/s/cc)

$r_{C_{\mathrm{MN}}}$	Rate of coke formation for methylnaphthalene (g/s/cc)
r_{DA}	Rate of hydrodealkyration (mol/s/cc)
ε_{e}	Volume fraction of emulsion phase in fluid-bed (–)
θ_{f}	Contact time (fluid-bed height/superficial gas velocity) (s)

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