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Reaction Modeling of Light Naphtha Aromatization (LNA) Process

Koichi KATO^{†1)*}, Satoshi FUKASE^{†2)}, Toru AMAYA^{†2)}, and Yasukazu SATO^{†2)}^{†1)} Engineering Dept., Petroleum Refining Div., Japan Energy Corp., 10-1 Toranomom 2-chome, Minato-ku, Tokyo 105^{†2)} Petroleum Laboratory, Japan Energy Corp., 17-35 Niizo-minami 3-chome, Toda, Saitama 335

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A kinetic reaction model has been developed for the light naphtha aromatization (LNA) process which employs zinc aluminosilicate catalyst. In order to develop the model, which represents the key reactions involved in the process, it is assumed that the catalyst activity is consistent, regardless of time or location in the reactor.

The kinetic model has been validated, using reaction rate coefficients fitted to match laboratory reactor data.

The kinetic model has been used with the process simulator to investigate reactor design and the optimal catalyst loading pattern for a commercial-scale unit consisting of three units of reactors with feed preheaters connected in series. The studies on catalyst loading were conducted for a total contact time of 1.429 h, with the feed to the reactor train, which is preheated to 520°C at each reactor inlet under the pressure of 3 kg/cm²G.

The optimal catalyst loading pattern, in terms of percentage of total catalyst volume into three reactors, was determined to minimize deviations from the results of isothermal reactor.

1. Introduction

The purpose of the naphtha aromatization process is to convert paraffins into aromatics, either for use in motor fuels (to increase octane ratings) or as a source of aromatic compounds. Aromatic product yield and selectivity depend on the operating conditions (temperature, pressure, contact time), naphtha feed property, catalysts type, and their ability.

Light paraffins are becoming attractive feedstocks for the production of aromatics. Several processes have been developed for this reaction: Cyclar^{1),2)} and Z-former³⁾. Zeolitic catalysts with MFI structure are generally chosen for this reaction, because of their lower coking tendency.

The aromatization of the paraffins in light naphtha into aromatic compounds takes place *via* a series of complex reactions on the surface of a catalyst containing various metal species (*e.g.*, Zn, Ga). There are many components/intermediates, such as paraffins (C₁ to C₉), olefins (C₂= to C₉=), aromatics (A₆ to A₉) and hydrogen, and several types of reactions involved in the transformation. Some of the reactions include cracking, hydrocracking, dehydrocracking, hydrogenation, dehydrogenation, oligomerization and dehydro-

cyclization. Furthermore, the catalyst activity deteriorates with time, which is due to decrease in the number of catalyst active sites by coking.

It has been reported that H-ZSM-5 combined with zinc or gallium cation enhanced aromatization of lower paraffins^{4),5)}. Several groups have reported on the mechanism of aromatization of lower paraffins over Zn- or Ga-loaded H-ZSM-5. Mole *et al.*⁶⁾ have studied the conversion of propane. Fujimoto *et al.*^{7),8)} have studied the conversion of *n*-butane. Nagamatsu *et al.*^{9),10)} have reported kinetic studies on hexane conversion on Zn/H-ZSM-5. Almost no work, however, has been reported, concerning pentane feedstock.

The authors have undertaken development of the light naphtha aromatization (LNA) process, to produce aromatics from pentane fraction¹¹⁾. After several years of laboratory study, the authors have proceeded with the design of a demonstration unit at the authors' refinery. The demonstration unit involves three fixed bed reactors connected in series with preheaters installed in between.

The objective of this study is to develop a reaction model of the light naphtha aromatization (LNA) process. The reaction model will be used in reactor design and to determine the optimal loading pattern of the LNA catalyst in the demonstration unit.

* To whom correspondence should be addressed.

2. Experimental

2.1. Catalysts and Feedstock

A Zn-ZSM-5 type zeolite was synthesized by method described in the previous paper¹¹⁾ and was solely used in the experiment.

Characterization of the synthesized materials was made by X-ray diffraction. The structure of zeolite was confirmed as that of ZSM-5.

The light naphtha used as feedstock in this experiment was composed of C₅-C₇ compounds. Its composition is shown in Table 1.

2.2. Apparatus and Procedure

Reactions were carried out in a continuous microflow fixed-bed reactor (1 cm in inner diameter, 55.5 cm in length) placed in a vertical furnace. Reaction temperatures were kept at 425, 450, 475, and 500°C at different runs while pressure was kept at 3 kg/cm²G, and contact time (W/F) was varied from 0.00167 through 0.1 h. It was not feasible to carry out the experiments for longer contact time as the reaction rates would be too high to be measured. Fresh catalyst was used in each experiment to minimize the effects of catalyst deactivation by coking. Analysis of the reaction products was conducted by gas chromatography. The changes in product selectivity and conversion with contact time were obtained.

Fractional conversion was defined as follows:

$$\text{Conversion} = (\text{Products} - AR_0) / (1 - AR_0) \quad (1)$$

where,

AR_0 = aromatics in the feed naphtha, weight percent

Products = (H₂ + (C₁ to C₄) + (C₅ + C₆) + aromatics) in product, weight percent

The results of experiment at 500°C are shown in Fig. 1.

3. Kinetic Analysis

3.1. Reaction Model

The reaction model which is used for this investigation is based on an extension of the kinetic studies on hexane by Nagamatsu *et al.*

The basic scheme for the aromatization of light naphtha is assumed to be as follows:

Paraffins → Lower Olefins → Higher Olefins → Aromatics

Table 1 Components of Reactant Naphtha

Components (code)	wt%
C1+C2	0
C3	0
isoC4	0
nC4	0
C4=	0
isoC5	15.36
nC5	32.27
C5=	0.06
C6	42.7
C6=	0
C7	7.10
C8	0
Benzene	2.06
Toluene	0.43
Ethylbenzene	0
<i>m,p</i> -Xylene	0
<i>o</i> -Xylene	0
A9+	0
Total	99.98

Fig. 1 Change in Product Selectivity and Conversion with Contact Time in the Conversion of Light Naphtha

According to this scheme, paraffins are cracked or hydrocracked to lower olefins which oligomerize to produce higher olefins. Aromatics are formed by successive cyclization/dehydrogenation of higher olefins. Hence, C₆= olefins will form A₆ aromatics, C₉= olefins will form A₉ aromatics, and so on. Some key elements of the reaction model, shown in Fig. 2, are summarized below:

1) Grouping are made for components which show the same dependence of concentration on contact time. This will allow the use of a smaller set of rate constants to describe the reaction kinetics.

C₁-C₂ light gas (LG)
 C₃-C₅ lower paraffins (LP)
 C₂=-C₅= lower olefins (LO)
 C₆-C₉ higher paraffins (HP)

Fig. 2 Reaction Model of Light Naphtha Aromatization

C₆=-C₉= higher olefins (HO)

A₆-A₉ aromatic hydrocarbons (AR)

2) Cracking of higher paraffins is carried out over zeolite catalyst to yield lower olefins and lower paraffins, or lower olefins and light gas. Furthermore, cracking of lower paraffins is carried out to yield lower olefins and light gas.

3) Dehydrocracking of higher and lower paraffins are carried out to give lower olefins.

4) Lower olefins oligomerize to form higher olefins, followed by successive dehydrocyclization of higher olefins to produce aromatics. The variety of aromatics produced could be ascribed to the formation of various higher olefins resulting from combinations of these reactions.

5) Lower and higher olefins are transformed to paraffins by hydride transfer, or are decomposed to lower paraffins or light gas by hydrocracking reactions.

6) Hydrogen atoms are combined to form hydrogen molecules. H₂* and H₂ represent hydrogen on the surface of catalysts and hydrogen in vapor phase, respectively.

7) Each reaction is assumed to be of first-order, with respect to concentration of hydrocarbon reactant. Furthermore, for hydrocracking and hydrogenation of olefins, reaction rates are assumed to comply with the first-order, not only with respect to concentration of hydrocarbon reactant, but also with respect to concentration of surface hydrogen, which are assumed to be at steady-state condition.

3. 2. Extension of Nagamatsu Kinetic Model

In the Nagamatsu model both rate constants and stoichiometric coefficients for the grouped

reactions were estimated from experimental data. The experimental stoichiometric coefficients used in the Nagamatsu kinetic scheme may be too specific for their system (catalyst type, feed quality, etc.). Rather than experimentally estimating a set of rates and stoichiometric coefficients, we propose to use the expanded form of the grouped reactions. Hence, the reactions are written for each component in the group. With this expansion, the stoichiometric coefficients will be fixed integer numbers and there is no need to estimate them from experimental data. The component groupings are still used for estimating/refining the rate constants for the different reaction types. That is, the reaction types have their own rate constants and every component grouped into a given type has the same rate constants as one another. The expanded form of the reactions are listed in Table 3. This approach will reduce the number of kinetic parameters that need to be estimated.

Laboratory data had shown that for short contact times (e.g., $W/F=0.005$) their amounts of some aromatics (toluene, *o*-xylene and ethylbenzene) in the product may be lower than their amounts in the feed. This signifies that there must be some demethylation/dealkylation reactions that transform these aromatic hydrocarbons to other aromatic hydrocarbons (e.g., toluene→benzene). These reactions are assumed to be negligible in the Nagamatsu kinetic scheme but appear to be important at short contact times. Hence, demethylation/dealkylation reactions have been added to the kinetic scheme.

In the Nagamatsu kinetic scheme, reaction rates of hydrocracking and hydrogenation of olefins are assumed to comply only with respect to concentration of surface hydrogen without respect to that of olefins. This leads to the situation that such reactions could occur even in the state of absence of hydrocarbon reactants. Hence, assumption for reaction rates of hydrocracking and hydrogenation are extended as described in section 3. 1.

3. 3. Components Used in the Model

All the components that may be included in the kinetic model are listed in Table 2. Not all of these components appear in the light naphtha feed and product data listed in Table 2. Some of the components are intermediates in the reaction scheme that may be present only in small amounts in the product, as their rate of production are approximately equal to their rate of consumption. Their components are included here for the sake of completeness, but may be removed from the component list, in the future, if the pseudo steady-state approximation would be applied for cal-

Table 2 Components Included in the LNA Model

Components (Code 1)	Nomenclature	Component (Code 2)
H2	hydrogen (in vapor phase)	H2
H2	hydrogen (on the catalyst)	H2A
C1	methane	CH4
C2	ethane	C2H6
C2=	ethylene	C2H4
C3	propane	C3H8
C3=	propylene	C3H6-2
C4	<i>n</i> -butane	C4H10-1
C4=	1-butene	C4H8-1
isoC5	2-methyl-butane	C5H12-2
<i>n</i> C5	<i>n</i> -pentane	C5H12-1
C5=	1-pentene	C5H10-2
C6	<i>n</i> -hexane	C6H14-1
C6=	1-hexene	C6H12-3
C7	<i>n</i> -heptane	C7H16-1
C7=	1-heptene	C7H14-7
C8	<i>n</i> -octane	C8H18-1
C8=	1-octene	C8H16-16
C9	<i>n</i> -nonane	C9H20-1
C9=	1-nonene	C9H18-3
Benzene (A6)	benzene	C6H6
Toluene (A7)	toluene	C7H8
Ethylbenzene (A8e)	ethylbenzene	C8H10-4
<i>m</i> -Xylene (A8m)	<i>m</i> -xylene	C8H10-2
<i>p</i> -Xylene (A8p)	<i>p</i> -xylene	C8H10-3
<i>o</i> -Xylene (A8o)	<i>o</i> -xylene	C8H10-1
A9+	<i>tri</i> -methylbenzene	C9H12-A

culating their concentration.

3. 4. The LNA Kinetic Scheme and Reaction Rates

Applying the extensions of the Nagamatsu kinetic scheme, described in section 3. 2. to the component list in Table 2, the LNA kinetic scheme listed in Table 3 was developed. The reactions, in Table 3, are listed by the reacting component having the same rate constant in the same reaction type. The kinetic scheme, in Table 3, was obtained by expanding, each component group reaction in the Nagamatsu kinetic scheme, to a set of reactions for each component in the group.

On the basis of the LNA kinetic scheme, the rate of reaction for each component could be written. The component reaction rates are listed in Table 4. The rate constant for each reaction (K_i) is written in the form of Eq. (2), below, in terms of a reference rate constant ($K_{i,\text{ref}}$ at T_{ref}) and an activation energy (ΔE_i).

$$K_i = K_{i,\text{ref}} \exp \left[-\frac{\Delta E_i}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (2)$$

Where:

- K_i : rate constant for reaction i at T
- $K_{i,\text{ref}}$: rate constant for reaction i at T_{ref}
- T_{ref} : reference temperature (K)
- ΔE_i : activation energy

3. 5. Parameter Estimation and Model Validation

In the LNA model there are 34 rate coefficient

Fig. 3 Plot of $\ln(k)$ vs. $1/T$ for HO Aromatization

parameters (reference rate constants and activation energies). The procedure for parameter estimation involves adjusting the parameter to minimize error between model predictions and experimental data. More exactly, as objective function of parameter estimation, the sum of the squared errors between model predictions and microflow reactor data for the component group mass fractions is considered. Typical examples of $\ln(k)$ vs. $1/T$ plots are shown in Fig. 3, in which the values for the rate coefficients are obtained from the parameter estimation runs at four temperatures (425, 450, 475 and 500°C). The reference rate constant is the value of the rate constant at 425°C, while the activation energy is given by the slope of plots, which show a least square linear regression, fit to the data points at the four temperatures (425, 450, 475 and 500°C). The final results of estimation, for the reference rate constants and activation energies, are given in Table 5.

Shown in Figs. 4 and 5 are some examples of model predictions compared to microflow reactor data for the component group, in weight percent. These figures show that the LNA model predicts the correct trends for different contact times and reactor temperatures. Although there are still some deviations, these are to be expected, considering the experimental uncertainties and scatter in the data. Further improvements may be possible, but this would require more data and estimation runs to finely tune the parameters.

Table 3 The LNA Kinetic Scheme Arranged by Reacting Component

Components	Grouping	Elementary reactions	Reaction rate
H ₂ '	H ₂ A	Vapor H ₂ formation	$k_{13} C_{H_2'}$
H ₂	H ₂	H ₂ dissociation	$k_{14} C_{H_2}$
C ₁	LG	n.a.	
C ₂	LG	n.a.	
C ₂ =	LO	LO hydrogenation	$k_6 C_{C_2=} C_{H_2'}$
		LO oligomerization	$k_8 C_{C_2=} C_{C_4=}$
			$k_8 C_{C_2=} C_{C_5=}$
C ₃	LP	LP cracking	$k_4 C_{C_3}$
		LP dehydrogenation	$k_5 C_{C_3}$
C ₃ =	LO	LO hydrogenation	$k_6 C_{C_3=} C_{H_2'}$
		LO hydrocracking	$k_7 C_{C_3=} C_{H_2'}$
		LO oligomerization	$k_8 C_{C_3=} C_{C_3=}$
			$k_8 C_{C_3=} C_{C_4=}$
			$k_8 C_{C_3=} C_{C_5=}$
C ₄	LP	LP cracking	$k_4 C_{C_4}$
		LP dehydrogenation	$k_5 C_{C_4}$
C ₄ =	LO	LO hydrogenation	$k_6 C_{C_4=} C_{H_2'}$
		LO hydrocracking	$k_7 C_{C_4=} C_{H_2'}$
		LO oligomerization	$k_8 C_{C_4=} C_{C_4=}$
			$k_8 C_{C_4=} C_{C_5=}$
isoC ₅	LP	LP cracking	$k_4 C_{C_{5i}}$
		LP dehydrogenation	$k_5 C_{C_{5i}}$
nC ₅	LP	LP cracking	$k_4 C_{C_{5n}}$
		LP dehydrogenation	$k_5 C_{C_{5n}}$
C ₅ =	LO	LO hydrogenation	$k_6 C_{C_5=} C_{H_2'}$
		LO hydrocracking	$k_7 C_{C_5=} C_{H_2'}$
			$k_7 C_{C_5=} C_{H_2'}$
			$k_7 C_{C_5=} C_{H_2'}$
C ₆	HP	HP cracking	$k_1 C_{C_6}$
			$k_1 C_{C_6}$
			$k_2 C_{C_6}$
			$k_2 C_{C_6}$
		HP dehydrocracking	$k_3 C_{C_6}$
			$k_3 C_{C_6}$
C ₆ =	HO	HO cracking	$k_9 C_{C_6=}$
		HO hydrocracking	$k_9 C_{C_6=}$
			$k_{10} C_{C_6=} C_{H_2'}$
			$k_{10} C_{C_6=} C_{H_2'}$
			$k_{10} C_{C_6=} C_{H_2'}$
			$k_{10} C_{C_6=} C_{H_2'}$
		HO aromatization	$k_{11} C_{C_6=}$
		HO hydrogenation	$k_{12} C_{C_6=} C_{H_2'}$
C ₇	HP	HP cracking	$k_1 C_{C_7}$
			$k_2 C_{C_7}$
			$k_2 C_{C_7}$
			$k_2 C_{C_7}$
		HP dehydrocracking	$k_3 C_{C_7}$
			$k_3 C_{C_7}$
C ₇ =	HO	HO cracking	$k_9 C_{C_7=}$
		HO hydrocracking	$k_9 C_{C_7=}$
			$k_{10} C_{C_7=} C_{H_2'}$
			$k_{10} C_{C_7=} C_{H_2'}$
			$k_{10} C_{C_7=} C_{H_2'}$
			$k_{10} C_{C_7=} C_{H_2'}$
		HO aromatization	$k_{11} C_{C_7=}$
		HO hydrogenation	$k_{12} C_{C_7=} C_{H_2'}$
C ₈	HP	HP cracking	$k_2 C_{C_8}$
			$k_2 C_{C_8}$
			$k_2 C_{C_8}$
		HP dehydrocracking	$k_3 C_{C_8}$
			$k_3 C_{C_8}$
C ₈ =	HO	HO cracking	$k_9 C_{C_8=}$
		HO hydrocracking	$k_9 C_{C_8=}$
			$k_{10} C_{C_8=} C_{H_2'}$
			$k_{10} C_{C_8=} C_{H_2'}$
			$k_{10} C_{C_8=} C_{H_2'}$
		HO aromatization	$k_{11} C_{C_8=}$

Table 3 (Continued)

Components	Grouping	Elementary reactions		Reaction rate
C9	HP	HO hydrogenation	$C8=+H2^{*} \rightarrow C8$	$k_{12} C_{C8=} C_{H2^{*}}$
		HP cracking	$C9 \rightarrow C5+C4=$	$k_2 C_{C9}$
C9=	HO	$C9 \rightarrow C4+C5=$	$C9 \rightarrow C4+=C5+=H2^{*}$	$k_2 C_{C9}$
		HP dehydrocracking	$C9= \rightarrow C4+=C5=$	$k_3 C_{C9}$
		HO cracking	$C9=+H2^{*} \rightarrow C4+C5=$	$k_9 C_{C9=}$
		HO hydrocracking	$C9=+H2^{*} \rightarrow C5+C4=$	$k_{10} C_{C9=} C_{H2^{*}}$
			$C9= \rightarrow A9+3H2^{*}$	$k_{10} C_{C9=} C_{H2^{*}}$
		HO aromatization	$C9=+H2^{*} \rightarrow C9$	$k_{11} C_{C9=}$
		HO hydrogenation		$k_{12} C_{C9=} C_{H2^{*}}$
Benzene	AR	n.a.		
Toluene	AR	demethylation	$A7+H2^{*} \rightarrow A6+C1$	$k_{15} C_{A7} C_{H2^{*}}$
Ethylbenzene	AR	demethylation	$A8e+H2^{*} \rightarrow A7+C1$	$k_{16} C_{A8e} C_{H2^{*}}$
<i>m,p</i> -Xylene	AR	n.a.		
<i>o</i> -Xylene	AR	demethylation	$A8o+H2^{*} \rightarrow A7+C1$	$k_{17} C_{A8o} C_{H2^{*}}$
A9+	AR	n.a.		

Table 4 Reaction Rates for the Components Included in the LNA Model

Component	Component reaction rate
H2	$k_{13} C_{H2'} - k_{14} C_{H2}$
H2'	$k_3 (C_{C6} + C_{C7} + C_{C8} + C_{C9}) + k_5 (C_{C3} + C_{C4} + C_{C5})$ $- k_6 C_{H2'} (C_{C2=} + C_{C3=} + C_{C4=} + C_{C5=}) - k_7 C_{H2'} (C_{C3=} + C_{C4=} + C_{C5=})$ $+ 3k_{11} (C_{C6=} + C_{C7=} + C_{C8=} + C_{C9=})$ $- (k_{10} + k_{12}) C_{H2'} (C_{C6=} + C_{C7=} + C_{C8=} + C_{C9=}) - k_{13} C_{H2'} + k_{14} C_{H2}$ $- (k_{15} C_{A7} + k_{16} C_{A8o} + k_{17} C_{A8e}) C_{H2'}$
C1	$k_1 C_{C6} + k_4 (C_{C3} + C_{C4} + C_{C5})$
C2	$+ (k_7 (C_{C3=} + C_{C4=} + C_{C5=}) + k_{10} C_{C6=} + k_{15} C_{A7} + k_{16} C_{A8e} + k_{17} C_{A8o}) C_{H2'}$
C2=	$k_1 (C_{C6} + C_{C7}) + k_4 (C_{C3} + C_{C4}) - k_6 C_{C2=} C_{H2'}$ $+ k_7 (C_{C4=} + C_{C5=}) + k_{10} (C_{C6=} + C_{C7=}) C_{H2'}$
C3	$(k_2 + k_3) (C_{C6} + C_{C7}) + k_4 (C_{C3} + C_{C4}) - k_6 C_{C2=} C_{H2'}$ $+ k_7 (C_{C3=} + C_{C4=} + C_{C5=}) C_{H2'} - k_8 (C_{C2=} + C_{C3=} + C_{C4=} + C_{C5=}) C_{C2=}$ $+ k_9 (C_{C6=} + C_{C7=}) + k_{10} (C_{C6=} + C_{C7=}) C_{H2'}$
C3=	$k_2 (C_{C6} + C_{C7} + C_{C8}) - (k_4 + k_5) C_{C3}$ $+ (k_6 C_{C3=} + k_7 C_{C5=} + k_{10} (C_{C6=} + C_{C7=} + C_{C8=})) C_{H2'}$ $- k_6 C_{C3=} C_{H2'} - k_7 (C_{C3=} - C_{C4=} - C_{C5=}) C_{H2'}$ $- k_8 (C_{C2=} + C_{C3=} + C_{C4=} + C_{C5=}) C_{C3=} + k_9 (2C_{C6=} + C_{C7=} + C_{C8=})$ $+ k_{10} (C_{C6=} + C_{C7=} + C_{C8=}) C_{H2'}$
C4	$k_2 (C_{C6} + C_{C7} + C_{C8} + C_{C9}) - (k_4 + k_5) C_{C4}$ $+ (k_6 C_{C4=} + k_{10} (C_{C6=} + C_{C7=} + C_{C8=} + C_{C9=})) C_{H2'}$
C4=	$k_1 C_{C6} + k_2 (C_{C7} + C_{C8} + C_{C9}) + k_3 (C_{C6} + C_{C7} + 2C_{C8} + C_{C9}) + k_4 C_{C5}$ $+ k_5 C_{C4} - k_6 C_{C4=} C_{H2'} - k_7 (C_{C4=} - C_{C5=}) C_{H2'} + k_8 C_{C2=} C_{C2=}$ $- k_8 (C_{C2=} + C_{C3=} + C_{C4=} + C_{C5=}) C_{C4=} + k_9 (C_{C6=} + C_{C7=} + 2C_{C8=} + C_{C9=})$ $+ k_{10} (C_{C6=} + C_{C7=} + C_{C8=} + C_{C9=}) C_{H2'}$
isoC5	$k_2 (C_{C7} + C_{C8} + C_{C9}) - (k_4 + k_5) C_{C5=}$ $+ (k_6 C_{C5=} + k_{10} (C_{C7=} + C_{C8=} + C_{C9=})) C_{H2'}$
nC5	$k_2 (C_{C7} + C_{C8} + C_{C9}) - (k_4 + k_5) C_{C5=}$ $+ (k_6 C_{C5=} + k_{10} (C_{C7=} + C_{C8=} + C_{C9=})) C_{H2'}$
C5=	$k_1 (C_{C6} + C_{C7}) + k_2 (C_{C8} + C_{C9}) + k_3 (C_{C7} + C_{C8} + C_{C9})$ $+ k_5 C_{C5} - k_6 C_{C5=} C_{H2'} - k_7 C_{C5=} C_{H2'} + k_8 C_{C2=} C_{C3=}$ $- k_8 (C_{C2=} + C_{C3=} + C_{C4=}) C_{C5=} + k_9 (C_{C7=} + C_{C8=} + C_{C9=})$ $+ k_{10} (C_{C6=} + C_{C7=} + C_{C8=} + C_{C9=}) C_{H2'}$
C6	$- (k_1 + k_2 + k_3) C_{C6} + k_{12} C_{C6=} C_{H2'}$
C6=	$k_8 (C_{C3=} C_{C3=} + C_{C2=} C_{C4=}) - (k_9 + k_{11}) C_{C6=} - (k_{10} + k_{12}) C_{C6=} C_{H2'}$
C7	$- (k_1 + k_2 + k_3') C_{C7} + k_{12} C_{C7=} C_{H2'}$
C7=	$k_8 (C_{C3=} C_{C4=} + C_{C2=} C_{C5=}) - (k_9 + k_{11}) C_{C7=} - (k_{10} + k_{12}) C_{C7=} C_{H2'}$
C8	$- (k_2 + k_3) C_{C8} + k_{12} C_{C8=} C_{H2'}$
C8=	$k_8 (C_{C3=} C_{C5=} + C_{C4=} C_{C4=}) - (k_9 + k_{11}) C_{C8=} - (k_{10} + k_{12}) C_{C8=} C_{H2'}$
C9	$- (k_2 + k_3) C_{C9} + k_{12} C_{C9=} C_{H2'}$
C9=	$k_8 C_{C4=} C_{C5=} - (k_9 + k_{11}) C_{C9=} - (k_{10} + k_{12}) C_{C9=} C_{H2'}$
Benzene	$k_{11} C_{C6=}$
Toluene	$k_{11} C_{C7=} - k_{15} C_{Tol} C_{H2'}$
Ethylbenzene	$k_{11} C_{C8=} - k_{16} C_{Eth} C_{H2'}$
<i>m</i> -Xylene	$k_{11} C_{C8=}$
<i>p</i> -Xylene	$k_{11} C_{C8=}$
<i>o</i> -Xylene	$k_{11} C_{C8=} - k_{17} C_{o-Xyl} C_{H2'}$
A9+	$k_{11} C_{C9=}$

Table 5 Final Results of Estimation for Reference Rate Constant and Activation Energy

Reaction type	Reference rate constant [1/sec]	Activation energy [kcal/mol]
HP cracking to LG and LO	4.749E-10	19.83
HP cracking to LP and LO	2.848E-3	25.22
HP dehydrocracking to LO	8.831E-6	19.93
LP cracking to LG and LO	6.109E-10	25.16
LP dehydrogenation LO	1.993E-3	25.16
LO hydrogenation to LG/LP	9.332 ^{a)}	17.90
LO hydrocracking	2.291 ^{a)}	39.78
LO oligomerization	8.666	35.64
HO cracking to LO	7.41E-6	19.80
HO hydrocracking	85.01 ^{a)}	46.19
HO aromatization	6.060E-2	53.14
HO hydrogenation	12.85 ^{a)}	46.19
H ₂ vapor formation	3.071E-2	20.69
H ₂ dissociation	1.891E-4	20.69
Toluene demethylation	1.020E-6 ^{a)}	15.79
Ethylbenzene demethylation	1.020E-6 ^{a)}	15.79
<i>o</i> -Xylene demethylation	1.020E-6 ^{a)}	15.79

a) The units for these rate constants are m³/kmol/sec. E-X corresponds to 10^x.

Fig. 4 Model Predictions Compared to Microflow Reactor Data at 425°C

Fig. 5 Model Predictions Compared to Microflow Reactor Data at 475°C

4. Reactor Modeling

4.1. The Processing Unit

A commercial-scale demonstration unit for LNA process involves three fixed bed reactors connected in series with preheaters installed in between¹¹⁾. A schematic diagram of the unit including reactor system is shown in Fig. 6. Because of the high level of endothermic heats of reaction, there could be substantial drop in temperature along the reactor bed. Hence, the catalyst is distributed over three fixed-bed adiabatic reactor vessels with feed preheaters installed in between the reactors.

4.2. Optimization of Catalyst Loading

The LNA kinetic model has been used with a process simulator to investigate reactor design and the optimal catalyst loading pattern for the unit. The ASPEN PLUS^{*1)} was used for the process

*1) ASPEN PLUS™ is the world's leading process simulation software and is developed and marketed by Aspen Technology of Cambridge, MA., USA.

Fig. 6 Simplified Flow Diagram of LNA Process

simulator, in this study.

A schematic simulator flow sheet used for the catalyst loading optimization study is very simple. It has three plug-flow reactors placed in series with preheaters located in between. The reactors are operated in an adiabatic manner. The preheaters in between the reactors are programmed to heat the feed to the next reactor to 520°C. A total contact time of 1.429 h (WHSV of 0.7 h⁻¹) is programmed. The volume ratio of catalyst charged to the reactors are corresponded to the ratio of reactor length in the simulation.

Two other flowsheets were set up to simulate the “best case” and the “worst case.” The “best case” corresponds to the reactor being maintained in isothermal state at feed temperature (520°C). The “worst case” corresponds to the reactor being adiabatic. The results from these cases are used to compare against optimal cases. The “best case” results are also used in formulating the objectives functions for the optimization.

The objective function for the investigation of the optimal catalyst loading is based on the squared deviations from the isothermal reactor results for conversion (in other word to get the maximum conversion). The length of the first and second reactors are varied to minimize the objective function subject to the total length. A FORTRAN block is used to calculate the length of the third reactor based on the current values of the first and second reactors.

The “optimal” catalyst loading pattern, in terms of percentage of total catalyst volume, was determined to be:

Fig. 7 Conversion Profile for Optimal Catalyst Loading Compared to Isothermal and Adiabatic Cases

Reactor	Optimal catalyst loading (volume percent)
R1	30.6
R2	31.2
R3	38.2

These results indicate that optimal distribution is nearly uniform to three reactors, in contrast to the well known examples of conventional fixed bed reforming unit.

Shown in Fig. 7 is the conversion for the optimal

Fig. 8 Temperature Profile for Optimal Catalyst Loading Compared to Isothermal and Adiabatic Cases

catalyst loading. The “best case” (isothermal operation) and the “worst case” (entirely adiabatic operation) results are also shown for comparison. The reactor temperature profiles are shown in **Fig. 8**.

Total aromatics yield for the optimal case is over 40 wt% at the third reactor outlet¹¹⁾.

In the commercial-scale unit (3 adiabatic reactors with heaters) the temperatures are 520°C at the reactor inlets but drop lengthwise of the reactor. The lower temperatures inside the reactor result in a lower overall conversion and the product selectivity might be different. In order to verify this effect, the model needs to be validated under operating conditions close to that used for the optimization studies.

5. Conclusion

A kinetic reaction model for the light naphtha aromatization (LNA) process, which uses pentane as a main feedstock was developed, assuming that the catalyst activity is fixed and does not vary with time or location in the reactor. The model which was validated using laboratory reaction data, has been used with the process simulator to investigate reactor design and the optimal catalyst loading pattern for a commercial-scale unit consisting of three reactors with feed preheaters arranged in series. The optimal catalyst loading pattern, in terms of percentage of total catalyst volume into three reactors, was determined to minimize deviations from the isothermal laboratory reactor results.

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要 旨

ライトナフサ芳香族化 (LNA) プロセス用反応モデルの開発

加藤恒一^{†1)}, 深瀬 聡^{†2)}, 天谷 徹^{†2)}, 佐藤保和^{†2)}^{†1)} (株) ジャパンエナジー 石油精製本部技術部, 105 東京都港区虎ノ門 2 丁目 10-1^{†2)} (株) ジャパンエナジー 石油研究所, 335 埼玉県戸田市新曽南 3 丁目 17-35

亜鉛アルミノシリケート触媒を用いたペンタンを主成分とするライトナフサの芳香族化反応における諸反応, 諸過程を表現するための反応モデルを開発した。触媒の劣化は考慮せず, 活性は反応器内で不変とした。反応モデルは, 永松らのヘキサンを用いた反応のモデル化を改良したものであり, 彼らのモデルにおいて実験的に定められている基本反応の量論係数を, 整数

値である素反応の量論係数に置き換え, かつ類似反応における反応速度定数を同一とみなし単純化したものである。実験室における等温系反応データを用いて反応モデルにおける諸パラメーターを決定し, 当モデルを用いて, 三個の断熱直列反応器からなる工業反応装置において転化率を最大とする最適触媒配分について検討した。

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Keywords

Light naphtha, Aromatization, Reaction modeling, Kinetics, Process development, Zinc aluminosilicate catalyst