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参考論文

1) "Kinetics of Isopentane Dehydrogenation on Chromia-Alumina Catalyst with Catalyst Fouling"
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3) "Optimal Controls of Catalytic Tubular Reactors with Catalyst Deactivation by Coke Deposition —— Applied to Isopentane Dehydrogenation—— "
（コーク蓄積による触媒劣化を伴なう管型反応器の最適政策 — イソペンタン脱水素反応への応用 — ）
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Optimal Operation of Chemical Reactor with Catalyst Fouling

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1975

PREFACE

The present studies have been carried out under the direction of Professor Tsutao Otake in his laboratory at Osaka University during 1970-1975. These are collected here as a thesis to be submitted to the Faculty of Engineering Science, Osaka University, in fullfilment of requirements for the Degree of Doctor Engineering.

The author wishes to express his deepest gratitude to Professor Tsutao Otake for his valuable guidance, helpful suggestions and encouragement throughout the work, and also to Asst. Professor Setsuji Tone for his valuable suggestions and stimulating discussion of the work as it progressed.

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Chapter 4. Optimal Operation of a Catalytic Reactor with Catalyst Fouling

General Introduction

Heterogeneous catalytic processes, using mainly solid catalysts, are very important for chemical industry. In operting the processes, the catalysts are usually decaying with process time and the yields of the products decrease as a result of the deactivation of the catalysts. When one is interested in the connections between the performance of the reactor and catalyst deactivation, one is generally not far from an optimization problem of some sort. It is necessary for the optimal control to develop a reaction model taking into account the reaction kinetics and deactivation mechanism and to know the parameters of the model precisely.

Research on catalyst deactivation has been concerned with three areas[1)] : (1) investigation of the fundamental mechanism and the kinetics of deactivation, (2) modeling the reaction and determination of the parameters of the governing equations, and (3) study of deactivation effects on the operation of real reaction system. It is necessary for the design and control of the chemical reactor with decaying catalyst to determine the reaction model considering the deactivation mechanism and to evaluate the parameters exactly. Such simple models, however, as a function of process time without considering the deactivation kinetics and as a function of the total amount of coke (carboneous material) deposited on catalyst have ever been used.

Since Jackson[2)] proposed and discussed the problem of the optimal temperature control, there have been a few studies of the optimal design and operation of the reactor with decaying catalyst. For the optimization problem, simple models have been used for the sake of the calculation, the analytical treatment and so on. It is, however, insufficient to apply such a simple model to the real reaction system subject to catalyst deactivation.

1. Purpose and contents of the thesis

The purposes of the present thesis are to make clear the reaction kinetics and deactivation mechanism of the reaction subject to catalyst decay, and sequently using the results to investigate the problems of the optimal temperature control.

In the first chapter, a reaction kinetics and deactivation mechanism are studied for isopentane dehydrogenation. A few models were presented for butane[3)] and isobutane[4)] dehydrogenation, while few models have been presented for isopentane dehydrogenation. This isopentane dehydrogenation is carried out over chromia-alumina catalyst. As process time proceeds the conversion of isopentane decreases accompanied with coke deposition and the changes of the profiles of the coke content in the reactor are observed. A kinetic model in which isopentane dehydrogenation takes place in a consecutive reaction (isopentane → isopentenes → isoprene) and coke formation is via both isopentenes and isoprene is proposed on the basis of the experimental results. A function of the total amount of coke content which is independent of catalyst activity profiles in the reactor has been used as a conventional expression of the deactivation. In this system the catalyst activity is also found to be proportional to the coke content, and the decrease of the kinetic parameters is expressed by a linear function of the point coke content which represents activity profile in the reactor. The kinetics parameters are determined by a non-linear least squares method using a hill climbing technique.

To test the applicability of the reaction kinetic model and the parameters, a wide range of experiments is carried out. The observed conversion and coke content agree fairly well with the calculated, which suggests that the kinetic model is useful for a design of the reactor.

In the first chapter the reaction model and the parameters are determined under a condition that the intraparticle diffusion is negligible, while the conversion and coke content change with catalyst size by the effect of the intraparticle diffusion. In the second chapter the effects of the intraparticle diffusion on the conversion and coke content in the reactor are studied using several catalyst sizes. During the reaction coke content in the catalyst pellet increases uniformly with process time. The diffusivity within the catalyst pellet is measured by the technique of transmittance of helium gas and also calculated from the nitrogen absorption data using the BET method. The observed effective diffusivity is found to be a linear function of the local coke content. The apparent diffusivity is determined by minimizing the variances between the observed conversion and the calculated, using a hill climbing method. The difference between the apparent and the observed diffusivity is recognized. Effects of the catalyst size on the conversion and coke content profiles in the fixed-bed reactor are explained by the proposed model.

In the third chapter, using the kinetic model and the parameters obtained in the first chapter, the problem of the optimal temperature control of the reaction subject to deactivation by coke deposition is theoretically studied for three kinds of reactors, an isothermal reactor, a non-isothermal reactor and a multi-bed reactor.

Most optimization studies have considered the problem of maximization of the total amount of product in a tubular reactor by manipulating reactor temperature with process time. From the view of post-treatment of the catalyst, it is necessary both to minimize the coke content and to maximize the total amount of product, and the objective functional is selected as matching the purpose. When the distributed maximum principle is applied to the optimization problem with deactivation by coke deposition, one has to solve two-point boundary value problems. The algorithm5) presented previously might not be applicable to the reaction accompanied by coke deposition.

A vector iteration method is chosen which is based on a gradient technique in spatial direction and in temporal direction based on the extremal technique[6]. The optimal policy for the single bed reactor calls for increasing temperature operation with process time, while that for the multi-bed reactor does not always call for the operation.

As shown in the preceding chapter, the optimal policy of the isothermal reactor called for a rising temperature operation, i.e. unsteady state operation. In the fourth chapter, the kinetic model obtained in the first chapter is examined using the optimal reactor experimentally. The optimal isothermal policy for isopentane dehydrogenation is calculated using the algorithm proposed in the preceding chapter. The reactor temperature is manipulating as the calculated optimal policy and the conversion and the coke content in the reactor are measured. The observed conversion and coke content in the reactor agree fairly well with the calculated, which suggests that the kineitc model obtained from isothermal experiments is useful for predicting unsteady operation and optimal control policies.

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Chapter 1

Kinetics of Isopentane Dehydrogenation on Chromia-Alumina Catalyst with Catalyst Fouling

Introduction

In catalytic reactions, cracking[20)], isomerization[22)], hydrogenation[19)], and so on, an activity distribution along the axial direction of the reactor usually occurs due to coke deposition on catalyst, and it varies with process time. Froment and Bischoff[4)] treated the distribution of the catalyst activity theoretically in the reactor. Several studies[9,14,17,19)] dealing with reactions with fouling, discussed the catalyst activity as a function of an average coke content. Recently, to aid process design[3,23,24)] and to obtain optimization[15,18)], an expression of the catalyst activity as a function of process time was introduced. The derived optimal policies or kinetic model would include uncertainties of the deactivation model and discrepancy between the observed and the evaluated values because of simplification of the catalyst fouling and coke formation. It is necessary to represent the catalyst activity profile precisely, but there have been only a few studies that analyze complex reaction kinetics with catalyst fouling. Gavalas et al.[7,8)] dealt with the problem of estimating catalyst activity profiles from current operating reactor data of naphtha reforming by a parametrization technique. Tone et al.[20)] developed a kinetic model for the relation between methylcyclohexane cracking and coke formation, and showed that by the activity factor, which was expressed as a function of coke content, the calculated values of both the product and coke content distribution in a fixed bed agreed fairly well with the observed values.

The purpose of this chapter was to develop a kinetic model for the dehydrogenation of isopentane that is useful for process design and optimization. The dehydrogenation of isopentane was studied in an integral packed reactor at various levels of temperature and space time, and the distribution of coke content was measured. A kinetic model including coke formation was assumed. The kinetic parameters in the model are estimated by a new algorithm which is constructed by two calculating steps. Firstly, under and assumption that the rate constants are uniform through the reactor, average or lumped kinetic parameters were evaluated by the non-linear least squares method. The function of activity factor was determined from the lumped rate constants, relating to the average coke content. Secondly, the activity factor with coke content could be used to represent the coke destribution in the catalytic bed, and as a result a simulation of the reactor kinetics was accomplished. From the best-fits between the experimental and calculated values, the proposed kinetic model was useful to simulate isopentane dehydrogenation with catalyst fouling.

1. Experimental

1.1 Catalyst

The catalyst used was a commercial chromia-alumina pellet catalyst (N-402, Nikki Chemical Co.) of a size 5 mm $\phi\times$ 5mm. The catalysts were crushed and sieved to three particle sizes— 8-10 mesh, 16-32 mesh and 40-60 mesh, and were calcined in an air stream for at least 3 hours at 550°C. Mainly the 16-32 mesh catalyst was used.

1.2 Apparatus and procedure for dehydrogenation of isopentane

To study the dehydrogenation of isopentane, a flow system was used as shown in Fig. 1, operating essentially at atmospheric pressure. The reactor, which was a 10 mm I.D. by 325 mm long quartz tube, contained catalysts fixed by quartz wool. The reactor was placed in a fluidized sand bath which was maintained at constant temperature by means of a P.I.D. controller. Two stainless sealed chromel-alumel thermocouples, 1 mm O.D., were positioned along the axis of the reactor to measure the temperatures within the catalyst bed; these temperatures were recorded continuously.

The hydrocarbons used were ultrapure grade isopentane, 2-methyl 2-butene (2M2B), 2-methyl 1-butene (2M1B), or isoprene. As the boiling points of the materials were close to 30°C, a syringe of a microfeeder was set in an ice bath to prevent the materials escaping in vapor. When the reactor reached a given temperature, nitrogen gas was exchanged with feed gas of definite composition of hydrocarbon diluted with nitrogen. A space time (τ) was defined by z/U_G on the space velocity at 300°C, ranging from 0.06 to 3.6 sec. The products were analyzed on line by

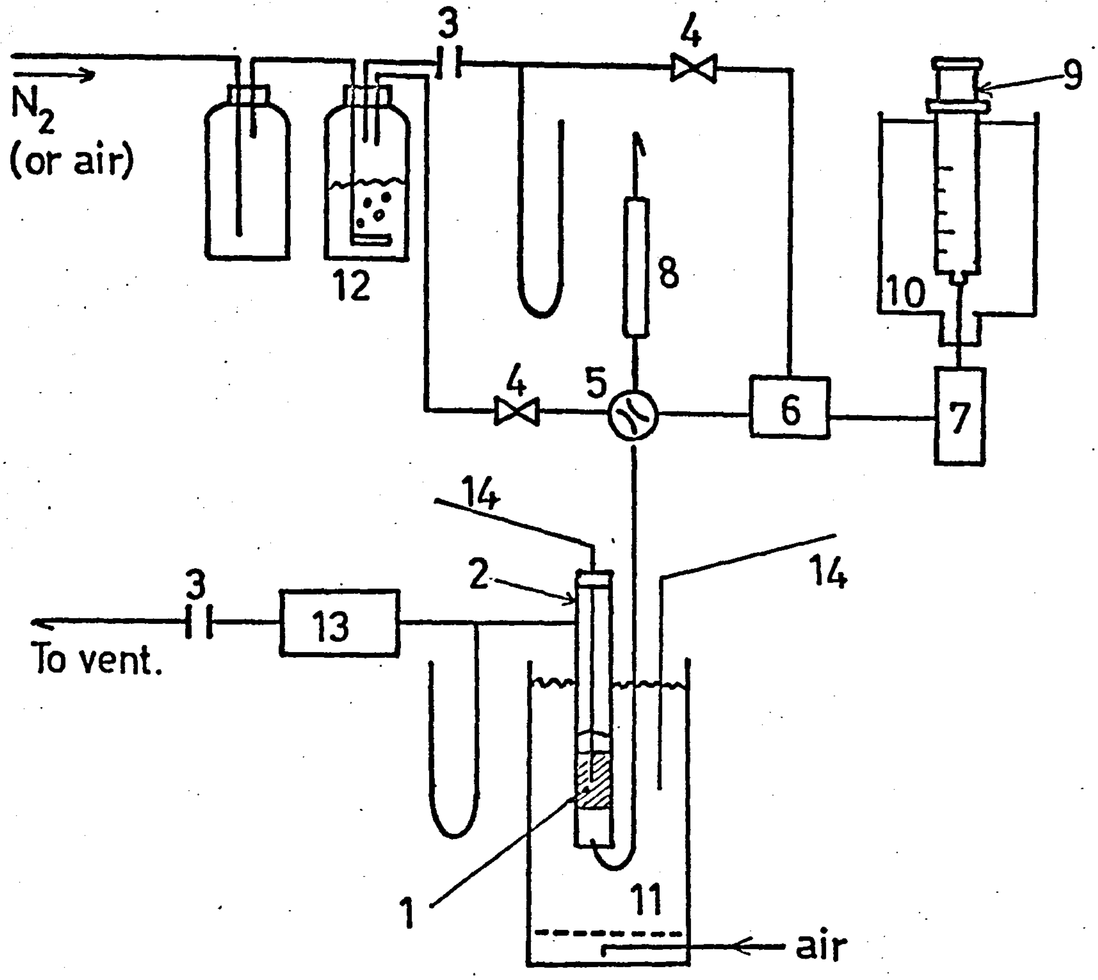

Fig.1 Flow diagram of experimental apparatus

1 Catalyst	2 Quartz reactor	3 Gas flow meter
4 Needle valve	5 Four way valve	6 Mixer
7 Vaporizer	8 Condenser	9 Microfeeder
10 Cooler	11 Fluidized bed	12 Drier
13 Heated gas sampler	14 Thermocouple	

gas chromatography; the total effluent from the reactor passed through the heated (at 50°C) gas sampler. Isopentane, isopentenes (2M1B, 2M2B and 3M1B) and isoprene were separated in a column containing 15% β-β'-oxydipropionitrile on α-alumina. The experimental conditions are shown in Table 1. Three sizes of catalysts and the pellet were tested to determine the resistance of intraparticle diffusion on conversion at a reaction temperature of 536°C. For catalyst particle less than 16-32 mesh, resistance of intraparticle diffusion was negligible, and the 16-32 mesh catalyst was used for measurement of reaction rates for all runs.

1.3 Measurement of coke content

After a reaction run was over, the catalyst bed was divided into equal sections about 1.5 cm long (about 1.0 g) along the reactor. The coke-deposited catalyst of the section was drawn out by vacuum line one after another. An average coke content of the m-th section from the inlet of the reactor was $\bar{n}_{cm}$. A coke content, n_{cm} as shown in Figs. 2-4, was given as an arithmetic mean of $\bar{n}_{cm-1}$ and $\bar{n}_{cm}$.

The weight of the coke on the catalyst was determined in a thermogravimetric balance by burning off coke with air. Furthermore, to measure the ratio of carbon to hydrogen in coke, experiments of coke combustion were carried out by the same apparatus as shown in Fig. 1. About 3 g of coke catalyst was placed into the reactor. After desorption of the adsorbed water

Table 1 Experimental Conditions

Concentration of hydrocarbon (Isopentane, Isopentenes, and Isoprene) diluted with nitrogen	0.143	[mole fraction]
Flow rate of nitrogen (Dilution gas)	200	[cc STP/min]
1) Differential Reactor		
Catalyst weight (w_{cat})	0.1 ∿ 1.0	[g]
Catalyst size	16 ∿ 32	[mesh]
Reaction temperature	536	[°C]
Space time (τ)	0.06 ∿ 0.6	[sec]
2) Integral Reactor		
Catalyst weight (w_{cat})	1.0 ∿ 12.0	[g]
Catalyst size	8∿10, 16∿32, 40∿60 and 5 mmϕ×5 mm pellet	[mesh]
Reaction temperature	488, 512, 536 and 560	[°C]
Space time (τ)	0.6 ∿ 3.6	[sec]

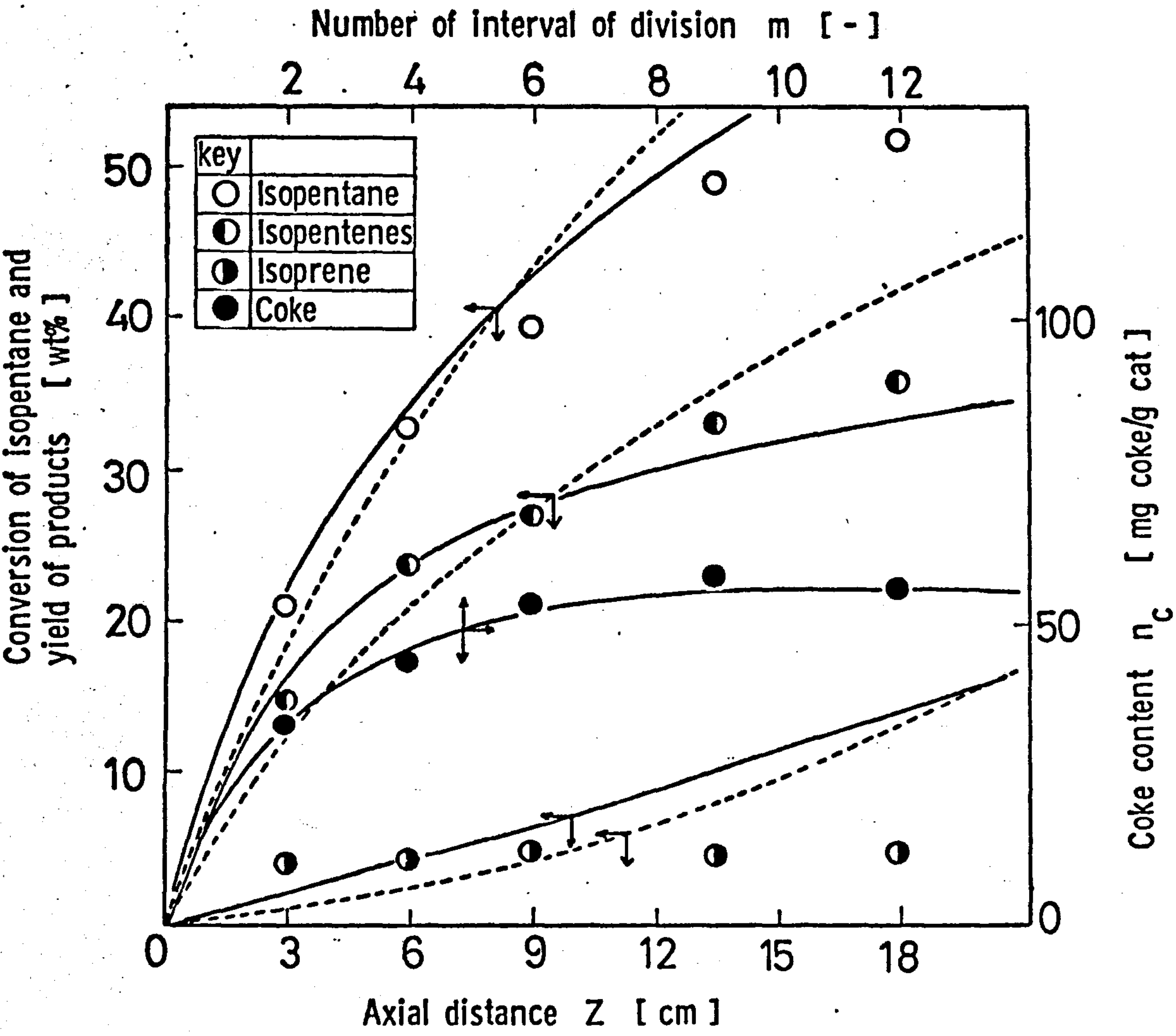

Fig.2 Axial distribution of reactant, products and coke content

----- calculated values from first step

——— calculated values from second step

Reaction temperature = 536°C

Process time = 70 min

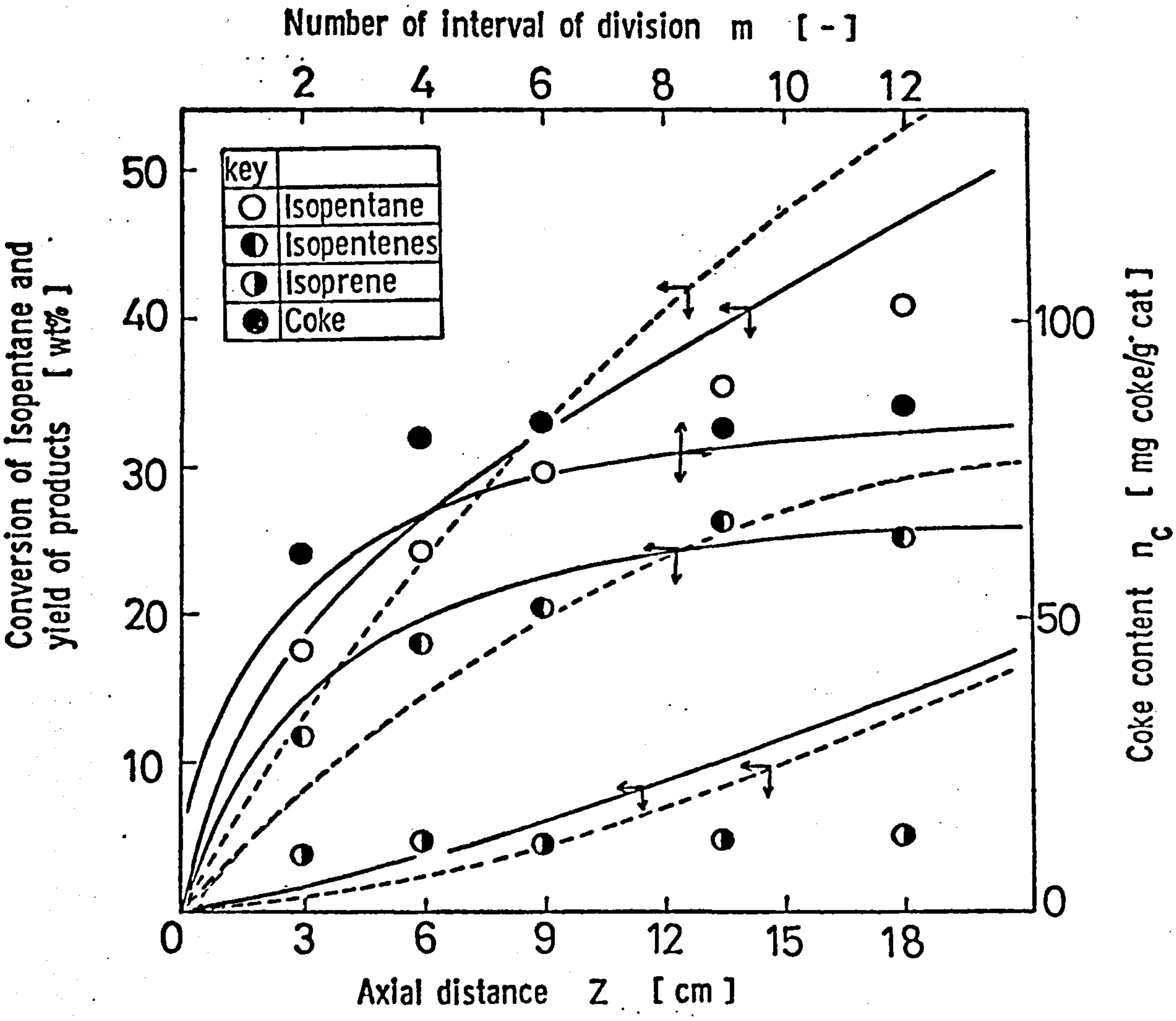

Fig.3 Axial distribution of reactant, products and coke content
----- calculated values from first step
—— calculated values from second step
Reaction temperature = 536°C
Process time = 130 min

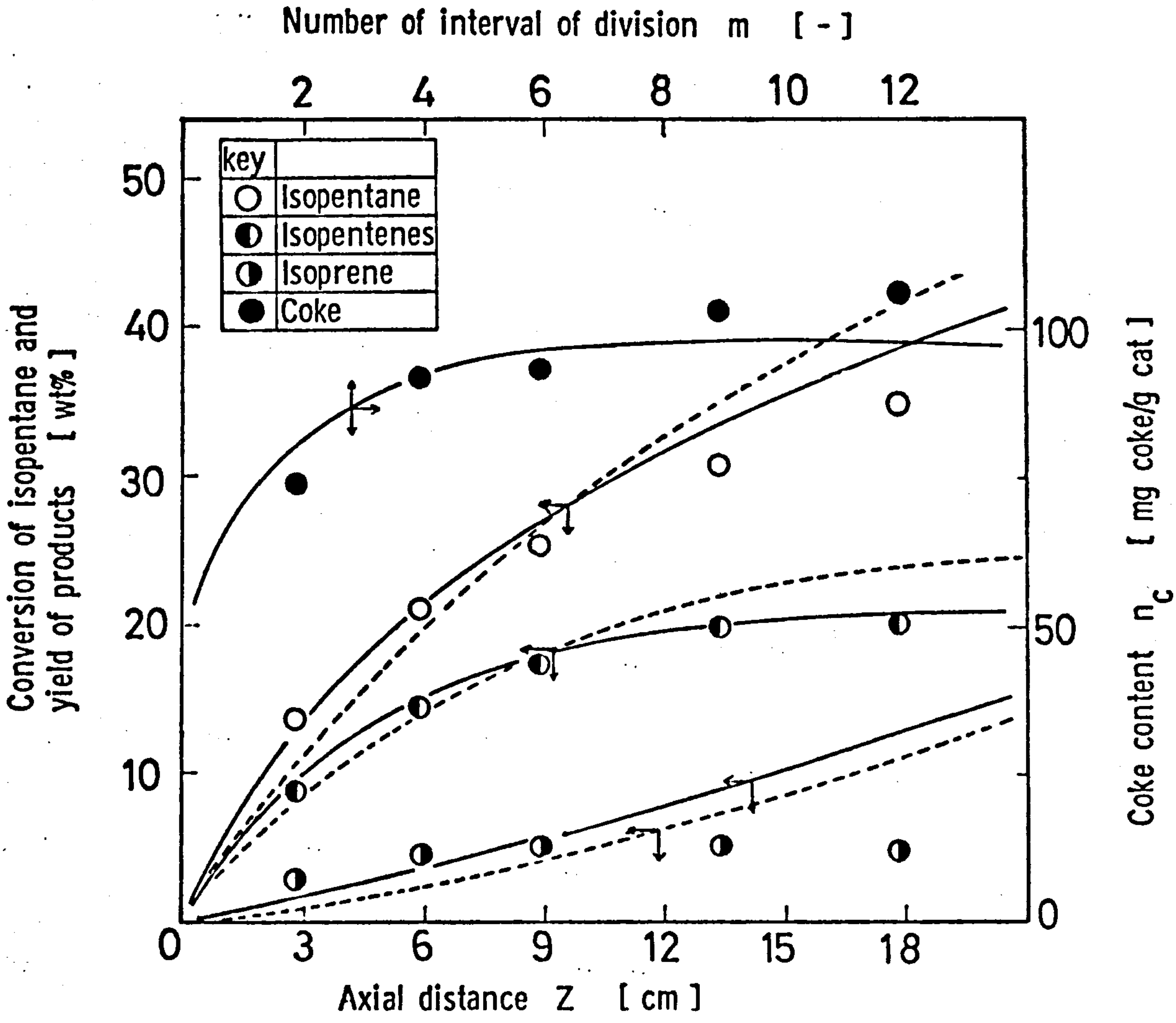

Fig.4 Axial distribution of reactant, products and coke content

----- calculated values from first step

——— calculated values from second step

Reaction temperature = 536°C

Process time = 190 min

by nitrogen at 250°C, 200 cc/min of dried air was passed through the reactor at about 620°C. CO and CO_2 were separated in a column containing silica gel-activated carbon with helium carrier gas while polyethylene glycol 20 M with hydrogen carrier gas was used to separate H_2O. The average composition of the coke was found to be from approximately $C_1H_{0.15}$ to $C_1H_{0.05}$.

2. Experimental Results

To examine the reaction models, three kinds of hydrocarbons, i.e. isopentane, 2M2B and isoprene, were used under differential reactor conditions. In the feed of isopentane, coke formation was negligible, but in the feed of 2M2B or isoprene considerable coke deposited on the catalyst. With an integral reactor (space time 0.6 sec, at 536°C and for process time 70 min), the average coke deposition from isopentane was about 40 mg-coke/g-cat., that from 2M2B was about 220 mg-coke/g-cat., that from isoprene was 250 mg-coke/g-cat. In the dehydrogenation of isopentane in an integral reactor, a rapid rise of temperature to 60°C was observed in the catalyst bed during 1 to 3 min of process time. It was considered that there might be exothermic reactions at an initial process time — rapid coke formation, polymerization and so on. At least five minutes were allowed for the system to reach steady state, so sample for reactant was taken ten minutes later.

Isopentenes were 2M1B, 2M2B and 3M1B, and ratios of each component were not dependent on process time, but only on temperature. Isopentenes (2M1B, 2M2B and 3M1B) are in equilibrium with each other as reported by Ishii et al.[11].

Figures 2-4 show the yields of products as a function of axial distance at three different process times. From these figures we see that the conversion of isopentane and the yield of isopentenes increase approximately exponentially with space time, but that of isoprene is almost constant. Fig. 5 illustrates typical plots of the conversion and the yields of products against the process time at three different temperatures. The conversion of isopentane and the yield of isopentenes decreased rapidly while that of isoprene did so slowly.

The distribution of the coke content n_{cm} is shown in Figs. 2-4. Plots of weight per cent of average coke content all over the catalyst bed against process time are shown in Fig. 6.

The average coke content is given by;

$$\bar{n}_c = \int_0^L n_c dz/L = m^{-1} \sum_{m=1}^{m} \bar{n}_{cm} \qquad (1)$$

Figures 5 and 6 indicate that the average coke content increases with both rising temperature and process time, while the conversion and the yields decrease.

3. Analysis of Experimental Results

3.1 Kinetic model

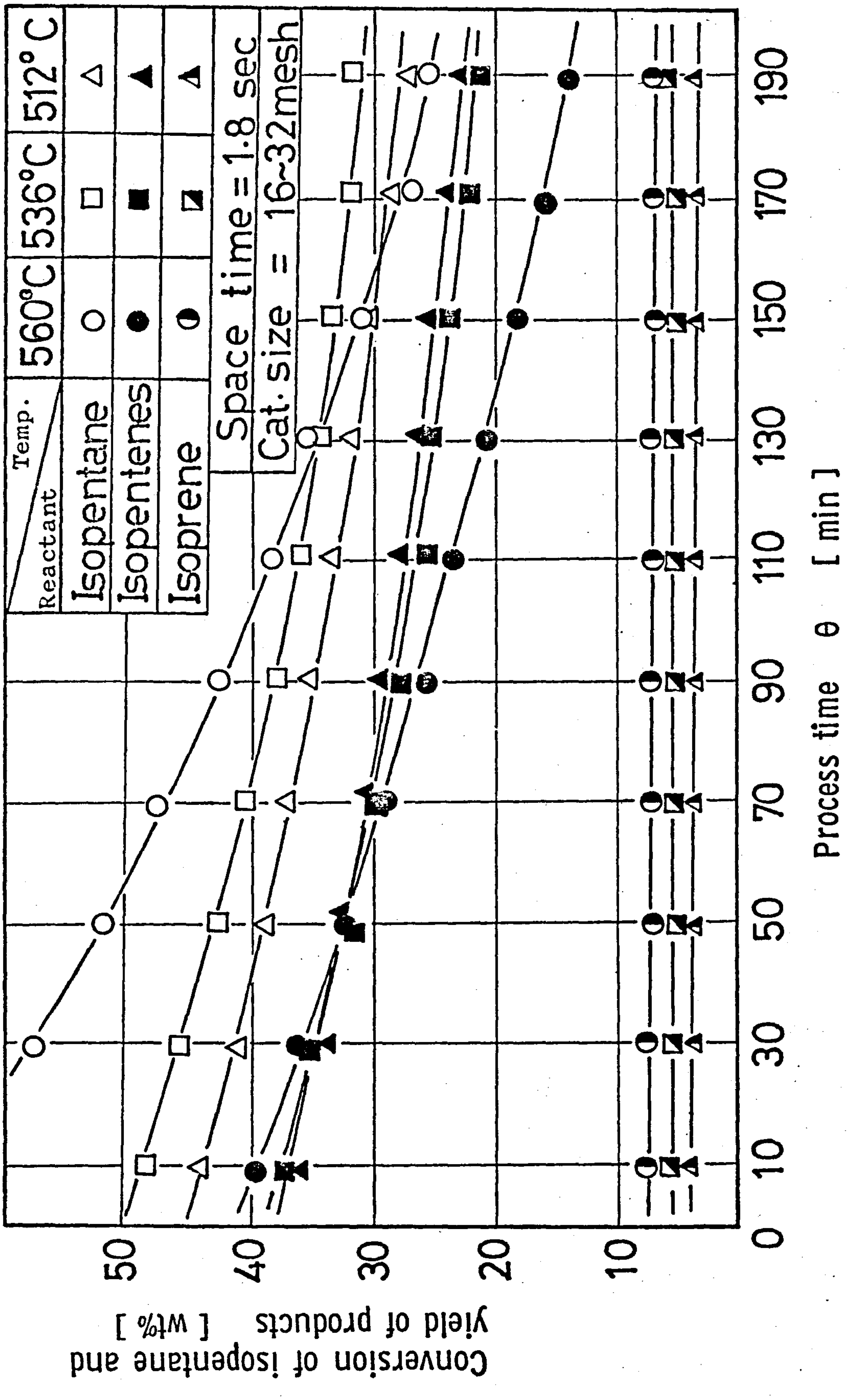

Fig. 5 Typical experimental data

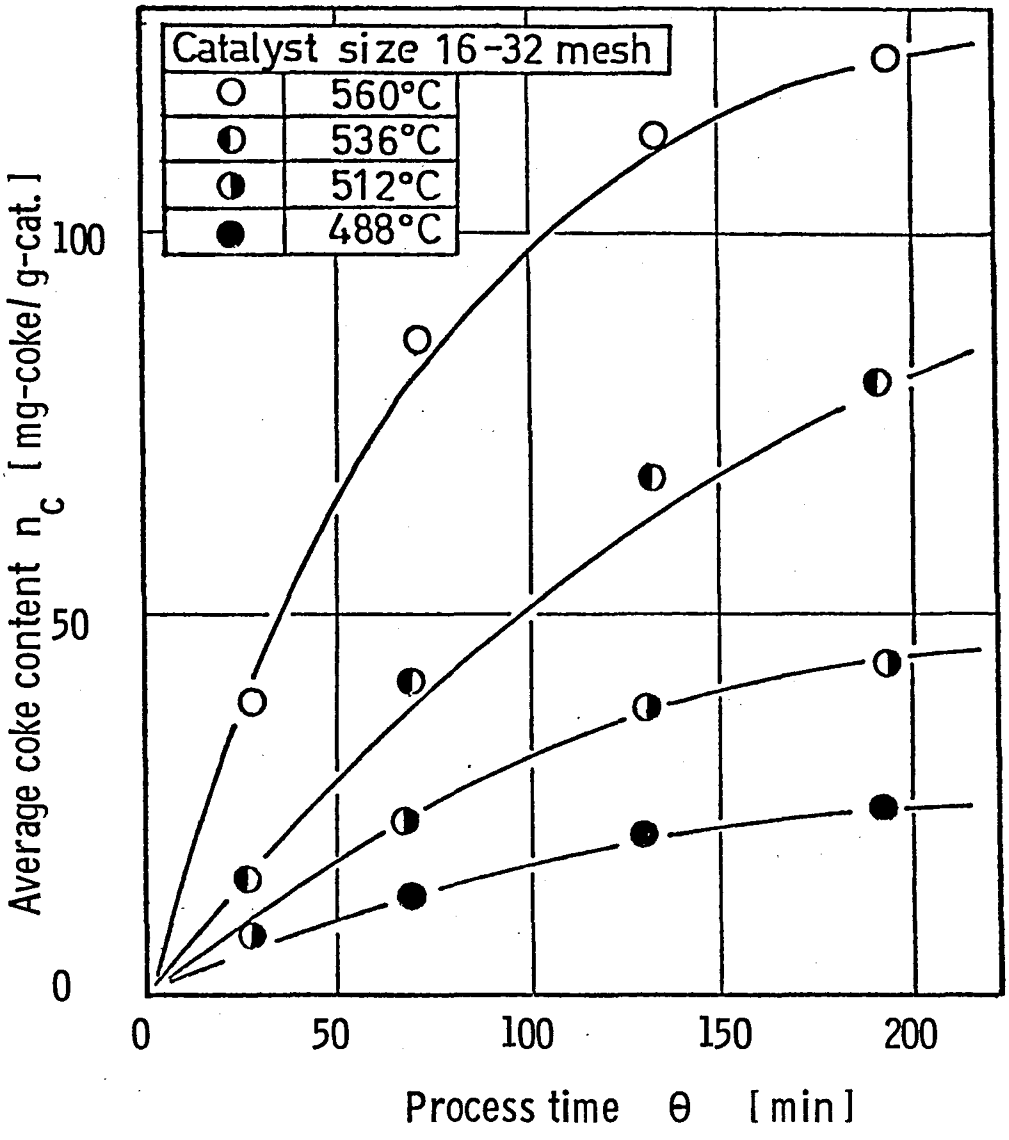

Fig. 6 Average coke content vs. process time

The dehydrogenation of isopentane was reported by Mavity et al.[12] as a consecutive reaction (isopentane → isopentenes → isoprene) under condition of various feed rates, pressure and so on. According to Ishii et al.[10,11] it was noted that dehydrogenation from isopentane to isopentenes was a first-order reaction, and that 2M1B and 3M1B were the intermediates to isoprene.

The dehydrogenation was accompanied by coke formation during the process. Coke is formed not only via olefin as reported by Takeuchi et al.[19], Eberly et al.[5], and Otake et al.[10], but also via diolefin, as obtained from the experimental results.

The reaction involves thermal cracking, isomerization, polymerization, etc. It is assumed that dehydrogenation of isopentane takes place in consecutive steps, that cracking occurs in parallel from isopentane, and that coke formation is via both isopentenes and isoprene. The kinetic scheme thus assumed is shown in Fig. 7.

1) The rate of isopentane disappearance is given as a first-order reaction;

$$r_A = (k_1 + k_2)C_A \qquad (2\text{-a})$$

$$r_{A1} = k_1C_A(\text{reaction rate for olefin}) \qquad (2\text{-b})$$

$$r_{A2} = k_2C_A(\text{reaction rate for other products}) \qquad (2\text{-c})$$

2) That of the dehydrogenation to isopentenes is given as a first-order reaction;

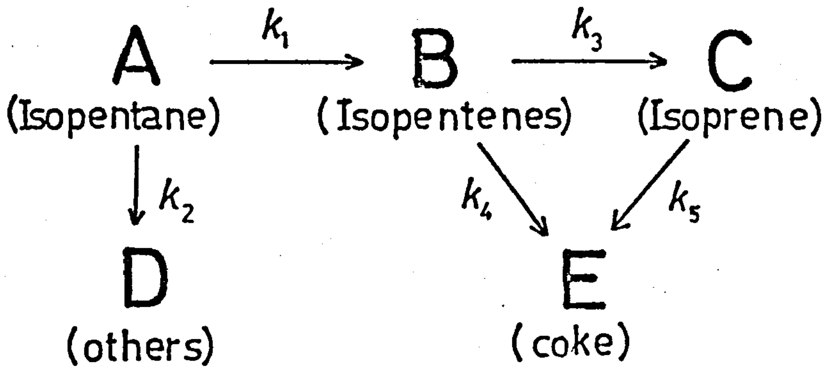

Fig.7 Reaction Scheme

$$r_B = k_1 C_A \tag{3}$$

3) That of the dehydrogenation to isoprene is given as a p-th order reaction;

$$r_C = k_3 C_B^p \tag{4}$$

4) That of the coke formation is given as a p-th order reaction from isopentenes and a q-th order reaction from isoprene;

$$r_{nc} = \nu(k_4 C_B^p + k_5 C_C^q) \tag{5-a}$$

$$r_{nc1} = k_4 C_B^p \text{ (reaction rate from isopentenes)} \tag{5-b}$$

$$r_{nc2} = k_5 C_C^q \text{ (reaction rate from isoprene)} \tag{5-c}$$

By introducing an activity factor, ϕ_i, the rate constants are defined as

$$k_i = k_{io}\,\phi_i \tag{6}$$

where k_{io} = initial rate constant at $n_c = 0$. In general, an activity factor is a function of process time and space time.

3.2 Simulation of reaction kinetics

Using the assumptions that (a) the feed gas is a plug flow, (b) there are negligible gradients of temperature and pressure through the reactor, (c) axial diffusion is negligible, (d) intraparticle diffusion is negligible, and (e) there is no interparticle or intraparticle mass and heat transfer rate limitation, it is possible to describe four coupled continuity equations given below;

$$\frac{\partial C_A}{\partial \theta} + U_G\frac{\partial C_A}{\partial z} = - r_A \tag{7}$$

$$\frac{\partial C_B}{\partial \theta} + U_G\frac{\partial C_B}{\partial z} = r_{A1} - r_C - r_{nc1} \tag{8}$$

$$\frac{\partial C_C}{\partial \theta} + U_G\frac{\partial C_C}{\partial z} = r_C - r_{nc2} \tag{9}$$

$$\frac{\partial n_C}{\partial \theta} = r_{nc} \tag{10}$$

As the integral reactor with coke formation is at unsteady state, and in general has an axial distribution of coke content, it is very difficult to determine the rate constants in distributed parameter system as described by Eqs.(7)-(10). In addition, we shall make an assumption that (f) space time is much shorter than process time for catalyst decay, so that the quasi-steady state approximation is valid.

Under this assumption, Eqs.(7)-(10) are reduced to

$$\frac{\partial C_A}{\partial \tau} = - (k_1 + k_2)C_A \tag{11}$$

$$\frac{\partial C_B}{\partial \tau} = k_1C_A - (k_3 + k_4)C_B^p \tag{12}$$

$$\frac{\partial C_C}{\partial \tau} = k_3C_B^p - k_5C_C^q \tag{13}$$

$$\frac{\partial n_C}{\partial \theta} = \nu(k_4 C_B^p + k_5 C_C^q) \qquad (14)$$

But Eqs.(11)-(14) are still distributed parameter system, so an algorithm, which is constructed by two calculating steps, for kinetic parameter estimation as shown in Fig. 8 is introduced.

3.2.1 The first calculating step

On the assumption that (g) the catalyst activity is uniform through the bed, the experimental data of the i-th component, $\hat{C}_{ijk}$, were compared with the calculated values, C_{ijk}, at process time (θ_k) and at space time (τ_j). That of coke content, n_{cj}, was plotted against process time and the rate of coke formation, r_{ncj}, was obtained by graphical differentiation.

The problem can be stated as one of finding $\bar{k}_1$ to $\bar{k}_5$ such that an objective function defined by Eq.(15) has a minimum value.

$$\psi_1 = \sum_{ij}\sum \{\omega_i(\hat{C}_{ijk} - C_{ijk})^2 + \omega_{nc}(\hat{r}_{ncj} - r_{ncj})^2\} \qquad (15)$$

where ω_i is a weighting factor for the i-th component. The objective function was minimized by a hill climbing method on a NEAC-2200/700 digital computer (at Osaka Univ. calculation center). The values of reaction order, p and q, were changed with four combinations of (1,1), (1,2), (2,1) and (2,2). As the result of calculations, the reaction orders p and q were found to be (1,1). The lumped rate constants, k_i, calculated from this step were related to average coke content, $\bar{n}_c$.

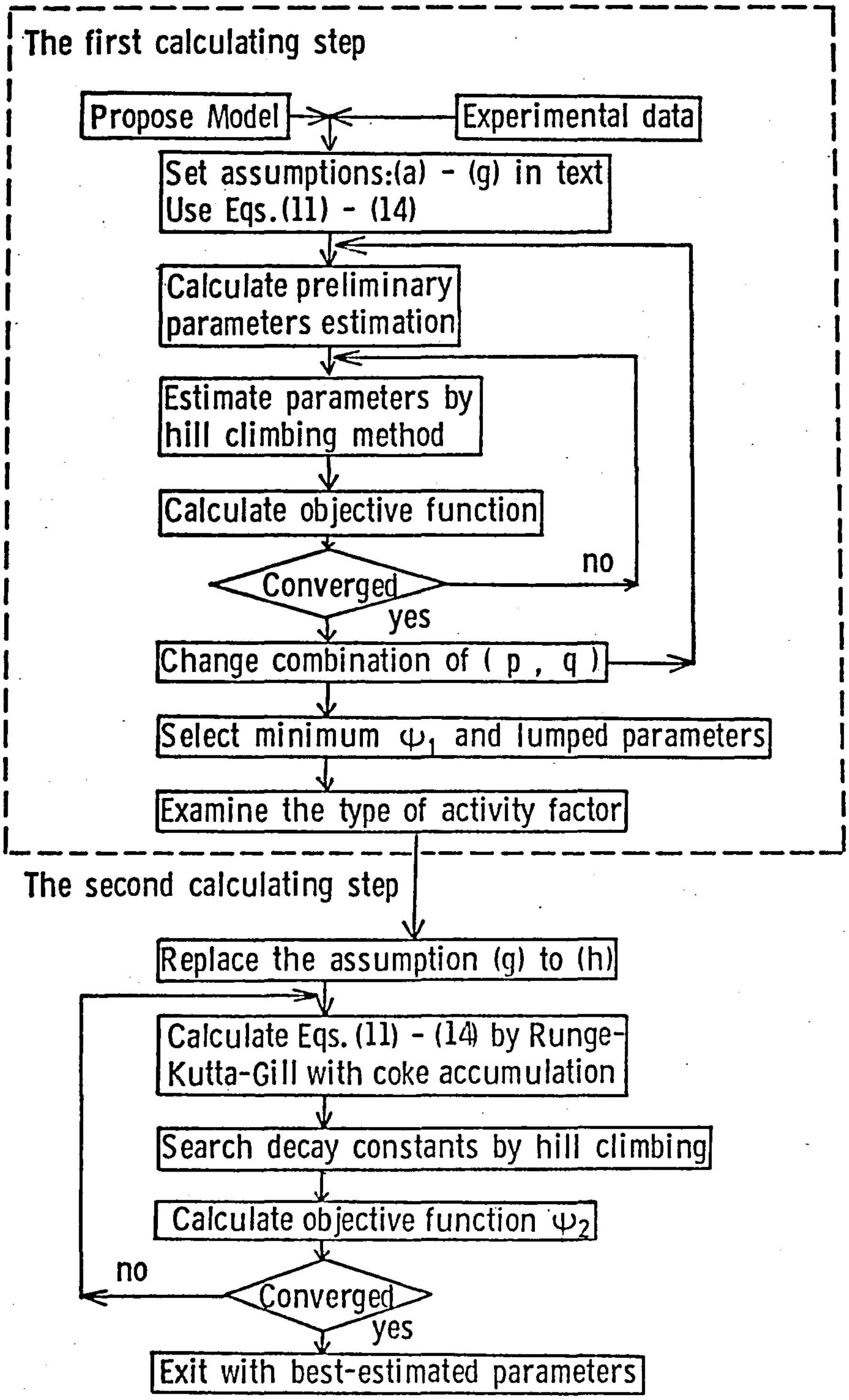

Fig.8 Algorithm for estimation of a distributed parameter system

From the linearity of the plots, the following relations were obtained.

$$\bar{k}_i = k_{io}\phi_i(\bar{n}_c) \qquad (16\text{-}1)$$

and

$$\phi_i(\bar{n}_c) = 1 - \bar{\alpha}_i\bar{n}_c \qquad (16\text{-}2)$$

where $\bar{\alpha}_i$ = lumped decay constant.

3.2.2 The second calculating step

The assumption(g) was replaced by a new assumption that (h) an activity factor, Eq.(17), the same as Eq.(16) could represent distribution of catalyst activity through the catalyst bed.

$$k_i = k_{io}\phi_i(n_c) \qquad (17\text{-}1)$$

and

$$\phi_i(n_c) = 1 - \alpha_i n_c \qquad (17\text{-}2)$$

Using the coke content a new objective function was defined by Eq.(18)

$$\psi_2 = \sum_{ijk}\sum\sum \{\omega_i(\hat{C}_{ijk} - C_{ijk})^2 + \omega_{nc}(\hat{n}_{cjk} - n_{cjk})^2\} \qquad (18)$$

where $\hat{n}_{cjk}$ and n_{cjk} are the experimental and calculated values of coke content, respectively, and ω_{nc} is a weighting factor for coke content. The $\phi_i(n_c)$ was substituted into Eqs.(7)-(10), and a set of Eqs.(7)-(10) could be integrated by a difference method, but by use of quasi-steady state assumption, Eqs.(11)-(14) were integrated by means of the Runge-Kutta-Gill method with coke accumulation. To minimize Eq.(18), ψ_2, the decay constants, α_i, and initial rate constant, k_{io}, were determined by a hill climbing method. The values of k_{io} were plotted against the reciprocal of absolute temperature, 1/T, on semilogarithmic ordinates as shown in Fig. 9. The value of the constant, α_i, was similarly plotted in Fig. 9, in the same way as by Takeuchi et al.19) and Ozawa et al.12). The rate constants and the decay constant, α_i, are summarized in Table 2. Campbell and Wojciechowski3) defined nonselective aging such that all rate constants were multiplied by the same activity factor, and selective aging such that each rate constant was multiplied by a different activity factor. Hano et al.9) showed that toluene disproportionation was selective aging. In this paper, isopentane dehydrogenation is also selective aging, as shown in Table 2.

4. Discussion

4.1 Coke and activation energy

From the chemical analysis of the coke component, $C_{1.0}H_{0.05} - C_{1.0}H_{0.15}$ was obtained. It was reported that the coke component on silica-alumina catalyst15) was $C_{1.0}H_{0.5} - C_{1.0}H_{1.0}$, and $C_{1.0}H_{0.5} - C_{1.0}H_{1.0}$ for the cracking of methylcyclohexane on

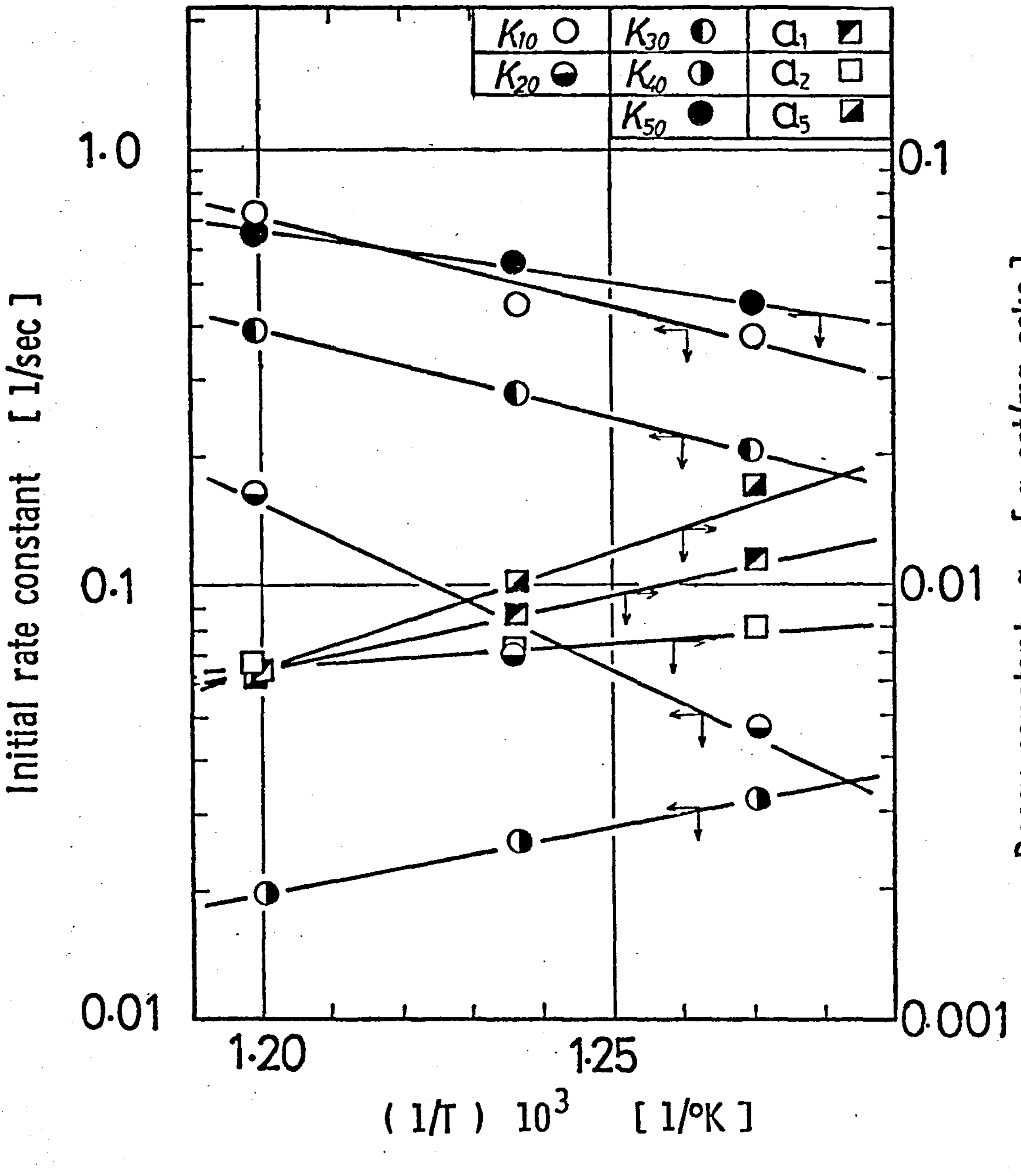

Fig. 9 Arrhenius plot

Table 2 Rate constants evaluated by simulation

$k = k_{1o}\phi_1 = \exp(10.0 - 17{,}300/RT)$ $\alpha_1 = \exp(-14.3 + 15{,}200/RT)$

$k = k_{2o}\phi_2 = \exp(19.4 - 35{,}200/RT)$ $\alpha_2 = \exp(-7.9 + 4{,}700/RT)$

$k = k_{3o}\phi_3 = \exp(9.2 - 16{,}800/RT)$ $\alpha_3 = 0.0$

$k = k_{4o}\phi_4 = \exp(-13.8 + 12{,}600/RT)$ $\alpha_4 = 0.0$

$k = k_{5o}\phi_5 = \exp(6.0 - 10{,}600/RT)$ $\alpha_5 = \exp(-20.1 + 24{,}900/RT)$

$\phi_i = 1 - \alpha_i n_c$; if $\alpha_i n_c > 1.0$ $\phi_i = 0.0$

where $\omega_A = \omega_B = 0.01$, $\omega_C = 0.1$, $\omega_{nc} = 1.0$

silica-alumina catalyst[21)] and $C_{1.0}H_{0.75}$ for the dehydrogenation of n-butane on chromia-alumina catalyst[13)]. The reason why the values of C/H (carbon/hydrogen) were different among investigators might be due to the complicated mechanism of such processes polymerization and adsorption. Ishii et al.[10,11)] reported that the reaction kinetics from isopentane to isopentenes was first-order with respect to each component and that the activation energy was 21.4 kcal/g-mol for isopentane with hydrogen carrier gas. The evaluated activation energy was 17.3 kcal/g-mol with nitrogen carrier gas. The difference between the former and the latter might be due to the influence of the kind of carrier gas. As to the activation energy of coke formation, it was reported that for the hydrogenation of n-butene[1)] and iso-butene[19)], respectively, the activation energies had values of - 3.3 kcal/g-mol and 1.5 kcal/g-mol. The values of 23.1 kcal/g-mol and 34.6 kcal/g-mol were reported, respectively, for the dehydrogenation of n-butane[16)] and cyclohexane[14)]. For the cracking of methylcyclohexane[20)], the activation energy of - 3.36 kcal/g-mol was reported. In the present work, for the activation energy of coke formation, the value of 12.6 kcal/g-mol via isopentenes and that of - 10.6 kcal/g-mol via isoprene were obtained. The differences among the values of the activation energy might come from the complexity of the coke formation mechanism for each reaction.

4.2 Kinetic parameters and expression of activity factor

For the expression of catalyst fouling, several types of function of coke content were presented by Anderson and Whitehouse[2)]. The lumped activity factor, Eq.(16-2), used in several studies because of its simple form, was shown to be useful for less coke content. Froment and Bischoff[6)] discussed theoretically in simple reaction models the differences of the distribution of the reactant and the coke content using the activity factor, Eq.(19). Morioka et al.[14)] derived the above activity factor by Poisson distribution of coke accumulation, and used it for cyclohexane dehydrogenation.

$$\phi_i = \exp(- \alpha_i n_c) \qquad (19)$$

If the decay constant, α, is small, Eq.(19) can be reduced to Eq.(16-2) or Eq.(17-2) by Taylor's expansion[16)]. In dehydrogenation of isopentane, Eqs.(16-2) and (17-2) were usable to estimate the changes of concentration. In the case of both lower temperature and less coke content, it is sufficient to use Eq.(16-2) and, also, it may be permissible that the reaction orders, (p,q), are (1,1) according to Fig. 10. Recently, the lumped activity factors as functions of process time have been developed for the design[3,23,24)] or the optimization[15,18)] of the reactor. Eq.(16-2) can be reduced to the lumped activity factor as a function of process time, but as shown in Figs. 2-4, if there are distributions of coke content in the reactor length, the activity factor, i.e. Eq.(17-2), is useful to predict distribution of catalyst activity through the reactor.

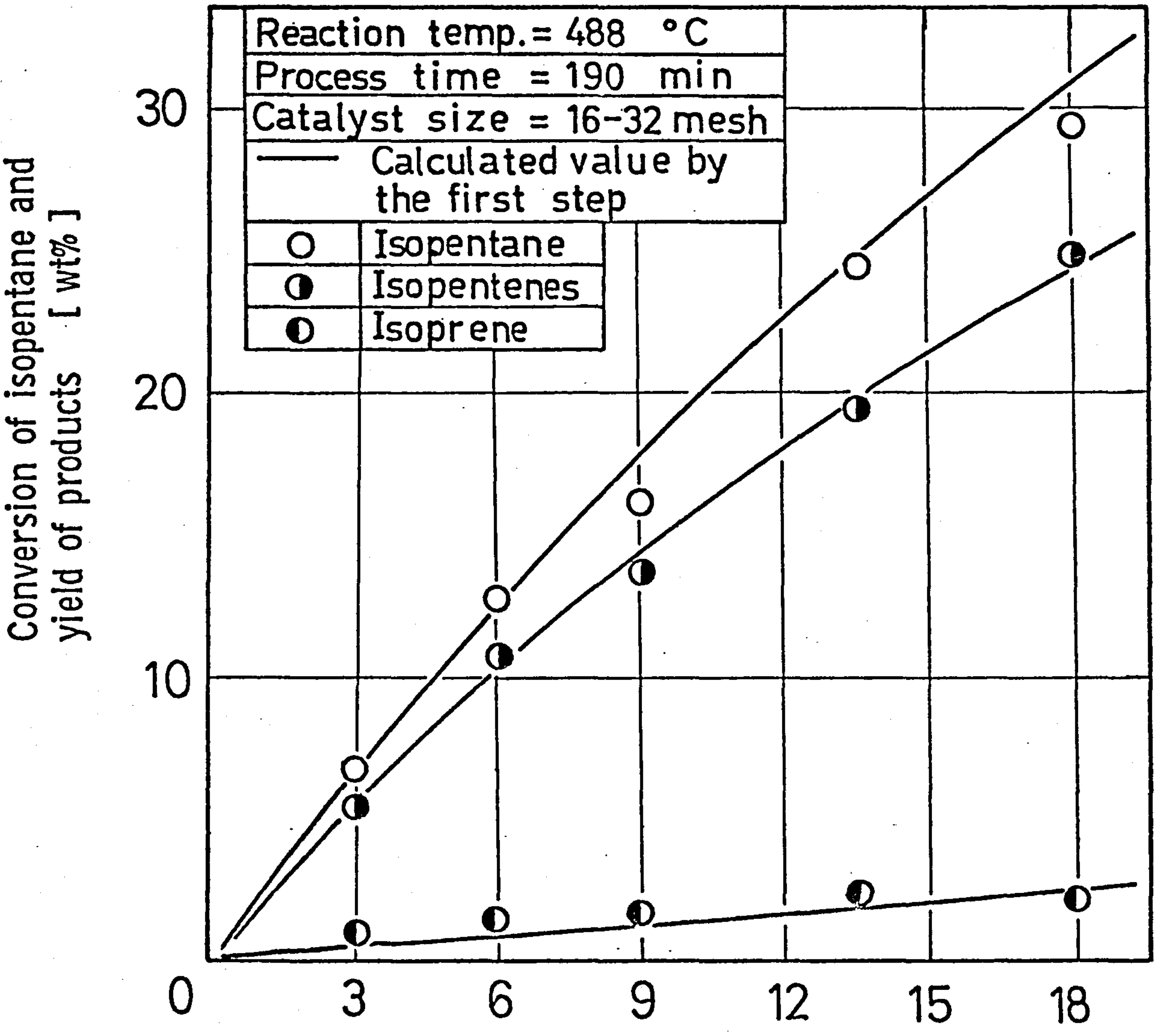

Fig.10 Axial distribution of reactant and products

Conclusion

In isopentane dehydrogenation over chromia-alumina catalyst, the conversion of isopentane and the yields of isopentenes decreased rapidly with process time while that of isoprene did so very slowly. Coke deposition on the catalyst and catalyst fouling occurred in an integral catalytic reactor, and axial coke distribution was observed along the reactor. For isopentane dehydrogenation a kinetic model was proposed in which the main reaction was consecutive and the subreaction was parallel. To evaluate distributed kinetic parameters with catalyst fouling, an algorithm involving two calculating steps was introduced. The parameter estimation method was applicable to isopentane dehydrogenation. Activity factors evaluated were different from each other, so the fouling was selective aging. The activity factor was revealed as a linear function of coke content. Using the kinetic parameters, the changes of concentration and the distribution of coke content with process time were simulated fairly well by the kinetic model.

Notations

C_i = weight fraction of the i-th component [g/cc]

$\hat{C}_i$ = observed weight fraction of the i-th component [g/cc]

F = feed rate [g/min]

k_{jo} = rate constant for the j-th reaction at zero coke deposit [1/sec]

k_j = rate constant for the j-th reaction at time [1/sec]

$\bar{k}_j$ = lumped rate constant for the j-th reaction [1/sec]

n_c = coke content on catalyst [mg-coke/g-cat.]

$\bar{n}_c$ = average coke content on catalyst [mg-coke/g-cat.]

n_{cm} = coke content on the m-th point of catalyst [mg-coke/g-cat.]

$\bar{n}_{cm}$ = average coke content on the m-th section of catalyst bed [mg-coke/g-cat.]

r_i = reaction rate with respect to the i-th component [g/cc·sec]

r_{nc} = rate of coke formation [mg-coke/g-cat.min]

$\hat{r}_{nc}$ = observed rate of coke formation [mg-coke/g-cat.min]

z = axial distance of the catalyst packed bed from the inlet of the reactor [cm]

U_G = vapor velocity of reactant fluid [cm/sec]

w_{cat} = catalyst weight [g]

Greeks

α_i = decay constant in activity factor [g-cat./mg-coke]

$\bar{\alpha}_i$ = lumped decay constant in activity factor [g-cat./mg-coke]

θ = process time [min]

ν = conversion factor [mg-come·g-feed·sec/g-cat·g-component·min]

τ = space time (= z/U_G) [sec]

ϕ_i = activity factor for the i-th reaction [—]

ψ = estimation function [—]

ω_i = weighting factor for each component [—]

Subscripts

A = isopentane

B = isopentenes

C = isoprene

n_C = coke

m = number of intervals of division

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Chapter 2

Effects of Intraparticle Diffusion on Catalyst Fouling

Introduction

The reaction model and the parameters were determined under a condition that the intraparticle diffusion is negligible[2,6,7,10] in the first chapter, while the profiles of the conversion change with catalyst size by the effects of the intraparticle diffusion. Many investigators[8,10,11] have studied the kinetics of catalytic reactions subject to fouling and presented several decay models as a function of average coke content.

To examine the kinetics of the reaction and the mechanism of deactivation, it is necessary to know the distribution of coke in the catalyst pellet. Murakami et al.[5] reported that distribution of coke content in a catalyst changed by disproportionation of n-butyl alcohol. Suga et al.[8] studied the effect of coke content on the effective diffusivity and expressed it as a linear function of the coke content in the n-butane dehydrogenation. Komiyama and Inoue[3] showed that the selectivity of the intermediate product of a consecutive reaction was explained by a micro-macro pore model using the Langmuir-Hinshelwood rate form. Masamune and Smith[4] showed that effectiveness factors could be useful for predicting the effect of fouling on the performance of a fixed-bed reactor.

The purpose of this chapter is to make clear the effects of the intraparticle diffusion in a catalyst pellet on the conversion in the fixed-bed reactor using the kinetic model developed previously for the isopentane dehydrogenation over chromia-alumina catalyst . The coke content in the catalyst pellet increases uniformly. The diffusivity within the catalyst pellet is measured by the technique of transmittance of helium gas and also calculated from the absorption data of nitrogen using the BET method. The observed effective diffusivity is found to be a linear function of the local coke content. The observed conversion ratio and coke content in the fixed-bed reactor are in agreement with the values calculated using the proposed model by choosing an apparent values of diffusivity, which is compared with the observed.

1. Experimental

1.1 Catalyst

The catalyst was prepared from the commercially available chromia-alumina pellets (N-401A and N402, Nikki Chem. Co.,) of the size 5 mmϕ×5 mm. The pellets were crushed and sieved to four sizes — 5 mmϕ×2.5 mm, 8-10 mesh, 16-32 mesh and 42-60 mesh, and they were calcined in an air stream at about 550°C for at least three hours.

1.2 Apparatus and procedure

The experimental apparatus used is shown in Fig. 1. Three kinds of reactor tubes were used; one was made of a stainless steel tube with 30 mm I.D. and the other two were quartz tubes

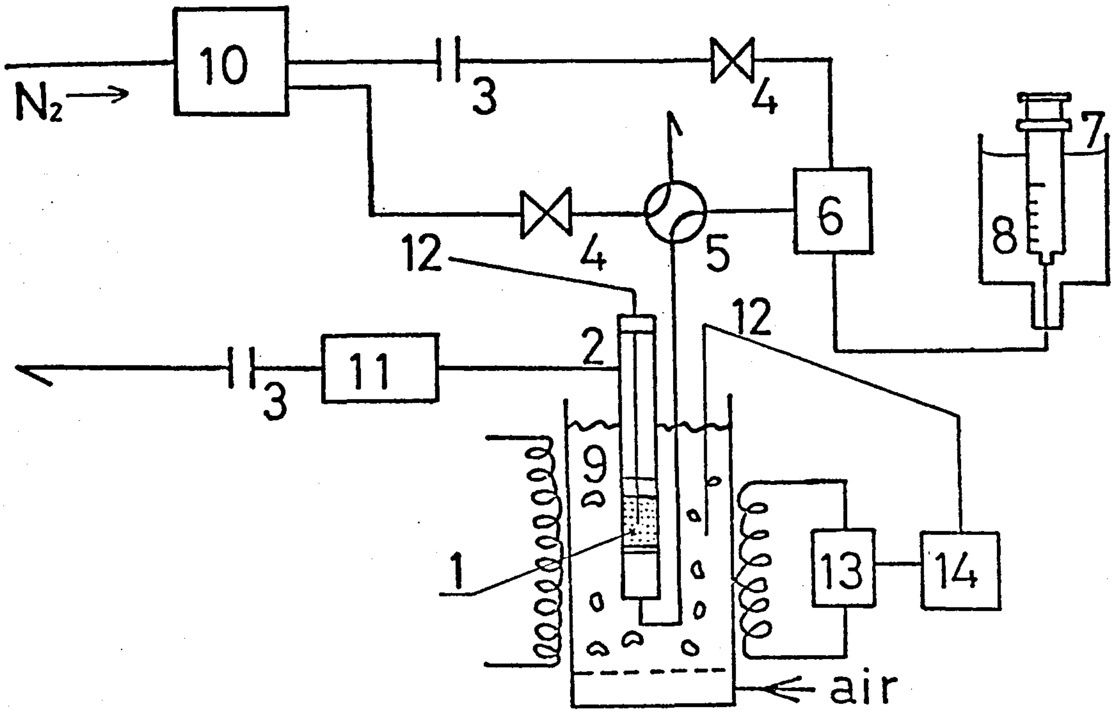


Fig. 1 Flow diagram of experimental apparatus

1 Catalyst bed
2 Reactor
3 Gas flow meter
4 Needle valve
5 Four way valve
6 Mixer
7 Microfeeder
8 Cooler
9 Fluidized bed
10 Drier
11 Heated gas sampler
12 Thermocouple
13 SCR unit
14 P. I. D. controller

of 10 mm I.D. and 26 mm I.D. The reactor was placed in a fluidized sand bath whose temperature was constantly maintained by a P.I.D. controller. Two stainless sealed alumel-chromel thermocouples of 1 mm O.D. were positioned along the axis of the reactor to measure the temperatures of the catalyst bed and another thermocouple was set in the bath. These temperatures were continuously recorded.

Ultrapure grade isopentane was used. As the boiling point of the isopentane was close to room temperature, the syringe (50 cc or 200 cc) of a microfeeder was set in an ice bath to prevent the reactant from escaping. When the reactor reached a specified temperature, nitrogen gas was replaced with the isopentane feed gas, of definite composition diluted with nitrogen. The space time (τ) was defined by z/U_G which was based on the space velocity at 300°C, and it varied from 0.06 to 4.2 sec. The products were analyzed by a gas chromatograph. A total effluent from the reactor passed through a heated (at about 50°C) gas sampler. The change in the volume of the reactant during the reaction was negligible. The experimental conditions are shown in Table 1.

1.3 Measurement of coke content

When the reaction was complete, the catalyst bed was divided into equal sections along the reactor axis. The catalyst in each section was withdrawn from the reactor, and the coke content on the catalyst was determined using a thermobalance

Table 1 Experimental conditions

Reaction temperature	488, 512, 536 and 560	[°C]
1) Pellet catalyst		
Catalyst size(R)	5 mmϕ×2.5 mm, 5 mmϕ×5 mm	
Catalyst weight(W_{cat})	17 ∿ 118	[g]
Bores of reactor	26 (quartz), 30 (stainless)	[mm]
Space time (τ)	0.6 ∿ 4.2	[sec]
Feed rate (F)	0.0101	[mole/min]
Nitrogen for dilution	0.0606	[mole/min]
2) Crushed catalyst		
Catalyst size(R)	42 ∿ 60, 16 ∿ 32 and 8 ∿ 10	[mesh]
Catalyst weight(W_{cat})	0.1 ∿ 12	[g]
Bores of reactor	10 (quartz)	[mm]
Space time (τ)	0.6 ∿ 4.2	[sec]
Feed rate (F)	0.0014	[mole/min]
Nitrogen for dilution	0.0084	[mole/min]

and burning off the coke with air.

1.4 Measurement of diffusivity

Diffusivity in a catalyst pellet was measured with apparatus$^{10,13)}$, which was similar to that described by Suga et al.$^{10)}$ The data were obtained by the countercurrent method of a nitrogen and helium system at 1 atm. and the apparatus was maintained at 25°C in the air bath of the gas chromatograph. The effluent gases were detected by the thermal conductivity cell of the gas chromatograph.

1.5 Pore size distribution in the catalyst

The relation between cumulative pore volume and pore radius was obtained by the mercury penetration technique using a porosimeter (model 1520, Carlo Erba). For calculating the pore size distribution from the adsorption isotherms on a porous catalyst, adsorption data were obtained using the BET method.

2. Results

2.1 Dehydrogenation of isopentane

Fig. 2 shows that conversion of isopentane and yields of isopentenes and isoprene changed with the size of the catalyst. The conversion and the yields of isopentenes decreased rapidly

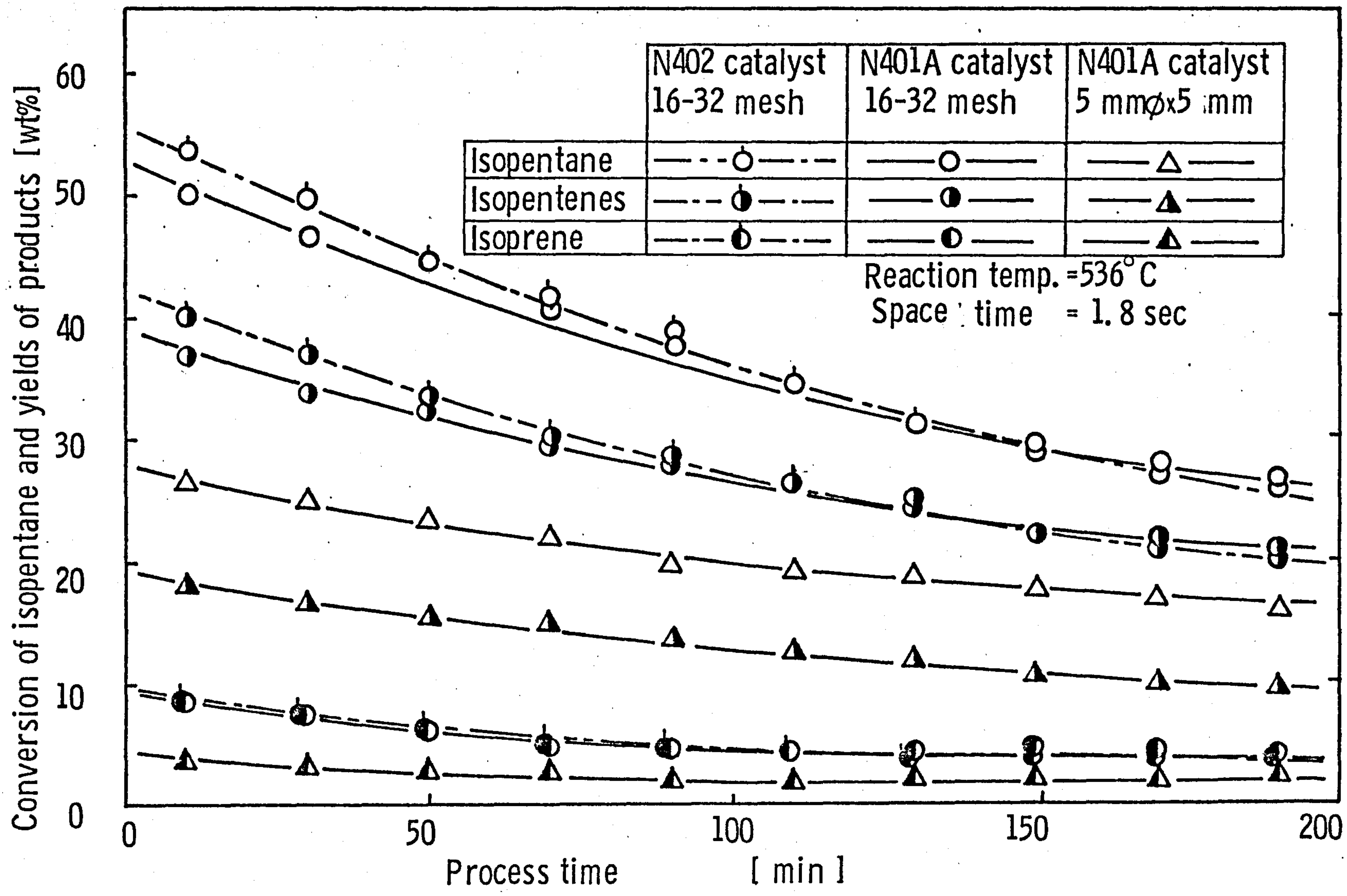


Fig. 2 Typical experimental data

with process time, while the yield of isoprene decreased slowly. But slight difference in the catalyst activity between type A (N402) and type B (N401A) was observed. The relation between the conversion profile and catalyst size in the reactor is shown in Fig. 3 for four catalyst sizes. The intraparticle diffusion is negligible as shown in Fig. 3, when the catalyst size is smaller than 16-32 mesh. Figs.4a and 4b show the conversion for three catalyst sizes at the process time of 130 minutes. Profiles of coke contents are also plotted in Figs.4a and 4b at reaction temperature 536°C.

2.2 Distribution of coke content in the reactor

The distribution curves of coke content in the reactor at the process time of 70 min are shown in Fig. 5 at four temperature levels for two catalyst sizes. The coke content increased from the inlet to the outlet of the reactor for the smaller size catalyst, while the content decreased for the larger size as shown in Figs. 4 and 5.

2.3 Coke distribution in pellet

To examine coke distribution in a catalyst pellet, a microphotometer and a thermobalance were used. A pellet was sliced into three parts in the radial direction (the outer, the intermediate, and the center core), then the coke content of each part was measured with the thermobalance. The cross-sectional photos of the catalyst pellet were scanned by the microphotometer

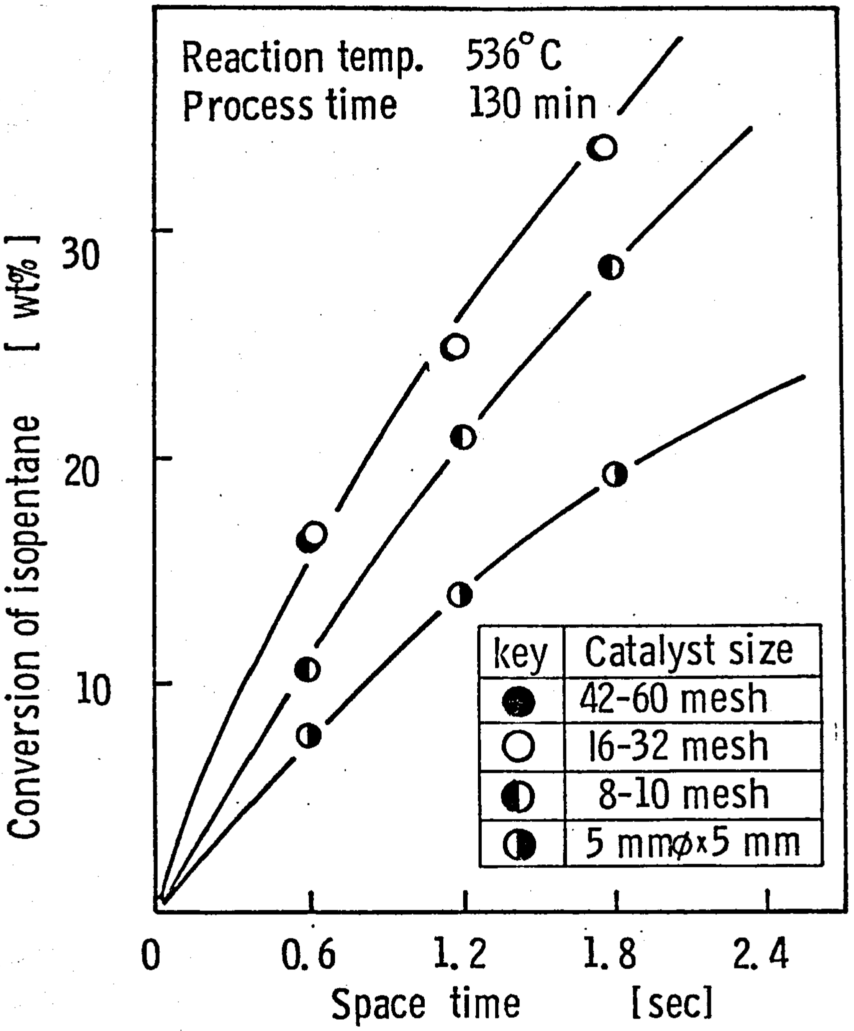


Fig. 3 Influence of catalyst size on conversion

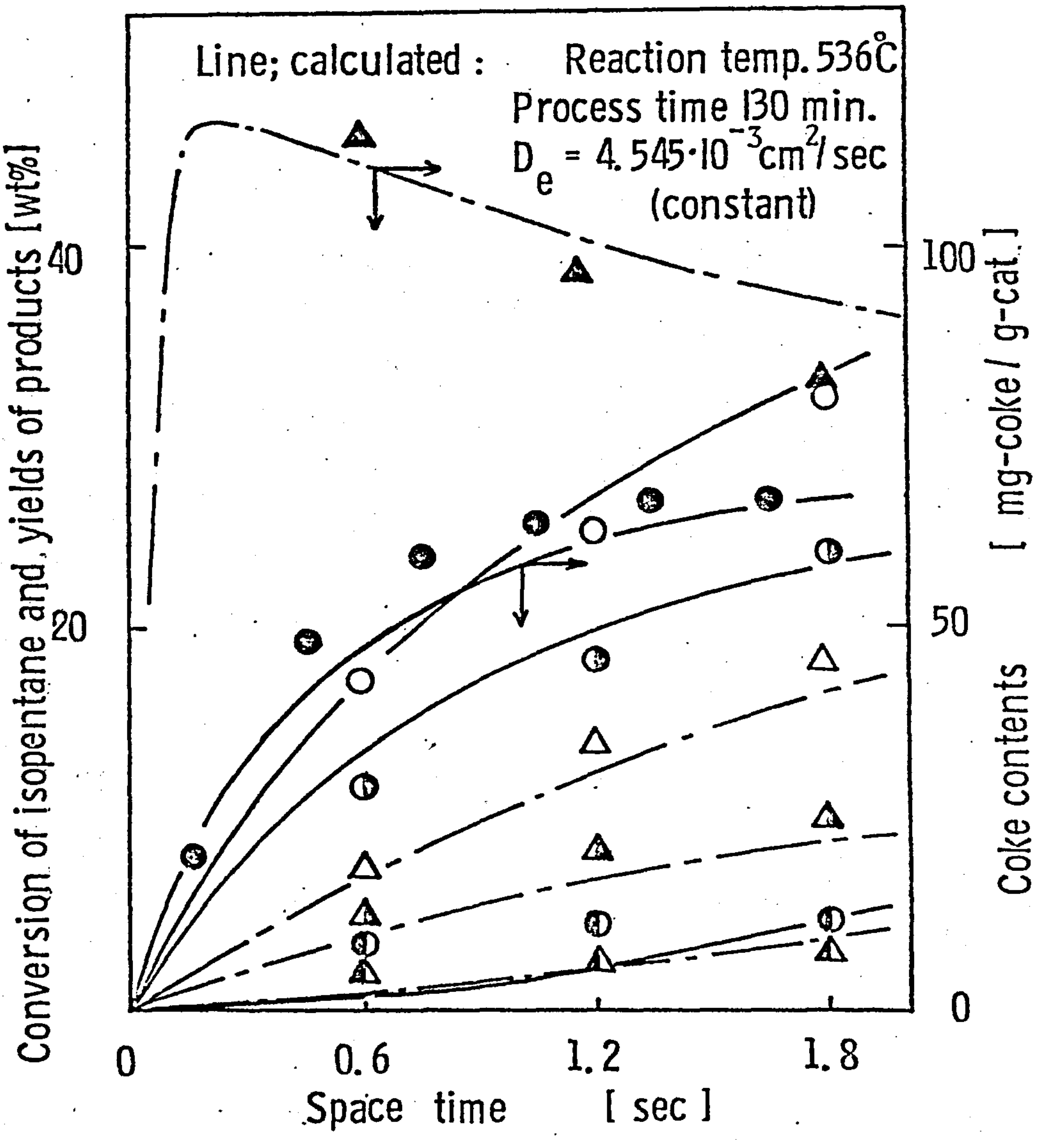


Fig. 4a Influences of the catalyst size on axial distributions of conversion, yields and coke contents

Catalyst Observed	N401A 16-32 mesh	N401A 5 mmØ×5mm
Isopentane	○	△
Isopentenes	◑	◭
Isoprene	◐	◮
Coke	●	▲

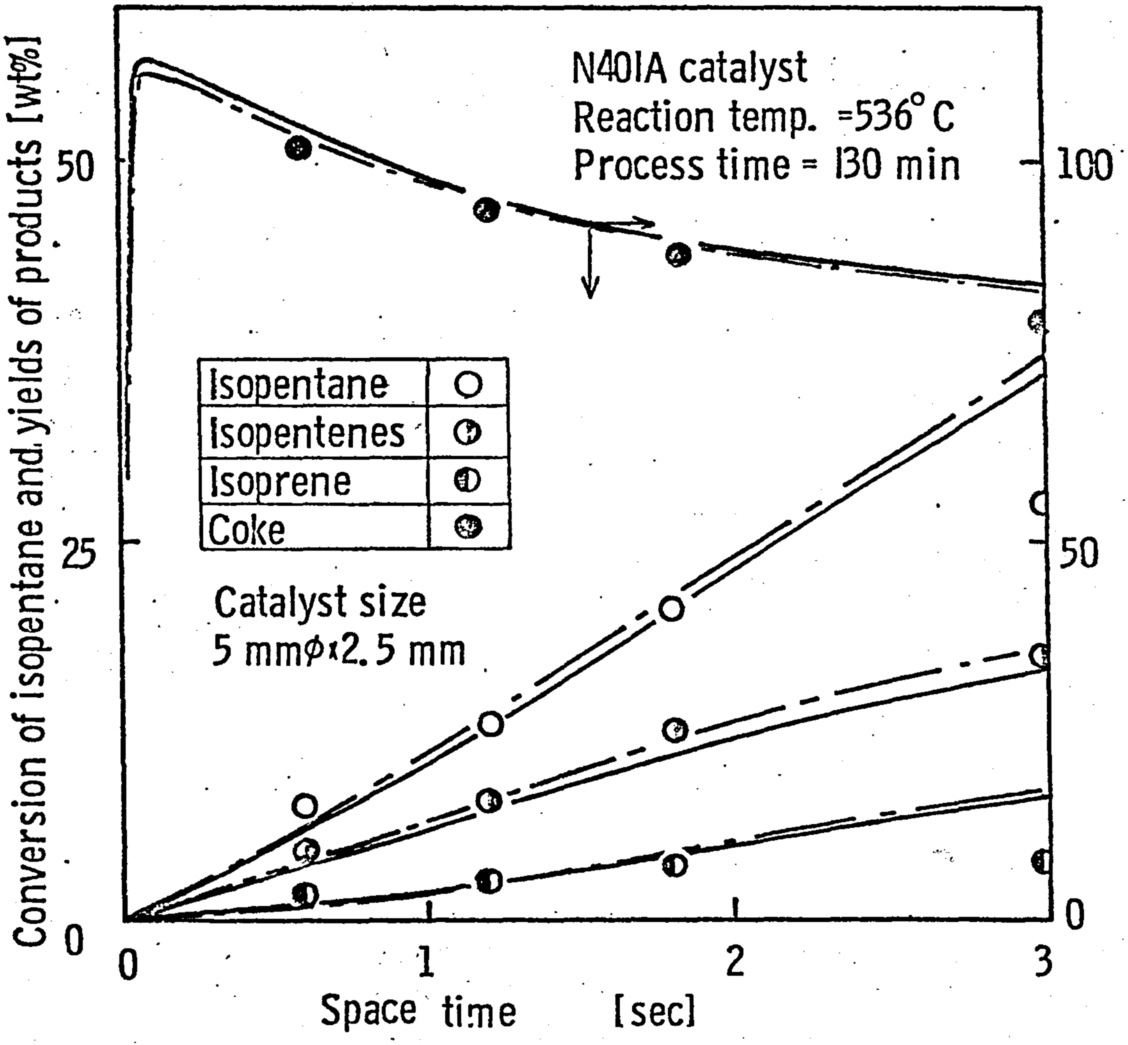


Fig. 4b Influences of the catalyst size on axial distributions of conversion, yields and coke contents

— - — - — ; calculated values, D_{ei} constant

——— ; calculated values using Eq. (3)

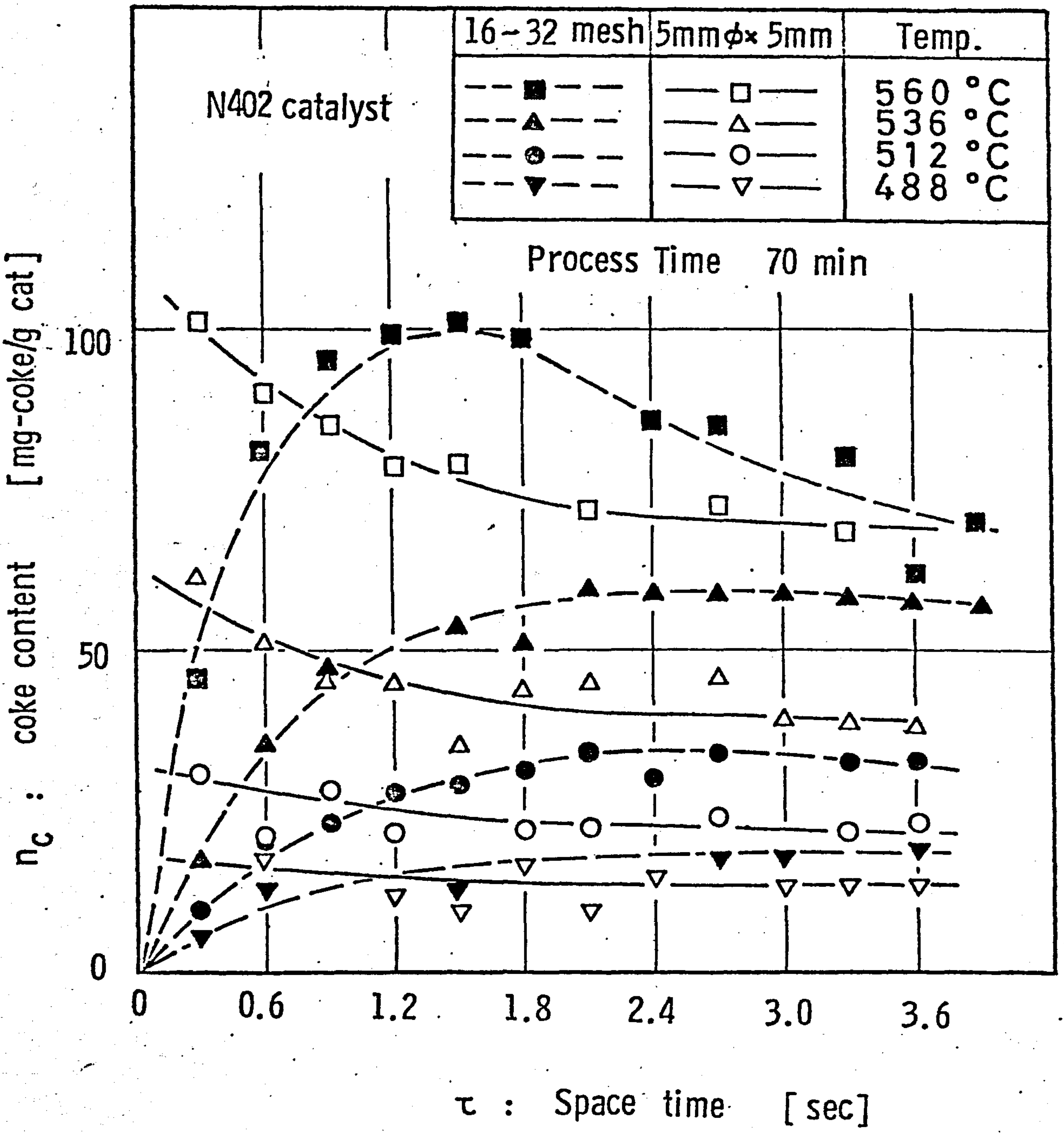


Fig. 5 Distribution of coke content in an axial direction

in a lateral direction. The radial coke distribution is indicated in Figs. 6a and 6b. It is shown that, at the initial stage, the coke accumulates in the outer part of the catalyst, then after about twelve minutes coke accumulation becomes uniform. This fact suggests that the use of a homogenous model for catalyst deactivation might be reasonable.

2.4 Diffusivity

The results of diffusivity which decreases with increasing coke content are shown in Fig. 7. The same relationship between diffusivity and coke content as reported by Suga et al.[10)] was obtained form the linearity of the plots:

$$D^p_e = D^p_{oe} (1 - 0.0063 n_c) \qquad (1)$$

where D^p_{oe} is the diffusivity at zero coke content, D^p_{oe} is determined as $1.03 \times 10^{-2} cm^2/sec$, and n_c is the coke content.

2.5 Distribution of pores in catalyst and calculation of Knudsen diffusivity

The porosimeter data showed that about 85% of the pores were micropores (smaller than 100 Å). To examine the micropore distribution, the data obtained by the BET method were analyzed by the Inkley and Cranelon's method[1)]. The results of distribution of pore sizes are shown in Fig. 8. The radius of the micropores becomes smaller with increasing coke content. The mean radius, $\bar{a}$, was calculated from the following equation,

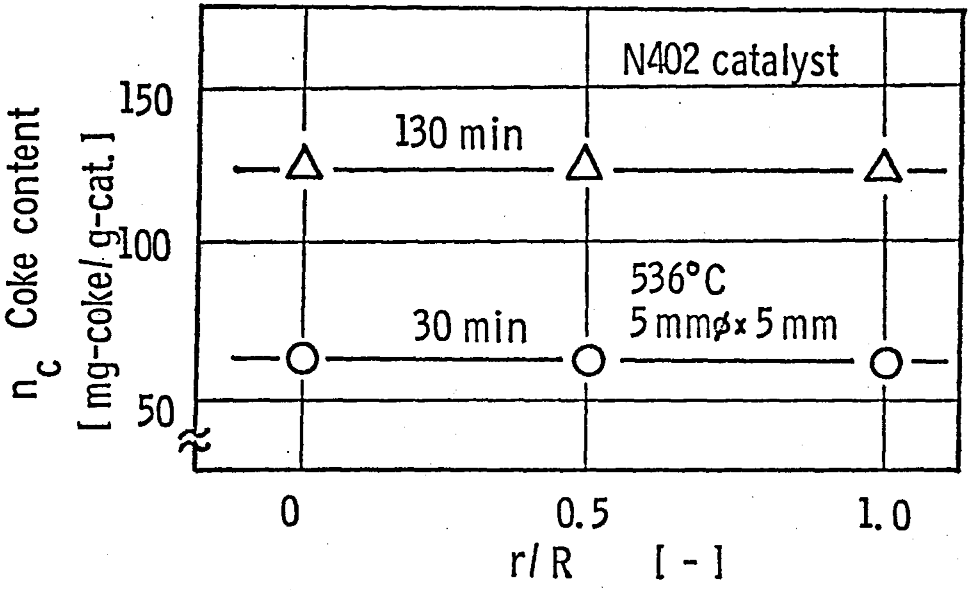


Fig. 6a Coke distribution in catalyst by thermobalance

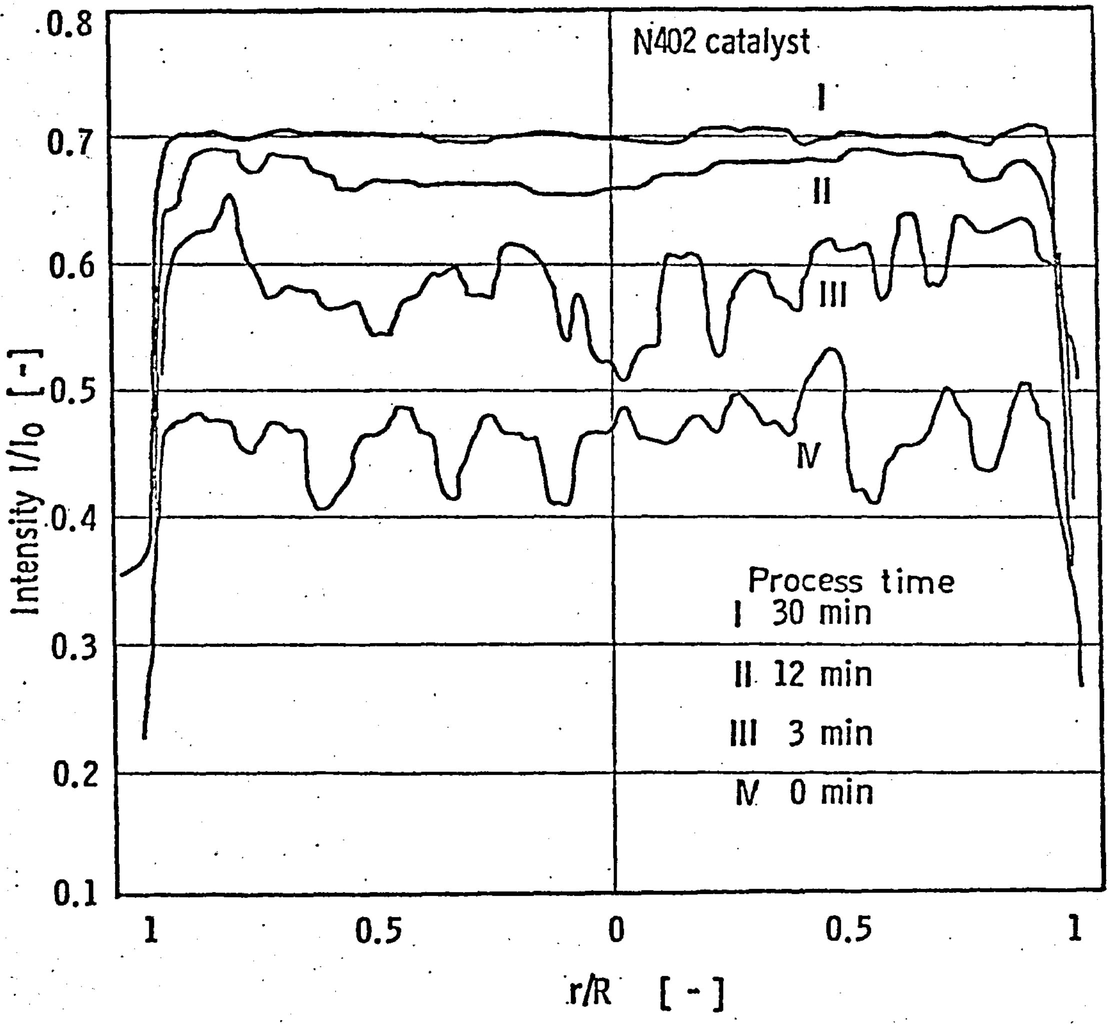


Fig. 6b Coke distribution in catalyst by microphotometer

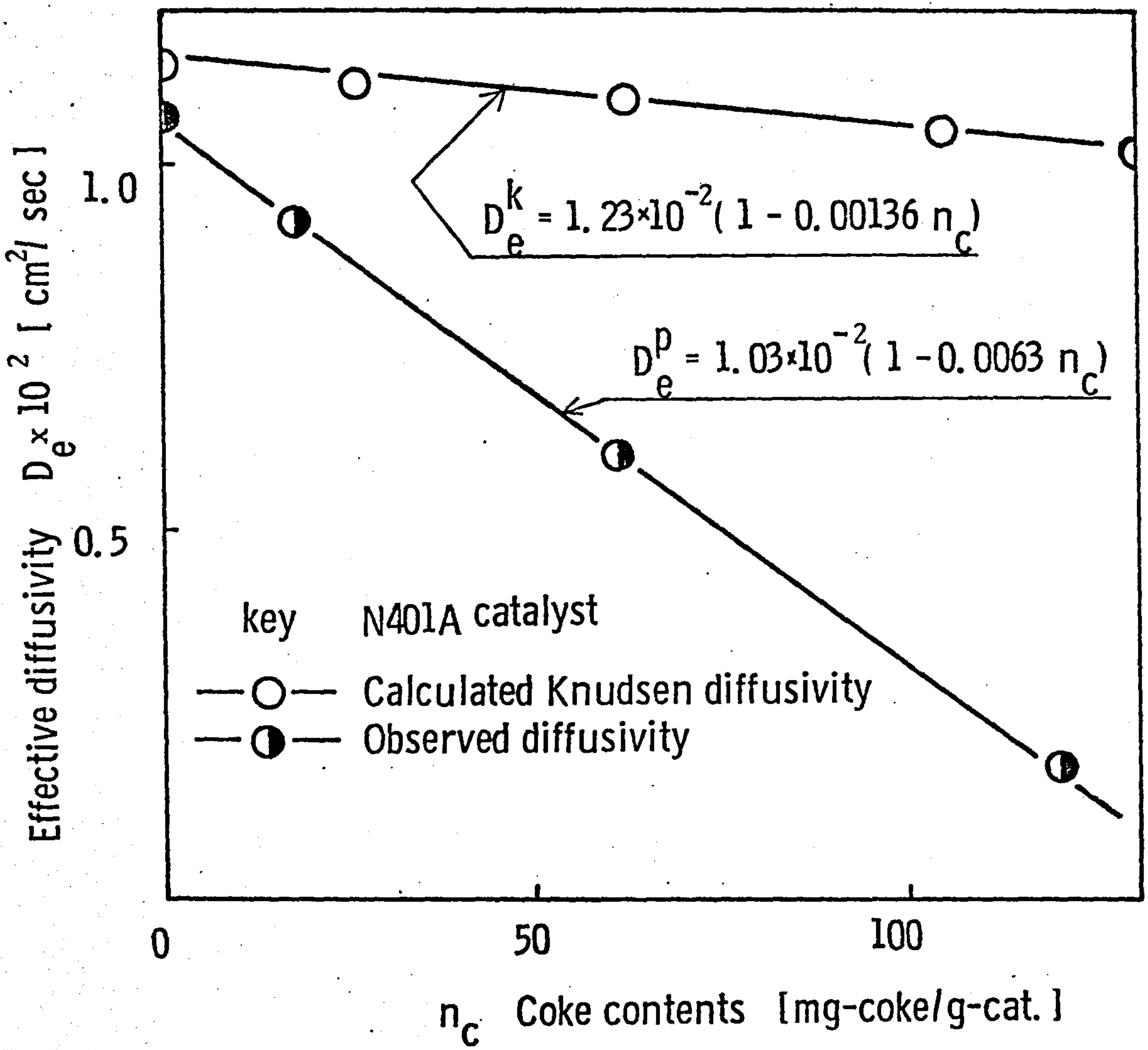


Fig. 7 Diffusivity vs. coke content

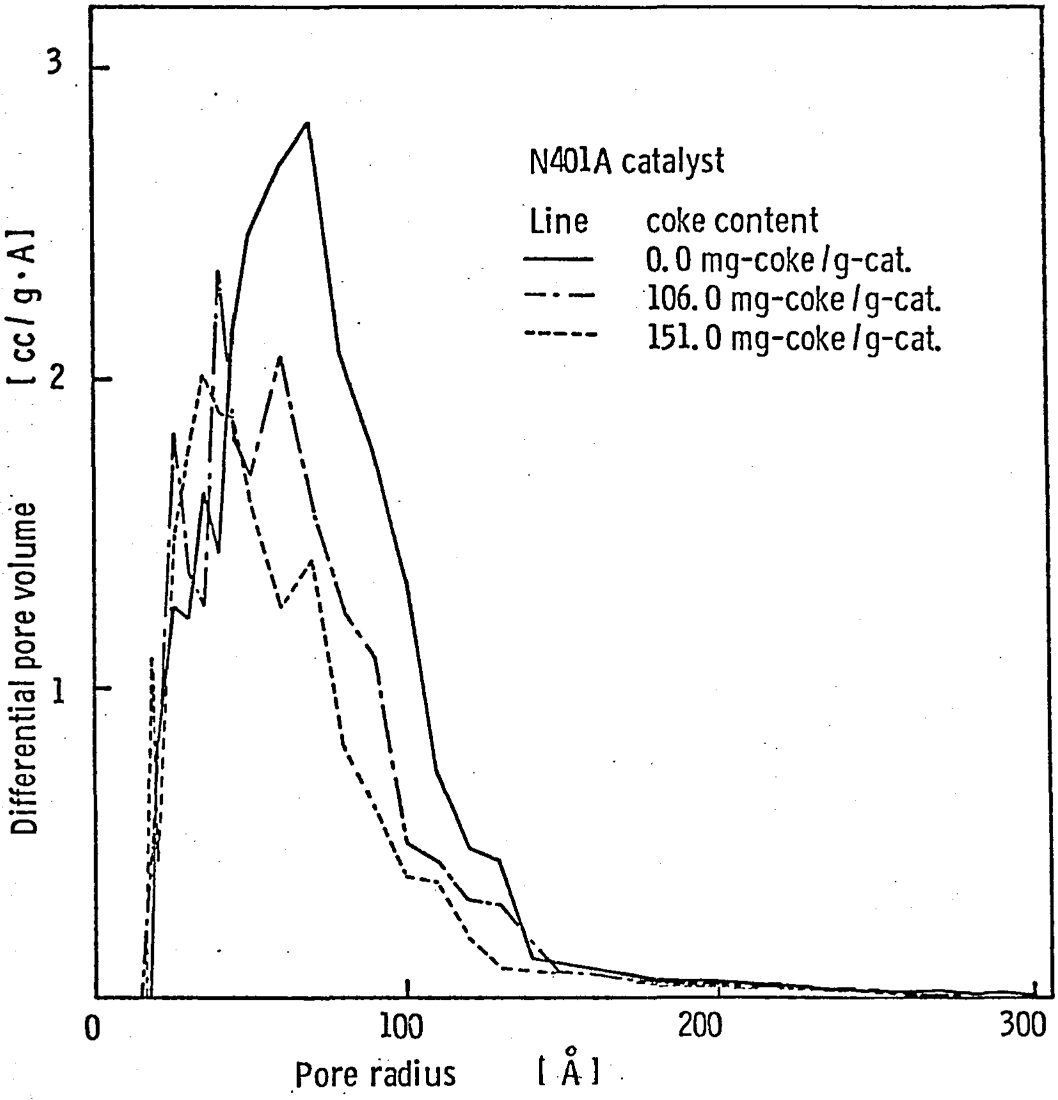


Fig. 8 Distribution of micropores in catalyst

$$\bar{a} = \sum_i a_i \, \Delta V_i \, / \, \sum_i \Delta V_i, \qquad (2)$$

where ΔV_i is the pore volume whose radius is between a_i and $a_i + \Delta a$. Fig. 8 shows that the calculated mean radius becomes smaller as the coke content increases. Diffusivity is calculated from the Knudsen equation using the mean pore radius, and is also shown in Fig. 7. From the linearity of the plots, the following relationship is obtained:

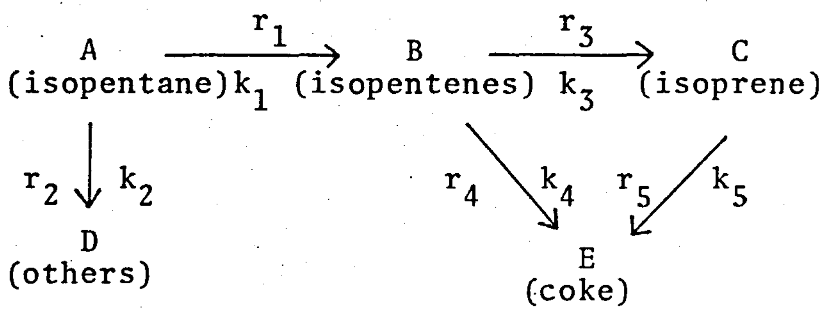
$$D_e^k = D_{oe}^k (1 - 0.00136 \, n_c), \qquad (3)$$

where D_{oe}^k is the initial diffusivity at zero coke content, and D_{oe}^k is determined as 1.23×10^{-2} cm^2/sec. The observed D_{oe}^p agrees fairly well with the calculated D_{oe}^k at zero coke content. The differnce between the observed and calculated values becomes larger with process time, and it might be due to the adsorption of nitrogen on coke.

3. Analyses and discussion

3.1 Kinetic model

The reaction scheme of isopentane dehydrogenation over chromia-alumina catalyst had been proposed in the first chapter as follows:



The overall disapperance of isopentane is the sum of the individual steps 1 and 2. These rates of reaction are of the first order with respect to the reactant;

$$r_A = r_1 + r_2 = - (k_1 + k_2) C_A \tag{4}$$

The net appearance of isopentenes is given as the difference of reaction rates between step 1, step 3 and step 4. These rates are also of the first order.

$$r_B = r_1 - r_3 - r_4 = k_1 C_A - (k_3 + k_4) C_B . \tag{5}$$

The rate of isoprene reaction is given by the difference of the rates between step 3 and step 5, that is,

$$r_C = r_3 - r_5 = k_3 C_B - k_5 C_c , \tag{6}$$

and that of coke formation is expressed in terms of step 4 and step 5,

$$r_{n_c} = r_4 + r_5 = k_4 C_B + k_5 C_c . \tag{7}$$

3.2 Basic equations for diffusion process

The material balance of the i-th component within a spherical catalyst may be written by

$$D_{ei}\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} \right) = \frac{\partial C_i}{\partial \theta} + r_i \ , \tag{8}$$

where D_{ei} is the effective diffusivity of the i-th component. Initial and boundary conditions are given by

$$\begin{aligned} C_i(z,R,\theta) &= C_{oi}(z,\theta) \quad ; \text{ at } \quad = 0,\ r=R \\ \frac{\partial C_i}{\partial r} &= 0 \quad ; \text{ at } r = 0, \text{ for } \theta > 0 \ . \end{aligned} \tag{9}$$

The reaction rate per unit reactor volume is given as follows, using the mass transfer into the pellet and the number of pellets per unit volume as;

$$\tilde{r}_i = \bar{n}\, r_{pi} = 3\,\bar{n}\,\frac{\rho_B D_i}{\rho\, R}\left(\frac{\partial C_i}{\partial r}\right)_{r=R}, \tag{10}$$

where $\bar{n}$ is the number of spherical pellets per unit volume of the bed. In an isothermal tubular reactor, the material balance of the i-th component can be expressed as

$$U_G \frac{\partial \tilde{C}_i}{\partial z} + \frac{\partial \tilde{C}_i}{\partial \theta} = \tilde{r}_i \ . \tag{11}$$

When a homogeneous model for a catalyst pellet is applicable, the coke content in the reactor is given by

$$\frac{\partial n_c}{\partial \theta} = \nu(\tilde{r}_4 + \tilde{r}_5), \tag{12}$$

where ν is the conversion factor that converts the dimension of the reaction rate from per unit volume to per unit weight.

The boundary conditions are given by

$$\begin{aligned} &\tilde{C}_i(z,0) = \tilde{C}_{oi} && \text{for } \theta \geq 0 \\ &\tilde{C}_i(z,\theta) = C_{oi}(z,R,\theta) && \text{for } \theta \geq 0, \text{ and } Z \geq z \geq 0 \\ &n_c(z,0) = 0 && \text{for } \theta = 0 \end{aligned} \tag{13}$$

According to the quasi-steady state the assumption that the rate of decay or coke accumulation would be negligible in comparison with the rate of change of the reactant in the reactor, and Eq. (8) is reduced to.

$$D_{ei}\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} \right) = r_i \tag{14}$$

Generally, the effect of intraparticle diffusion on the reaction rate is represented by the effectiveness factor, but for a complex reaction it is not readily representable by this factor. The effect is directly expressed by Eq. (14) with the effective diffusivity, D_{ei}, and Eq. (11) is reduced to the following equation,

$$\frac{\partial \tilde{C}_i}{\partial \tau} = \tilde{r}_i. \tag{15}$$

As the density of reactant ρ_G is constant during the reaction, and C_i is $\rho_G\, y_i$, Eqs. (14) and (15) are reduced to

$$D_{ei}\left(\frac{\partial^2 y_i}{\partial r^2} + \frac{2}{r}\frac{\partial y_i}{\partial r} \right) = r_i \,/\, \rho_G, \tag{16}$$

where y_i is the weight fraction of the i-th component, and the boundary conditions are,

$$\left.\begin{array}{ll} y_i(z,R,\theta) = \tilde{y}_{oi}(z,\theta) & \text{for } \theta > 0 \\ \dfrac{\partial y_i}{\partial r} = 0 & \text{at } r = 0, \theta > 0. \end{array}\right. \tag{17}$$

The material balance equations in the fixed-bed reactor can also be rewritten as

$$\rho_G \frac{\partial \tilde{y}_i}{\partial \tau} = \tilde{r}_i \tag{18}$$

$$\rho_G \frac{\partial n_c}{\partial \theta} = \tilde{r}_{n_c} \tag{19}$$

and the boundary conditions are

$$\left.\begin{array}{ll} \tilde{y}_i(0,\theta) = \tilde{y}_{oi} & \text{for } \theta > 0 \\ n_c(\tau,0) = 0 & \text{for } \theta = 0 \end{array}\right. \tag{20}$$

3.3 Chemical rate constants and activity factors

For the changes of reaction rate constants with catalyst deactivation, the following relation is used:

$$k_i = k_{io}\,\phi_i\,, \tag{21}$$

where k_{io} is the initial rate constant at zero coke content and ϕ_i is the activity factor. The kinetic parameters have been estimated by two calculation steps$^{6)}$. The activity factor is given by a linear function of coke content,

$$\phi_i = 1 - \alpha_i\,n_c\,, \tag{22}$$

where α_i is the decay constant and n_c is the coke content. The calculated rate and decay constants are shown in Table 2. There are four different α's, so this reaction system is selective aging. The decay constants for step 3 and step 4 are found to be zero.

3.4 Apparent diffusivity under chemical reaction subject to catalyst fouling

To study the effect of catalyst size on conversion, the observed conversion was compared with that of the calculated. The conversions were numerically evaluated using Eqs. (16)-(20) by taking into account the effect of coke deposition on the catalyst activity. The observed values were compared with those of calculated, using two different values of observed and Knudsen diffusivity, but there was only a little difference between them. Apparent diffusivity was determined by minimizing the variances between the observed conversion and the calculated,

Table 2 Reaction rate and decay constants

N402 catalyst

$k_{1o}=\exp(10.0-17{,}300/RT)$; $\alpha_1= \exp(-14.3+15{,}200/RT)$
$k_{2o}=\exp(19.4-35{,}200/RT)$; $\alpha_2= \exp(-7.9+4{,}700/RT)$
$k_{3o}=\exp(9.2-16{,}800/RT)$; $\alpha_3= 0.0$
$k_{4o}=\exp(-13.8+12{,}600/RT)$; $\alpha_4= 0.0$
$k_{5o}=\exp(6.0-10{,}600/RT)$; $\alpha_5= \exp(-20.1+24{,}900/RT)$

N401A catalyst

$k_{1o}=\exp(9.95-17{,}400/RT)$; $\alpha_1= \exp(-14.2+15{,}400/RT)$
$k_{2o}=\exp(19.4-35{,}500/RT)$; $\alpha_2= \exp(-7.95+5{,}300/RT)$
$k_{3o}=\exp(9.2-17{,}500/RT)$; $\alpha_3= 0.0$
$k_{4o}=\exp(-13.8+12{,}600/RT)$; $\alpha_4= 0.0$
$k_{5o}=\exp(6.0-10{,}600/RT)$; $\alpha_5= \exp(-20.0+24{,}400/RT)$

using a hill climbing method. The apparent diffusivity was about one fifth of that observed. This fact may suggest that diffusivity is affected by chemical reactions.

For the 16-32 mesh and 42-60 mesh catalysts, the influences of intraparticle diffusion could be ignored as confirmed by calculation and by the experiments as shown in Fig. 3. Some of the results of simulation were shown in Fig. 4. The computing time for one iteration from 0 minute to 190 minutes for process time was about 50 second on a NEAC 2200/700 at the Calculation Center, Osaka Univ.

Conclusion

In the dehydrogenation of isopentane over chromia-alumina catalyst, the conversion of isopentane and the yields of isopentenes decreased rapidly with process time, while the yield of isoprene decreased very slowly. The evaluated activity factors were different for different reactions, so the fouling was selective aging. Moreover, in the reaction, the coke content in the catalyst pellet was found to be uniform. The observed effective diffusivity was a linear function of coke content. The apparent diffusivity for the chemical reaction was determined by fitting the observed conversion ratio in the fixed-bed reactor with the values obtained from a proposed model. The difference between the apparent and the observed diffusivity was recognized. Effects of the catalyst size on conversion and coke content profiles in the fixed-bed reactor were explained by the proposed model.

Notations

a = pore radius in a catalyst [Å]

C_i = concentration of i-th component [g/cc]

$\hat{C}_i$ = concentration of i-th component in a catalyst [g/cc]

D_{ei} = apparent diffusivity evaluted by simulation [cm^2/sec]

D_e^k = evaluated diffusivity by BET method [cm^2/sec]

D_e^p = observed diffusivity by diffusion method [cm^2/sec]

F = feed rate of reactant [g/min]

k_j = rate constant for the j-th reaction [1/sec]

n_c = coke content on catalyst [mg-coke/g-cat.]

$\bar{n}$ = number of spherical catalyst per unit volume [number/cc]

r_i = reaction rate of i-th component per unit volume [g/cc·sec]

r_{pi} = reaction rate per unit pellet [cc/g·sec·number]

r_{n_c} = rate of coke formation [mg-coke/g-cat·min]

R = radius of a spherical catalyst [mm]

y_i = weight fraction of i-th component [-]

z = axial distance of the fixed-bed reactor from inlet [cm]

Z = reactor length [cm]

U_G = superficial velocity of reactant [cm/sec]

W_{cat} = weight of catalyst [g]

Greeks

α_i = decay constant [g-cat./mg-coke]

θ = process time [min]

ν = conversion factor [mg-coke·g-feed·sec/g-cat.g-component·min]

τ = space time (= z/U_G) [sec]

ρ = density of catalyst pellet [g/cc]

ρ_B = density of catalyst bed [g/cc]

ρ_G = density of reactant gas [g/cc]

ϕ_i = activity factor for the i-th reaction [-]

Subscripts

A = isopentane

B = isopentenes

C = isoprene

m = number of intervals of division of the reactor

n_c = coke

o = initial (at zero coke content)

f = final

Superscripts

- = average

^ = observed

∿ = bulk

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Chapter 3

Optimal Control Policy of Chemical Reactors with Catalyst Deactivation

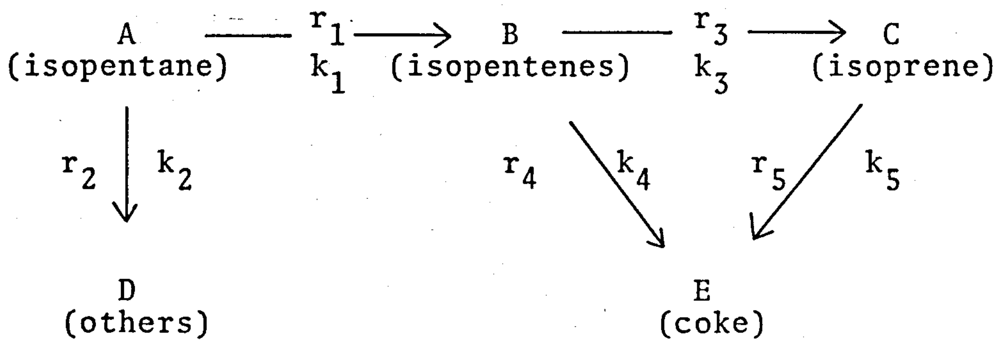
Introduction

It is important for improvements of product yield and catalyst life to operate and to design a catalytic reactor subject to deactivation[1,10] optimally. Since Jackson[6,7] discussed and proposed the problem of optimal temperature control of a reactor subject to the catalyst decay, there have been a few studies concerning with the problem. Szépe and Levenspiel[16], Chou et al.[2] and Haas et al.[5] have studied the problems of obtaining the isothermal optimal temperature histories using a lumped reaction model in which the catalyst decay is independent of reactant using Bolza method of calculus of variations. Ogunye and Ray[11] and Crowe[3] treated the problem using the maximum principle. In a class of distributed parameter system, Volin and Ostrovskii[17], Jackson[6,7] and Ogunye and Ray[12] derived the distributed maximum principle and proposed the computational algorithms. Ogunye and Ray[14] also applied their algorithm to vinyl chrolide monomer reactor and solved the problem of catalyst loading. Kumbilieva and Peshev [9] evaluated the optimal temperature control of a tubular reactor in which two parallel irreversible reaction occurred. Extensions of the basic problem have been given by Ogunye and Ray[13], Paynter[15] and Crowe[4] for multi-bed reactors. Simple reaction models have been used for the sake of the calculation, the analytical treatment and so forth. It is, however, insufficient to apply such a simple model to the real reaction system with catalyst decay.

In this chapter, using the kinetic model obtained in the first chapter, the problem of the optimal temperature control of the reaction subject to deactivation by coke deposition is theoretically studied for three kind of reactors, that are an isothermal reactor, a non-isothermal reactor and a multi-bed reactor. Most optimization studies have considered the problem of maximization of the total amount of reaction in a catalytic reactor by manipulating reactor temperature with process time. From the view point of post-treatment of the catalyst, it is necessary both to minimize the coke content and to maximize the total amount of product, and the objective functional has to be selected as matching the purpose. When the distributed maximum principle is applied to the optimization problem with deactivation by coke deposition, one has to solve a two-point-boundary value problem. The algorithm proposed by Ogunye and Ray12), however, might not be applicable to the reaction accompanied with coke deposition. A vector iteration method is proposed that is based on a gradient technique in spatial direction and in temporal direction based on an extremal technique8). The optimal policy for the single bed reactor calls for increasing temperature operation with process time, while for the multi-bed reactor does not always call for the operation.

1. Reaction model

The previously obtained reaction kinetic model and the parameters are used for the studies of optimal temperature policy with catalyst decay. The reaction model[10)] had been proposed as follows:



Each step is a first order reaction. The reaction is deactivated due to coke deposition. For changes of reaction rate constants, the following relation is used:

$$k_i = k_{io}\ \phi_i \tag{1}$$

where k_{io} is an initial rate constant and ϕ_i is an activity factor. The activity factor was given by a linear function of the local coke content which represents activity profiles in the reactor:

$$\phi_i = 1 - \alpha_i\ n_c(\tau,\theta) \tag{2}$$

where α_i is a decay constant. The rate constant k_i is temperature dependent and is represented by the Arrhenius formula:

$$k_{io} = \exp(\ A_i - E_i/RT) \tag{3}$$

The activity factor is also temperature dependent and the decay constant is represented by the Arrhenius form. Used rate

Table 1 Reaction rate and decay constants

$k_{1o} = \exp(10.0 - 17,300/RT)$ $\qquad \alpha_1 = \exp(-14.3 + 15,200/RT)$

$k_{2o} = \exp(19.4 - 35,200/RT)$ $\qquad \alpha_2 = \exp(-7.9 + 4,700/RT)$

$k_{3o} = \exp(9.2 - 16,800/RT)$ $\qquad \alpha_3 = 0.0$

$k_{4o} = \exp(13.8 + 12,600/RT)$ $\qquad \alpha_4 = 0.0$

$k_{5o} = \exp(6.0 - 10,600/RT)$ $\qquad \alpha_5 = \exp(-20.1 + 24,900/RT)$

$$\phi_i = 1 - \alpha_i n_c \text{ ; if } \alpha_i n_c \geq 1.0 \text{ , } \phi_i = 0.0$$

and decay constants are shown in Table 1.

2. Reactor Model and System Equation

For the tubular reactor three assumptions are made that the reactor is in plug flow, that the intraparticle and interparticle mass and heat transfer is negligible and that the space time scale is much shorter than the process time scale for catalyst decay by the coke deposition so that the quasi-steady state is valid.[10,12] Under these assumptions the extent of reaction for each component is given as:

$$\frac{\partial x_A}{\partial \tau} = -(k_1 + k_2) x_A = f_1 \tag{4}$$

$$\frac{\partial x_B}{\partial \tau} = k_1 x_A - (k_3 + k_4) x_B = f_2 \tag{5}$$

$$\frac{\partial x_C}{\partial \tau} = k_3 x_B - k_5 x_C = f_3 \tag{6}$$

$$0 \leq \theta \leq \theta_f, \quad x(0,\theta) = x(1,0,0)^T \tag{7}$$

and coke content in the reactor is given as:

$$\frac{\partial n_c}{\partial \theta} = \nu(k_4 x_B + k_5 x_C) = g \tag{8}$$

$$0 \leq \tau \leq \tau_f, \qquad n_c(\tau,0) = n_{co}(\tau) \tag{9}$$

3. Optimization Problem

The general form of the objective functional stated by Ogunye and Ray[12)] (for a fixed value of θ) is rewritten for the coke deposition as follows:

$$I = \int_0^{\theta_f} G_1(x_i(\tau_f,\theta))\,d\theta + \int_0^{\tau_f} G_2(n_c(\tau,\theta_f))\,d\tau + \int_0^{\theta_f}\int_0^{\tau_f} G(x,n_c,T)\,d\theta d\tau \qquad (10)$$

where G_1 accounts for the value of product concentrations, feed costs, etc; G_2 accounts for catalyst cost, regeneration cost, coke content, etc, and G accounts for heating and cooling cost, etc. The total amount of reaction products isopentenes, is maximized, and simultaneously the coke content that accounts for the catalyst fouling is minimized. The objective functional is reduced as follows;

$$I' = \int_0^{\theta_f} x_B(\tau_f,\theta)\,d\theta - p\int_0^{\tau_f} n_c(\tau,\theta_f)\,d\tau \qquad (11)$$

where p is an economic parameter that accounts for the catalyst cost, regeneration cost, etc. The optimal control of the temperature, T, which maximizes the objective functional Eq.(11) subject to Eqs.(4)-(9) according to maximum principle, is treated.

4. Maximum Principle

A Hamiltonian is defined by the following function;

$$H = \sum_i \lambda_i f_i + \mu g \tag{12}$$

where f_i and g are Eqs.(4)-(9), and λ_i and μ are adjoint variables defined below,

$$\frac{\partial \lambda_A}{\partial \tau} = - \frac{\partial H}{\partial x_A} \tag{13}$$

$$\frac{\partial \lambda_B}{\partial \tau} = - \frac{\partial H}{\partial x_B} \tag{14}$$

$$\frac{\partial \lambda_C}{\partial \tau} = - \frac{\partial H}{\partial x_C} \tag{15}$$

$$\frac{\partial \mu}{\partial \theta} = - \frac{\partial H}{\partial n_c} \tag{16}$$

Eqs.(13)-(16) have to satisfy the boundary conditions,

$$\lambda\ (\tau_f, 0) = (0,1,0)^T\ ,\ \mu(\tau,\theta_f) = p \tag{17}$$

For T to be optimal when T is unconstrained, it is necessary that,

$$\frac{\partial H}{\partial T} = 0 \tag{18}$$

When T is constrained as $T_* \leq T \leq T^*$, it is necessary that Eq.(12) is to be a maximum with respect to T.

5. Algorithm for an Optimizaiton with Fouling by Coke Deposition

To determine an optimal temperature, it is necessary that the simultaneous partial differential equations (4)-(9) and (13)-(16) may be solved with the boundary conditions, while Eq.(18) is satisfied. In the procedure the coke accumulation had to be taken into account and also change of the catalyst activity along the reactor was taken into consideration. The algorithm presented by Ogunye and Ray[12)] might not be applicable to the reaction accompanied by coke deposition. A control vector iteration method was chosen that was based on a gradient technique in spatial, z-direction and in temporal, θ-direction based on the extremal technique[8)]. The flow chart of the calculation is shown in Fig. 1.

6. Results

Firstly it was assumed that at an initial process time, coke content was zero, $n_c(\tau,0) = 0.0$, that a run was started with new or completely regenerated catalysts, and that pure isopentane was supplied from the inlet of the reactor, $x(0,\theta) = (1,0,0)^T$. The upper limit of the reactor temperature was kept at 900°C, because of the experimental conditions. The economic parameter p in Eq.(11) and the final process time θ_f were chosen 1.0 and 130 min, respectively. The partial differential equations were numerically integrated by the Runge-Kutta-Gill method, the spatial direction was divided into 50 intervals and the time axis divided into 26 intervals.

6.1 Ideal optimal reactor

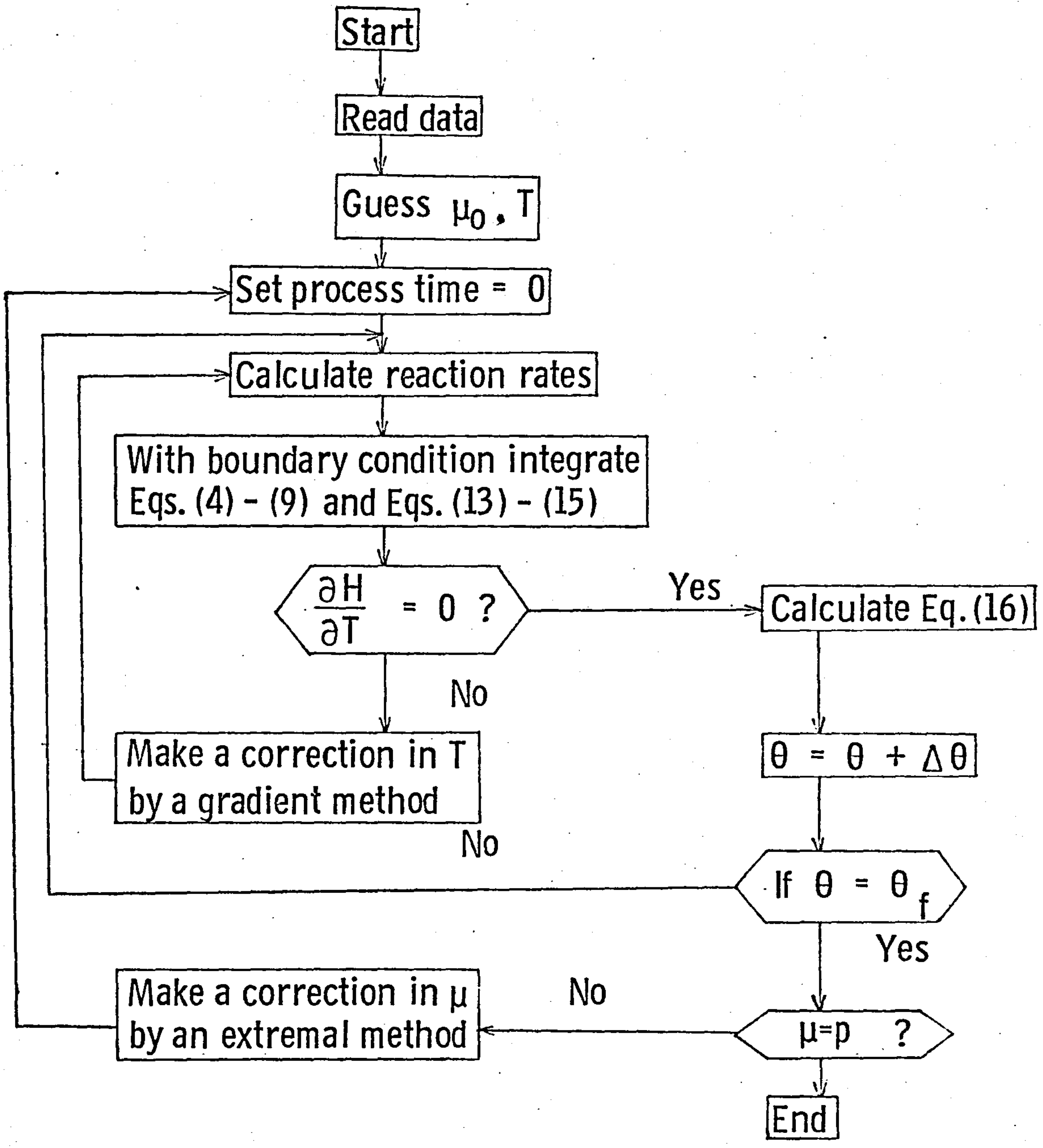


Fig. 1 Flow chart of the calculation steps for optimal control policy

The ideal optimal reactor was defined as a reactor that has both ideal temperature profiles along the spatial direction of the reactor and with optimal histories in the temporal direction. The algorithm was applied to the optimization problem of the ideal optimal reactor. The space times chosen were 1.8, 2.4 and 3.0 sec. Fig.2 shows that the conversion of isopentane for space time 3.0 sec is almost constant as reported by Chou et al.[2)], Crowe[3)], etc., for a first order irreversible reaction using an isothermal optimal reactor, which has an optimal temperature history with process time. The best yield of isopentenes is obtained from the reactor at space time 3.0 sec, while the best yield of isoprene is obtained from that at 1.8 sec among three ideal optimal reactors. The conversion of isopentane for 2.4 sec and 1.8 sec slightly decrease as the process time proceeds because of the upper temperature limit. As can be seen from Fig. 3, the ideal optimal reactors have rising temperature profiles toward the upper temperature limit, and the coke content increases from the inlet to the outlet of the reactor. Significant increases of the temperature profiles are recognized with the shorter space time.

6.2 Isothermal optimal reactor

For the optimal control of the isothermal reactor, the control variable is a reactor temperature and it varies according to an optimal control history. The gradient method was modified as follows;

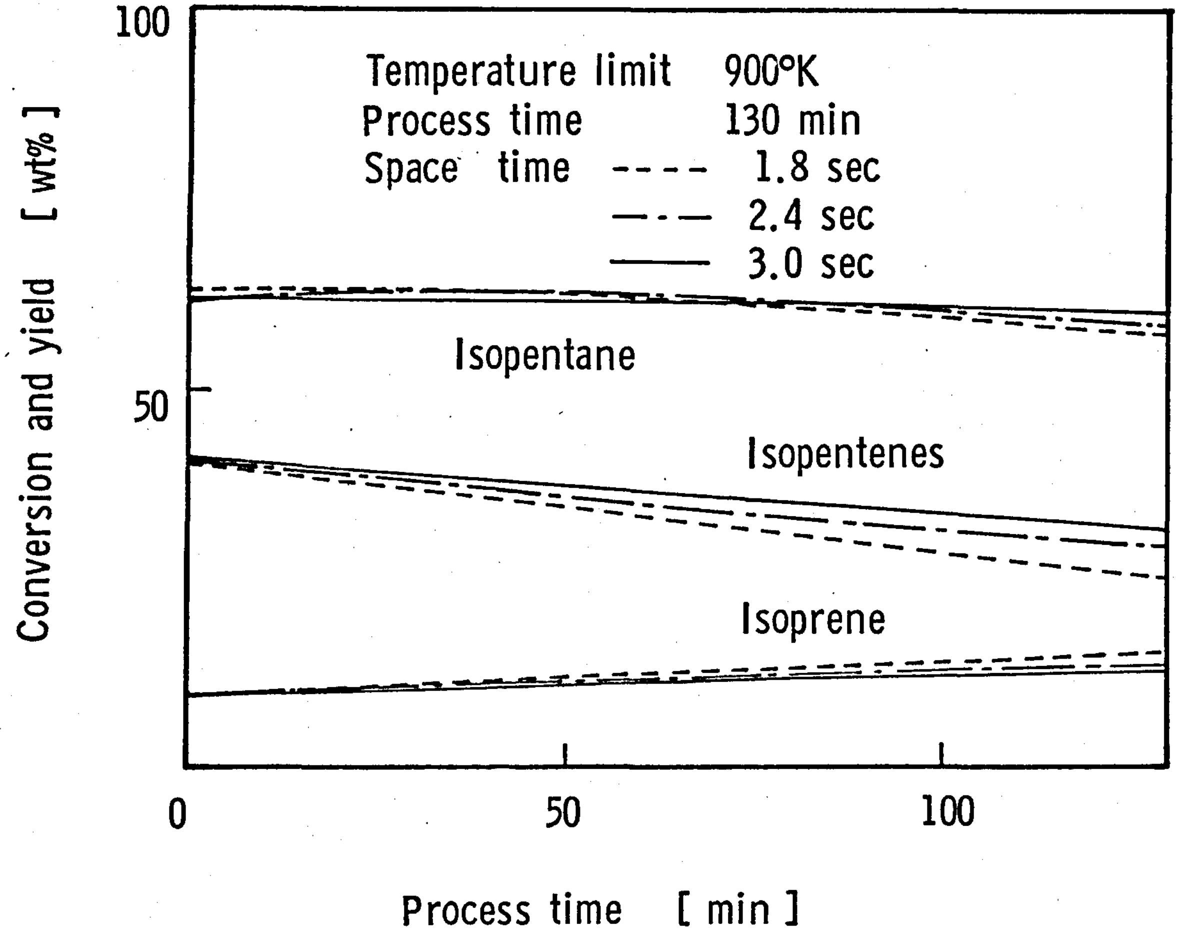


Fig. 2 Changes of the conversion of the ideal optimal reactor

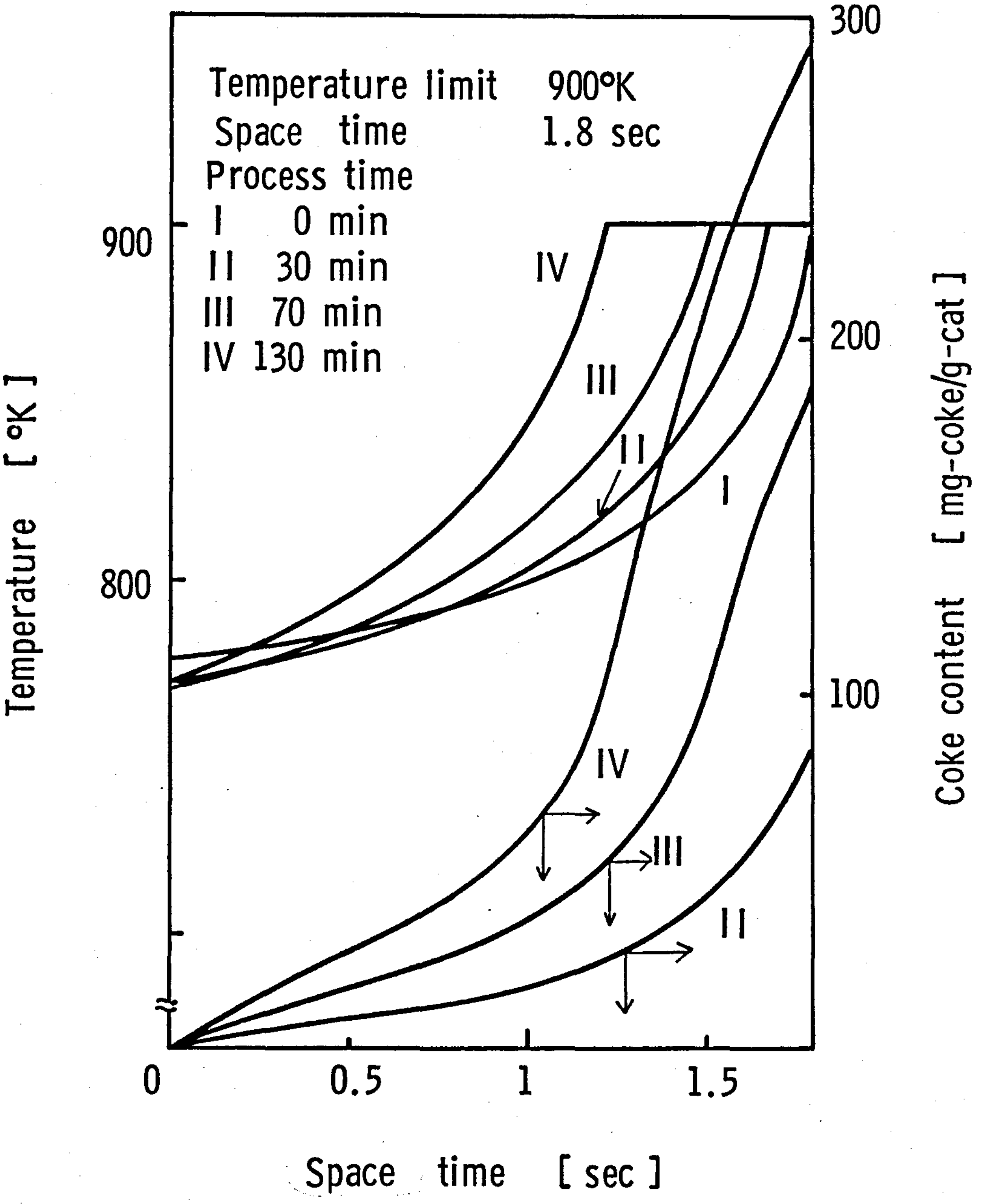


Fig. 3(a) Optimal temperature and coke content profiles in the ideal optimal reactor

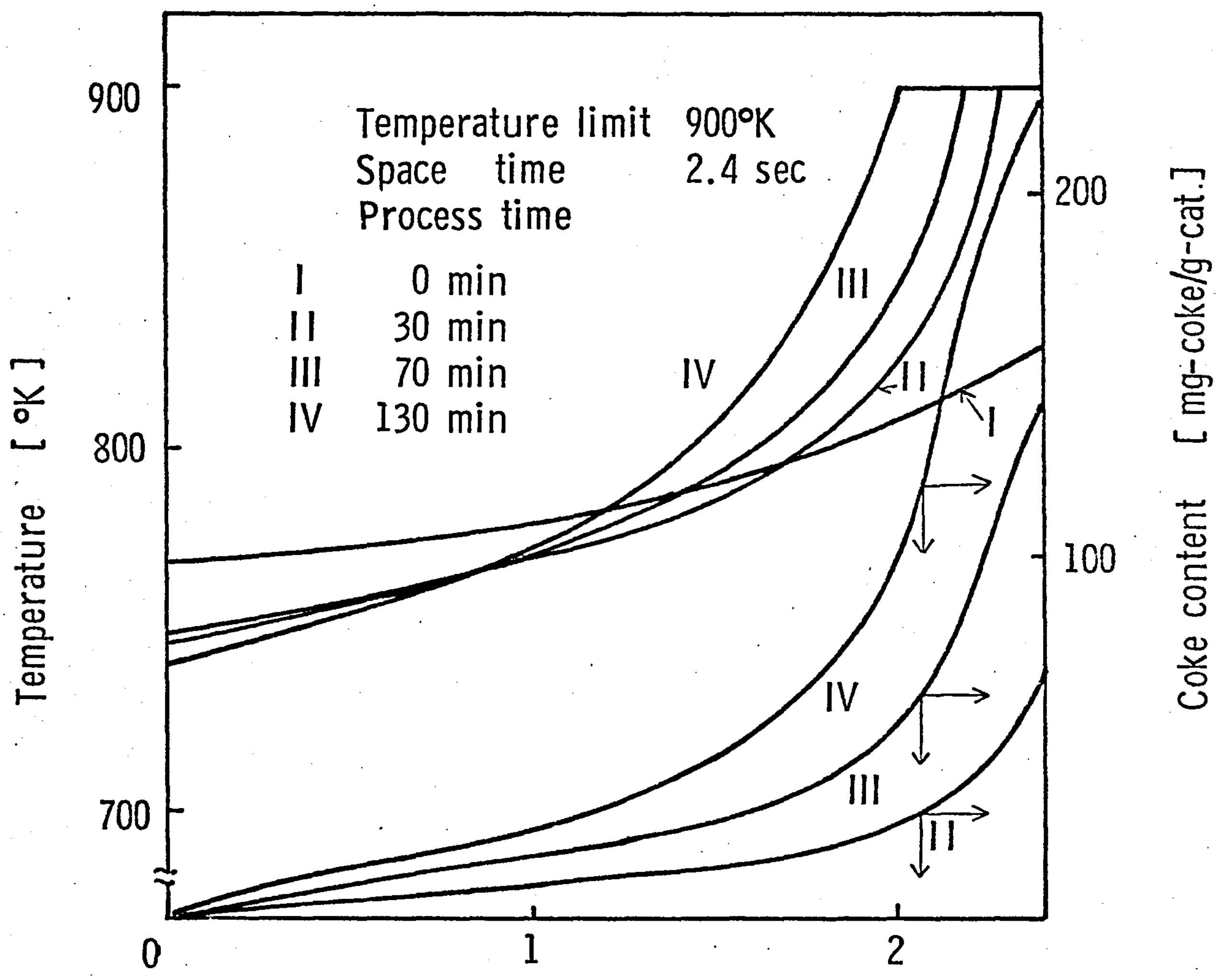


Fig. 3 (b) Optimal temperature and coke content profiles in the ideal optimal reactor

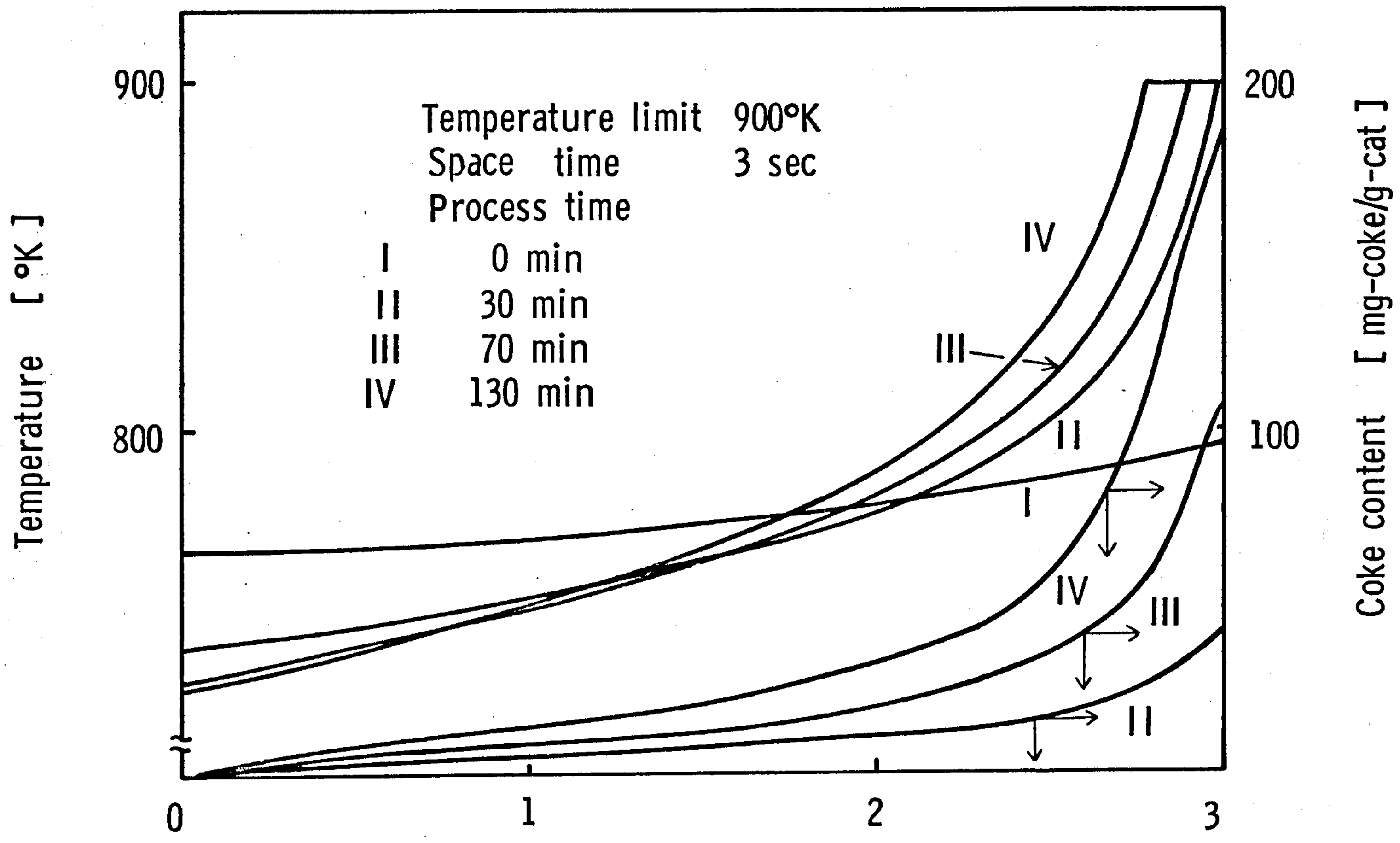


Fig. 3 (c) Optimal temperature and coke content profiles in the ideal optimal reactor

$$T(\theta) = T(\theta) + \varepsilon \int_{o}^{\tau_f} \frac{\partial H}{\partial T(\theta)} d\tau \tag{19}$$

where ε is a step size factor. The optimal policy is rising temperature history. The conversion and the optimal policy are shown in Fig. 4. The changes of the coke content profiles with process time are shown in Fig. 5. The conversion of isopentane and the yield of isopentenes decrease gradually, while that of isoprene increases.

6.3 Multi-bed reactor

The multi-bed reactor system is shown in Fig. 6. Each reactor is isothermally and also optimally controlled with process time. The reactor length is L;

$$L = \sum_{i} L_i \tag{20}$$

where L_i represents the i-th bed length. The boundary conditions of state variables x from bed to bed are given by,

$$x_{i,j}(\tau_j,0) = x_{i,j+1}(\tau_j,0) \tag{21}$$

and the discontinuities in the adjoint variable from bed to bed are also given by,

$$\lambda_{i,j}(\tau_j,0) = \lambda_{i,j+1}(\tau_j,0) \tag{22}$$

The control correction for i-th bed temperature is made by the same gradient method as for the isothermal optimal control,

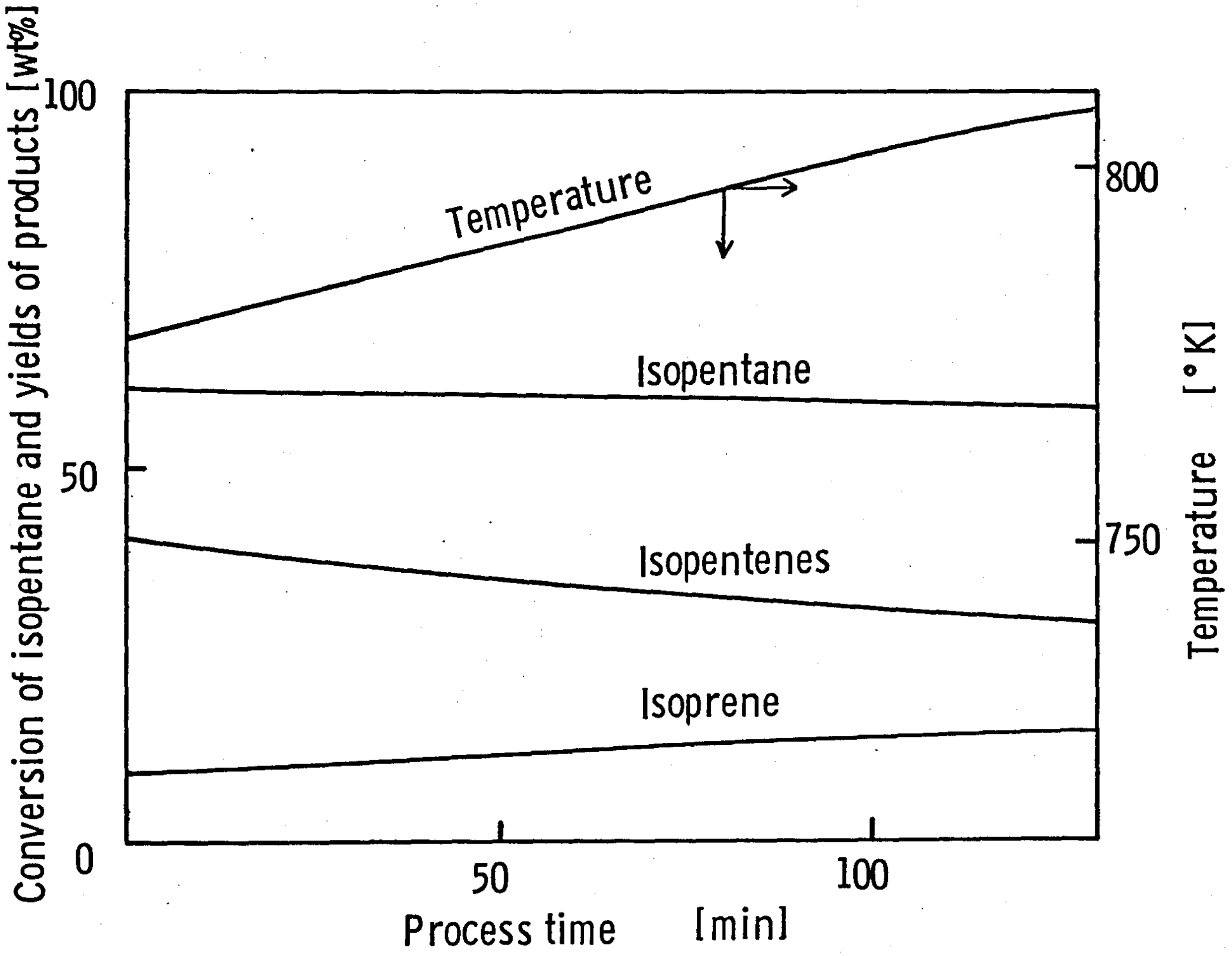


Fig. 4 Optimal temperature and the conversion history of the isothermal optimal reactor
Space time = 3.0 sec ; p = 1.0

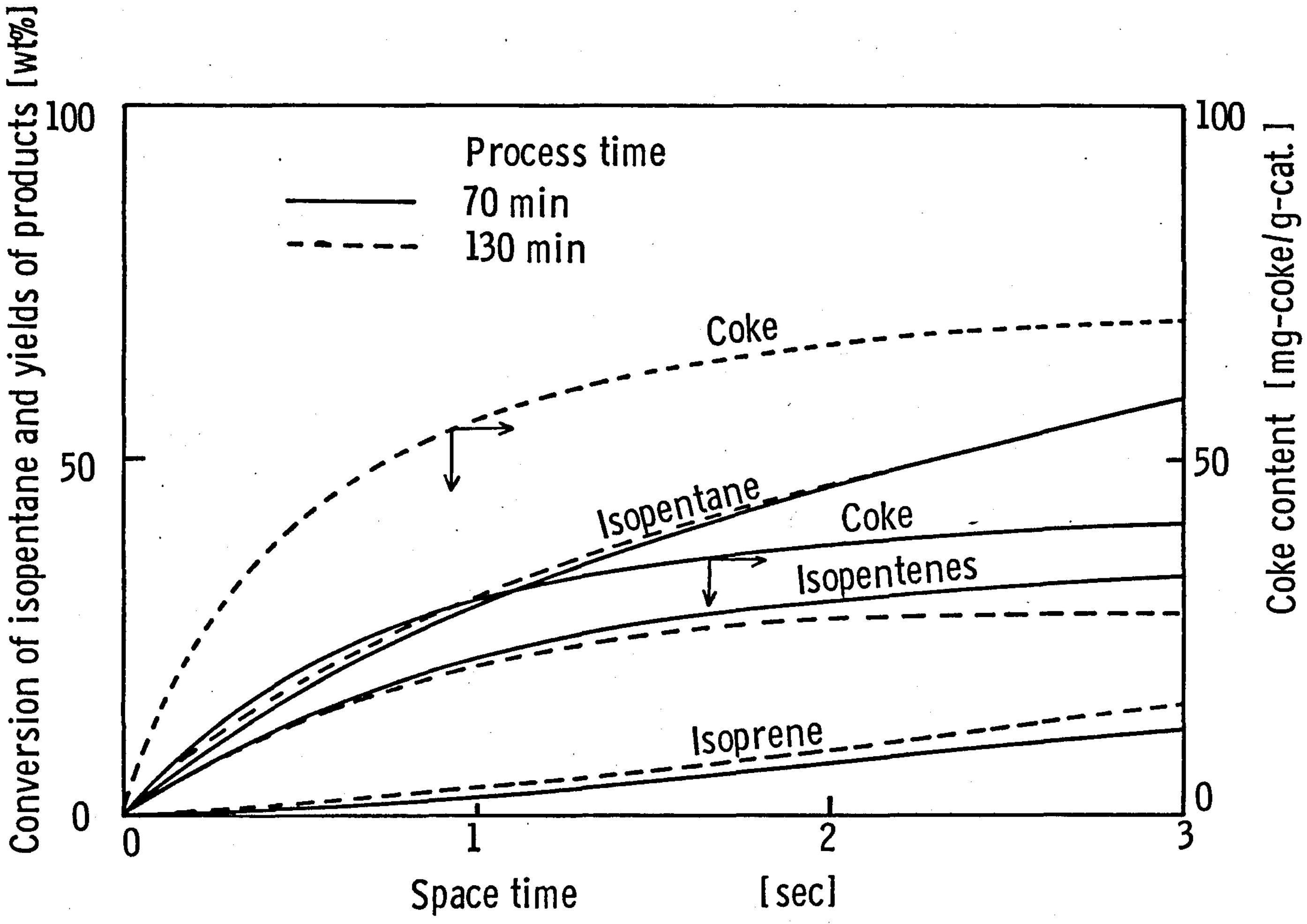


Fig.5 Conversion and coke content profiles in the isothermal optimal reactor

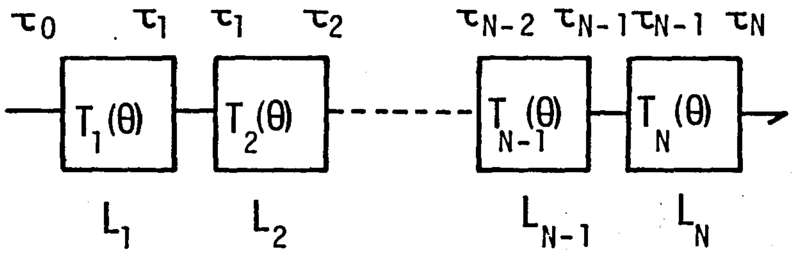


Fig.6 Multi-bed reactor system

$$T_j(\theta) = T_j(\theta) + \varepsilon \int_{\tau_j}^{\tau_{j+1}} \frac{\partial H}{\partial T_j(\theta)} \, d\tau \qquad (23)$$

In this example the bed number and space time were chosen 2 and 3 sec, respectively. The ratios of the bed length were chosen, (A) $L_1 : L_2 = 1 : 4$, (B) $L_1 : L_2 = 1 : 1$ and (C) $L_1 : L_2 = 3 : 1$. As can be seen from Fig. 7, the conversion of isopentane is almost constant independent of the ratios of the bed length. As shown in sections 6.1 and 6.2, the yield of isopentenes decreases and the yield of isoprene increases gradually as process time proceeds. In Fig. 8 the profiles of the conversion and coke content are shown at process time 70 min for reactor (A). On the first bed coke deposited scarcely, and on the second bed it deposited considerably. The reactor (C) gives the best yield of isopentenes and the best catalyst activity at the process time 130 min as shown in Fig. 9 among three kinds of multi-bed reactor.

6.4 Comparison among the three types of the optimal reactor

As can be seen from Figs. 2, 4 and 7, the best yield of isopentenes is obtained by the ideal optimal reactor at space time 3 sec, while the best yield of isoprene is obtained by the ideal optimal reactor at space time 1.8 sec. The coke content profiles increase from the inlet to the outlet of each reactor at any process time. The average coke content which is a measure of the catalyst activity is shown in Fig.9. The average coke content is defined by the following equation,

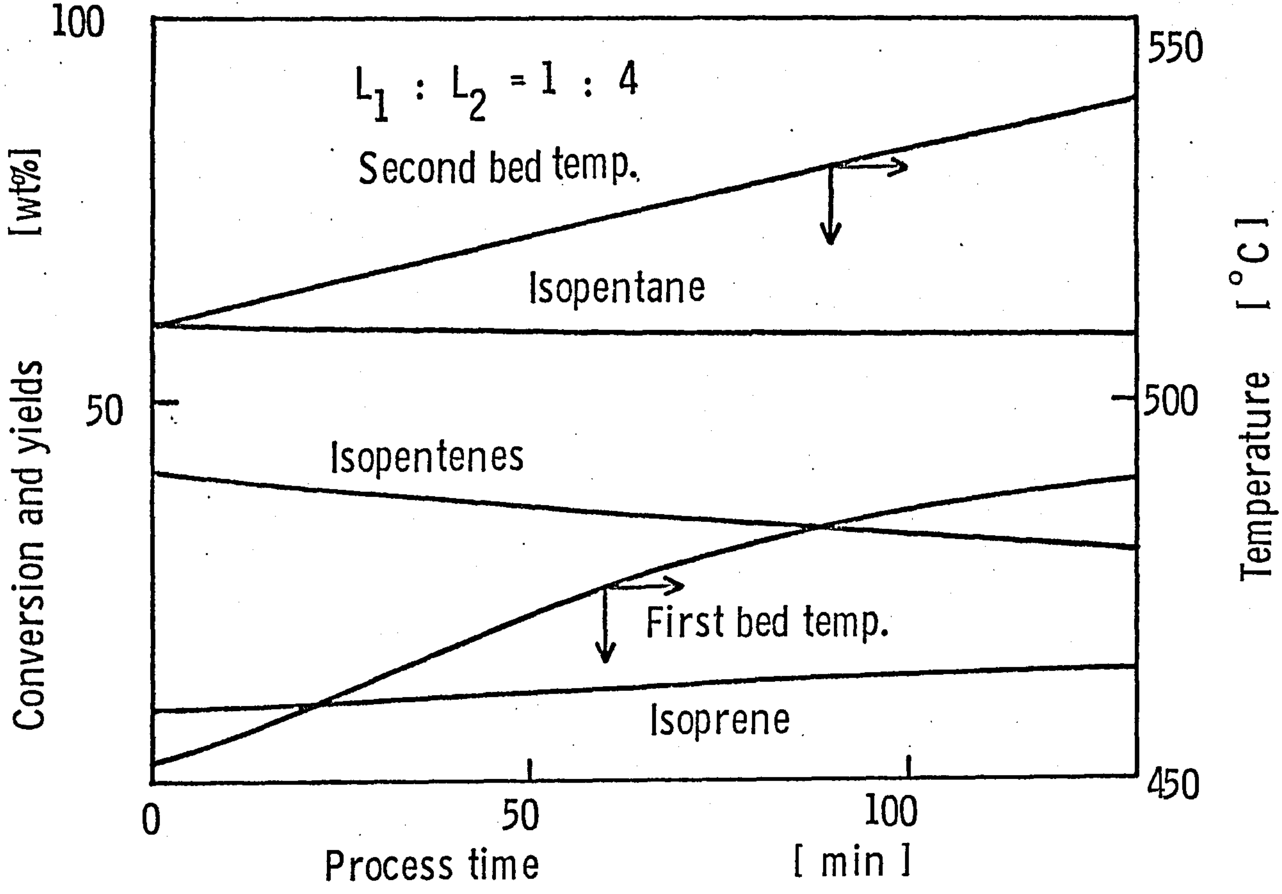


Fig. 7(a) Optimal temperature control for two beds reactor
$p = 1$; $L_1 : L_2 = 1 : 4$

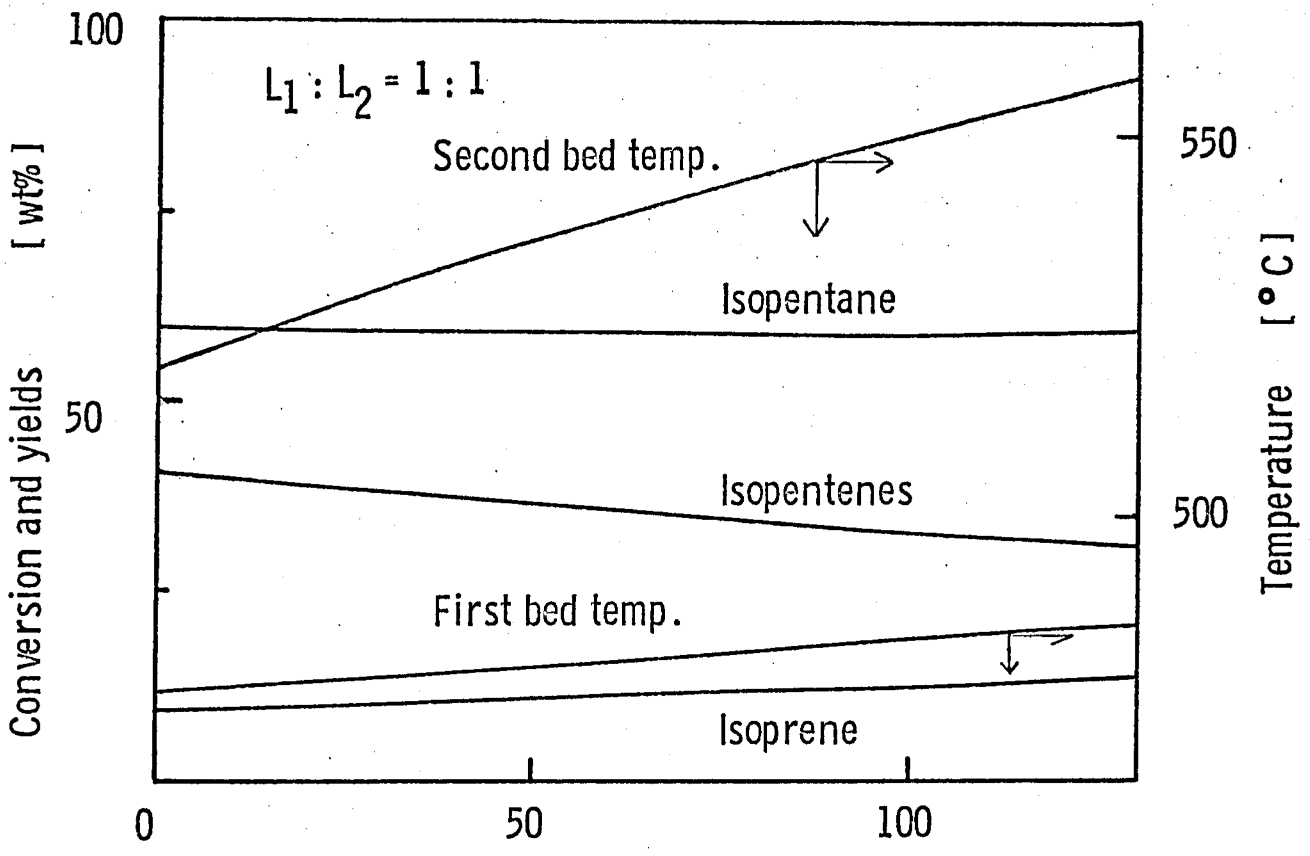


Fig. 7 (b) Optimal temperature control for two beds reactor
Space time = 3.0 sec ; p=1

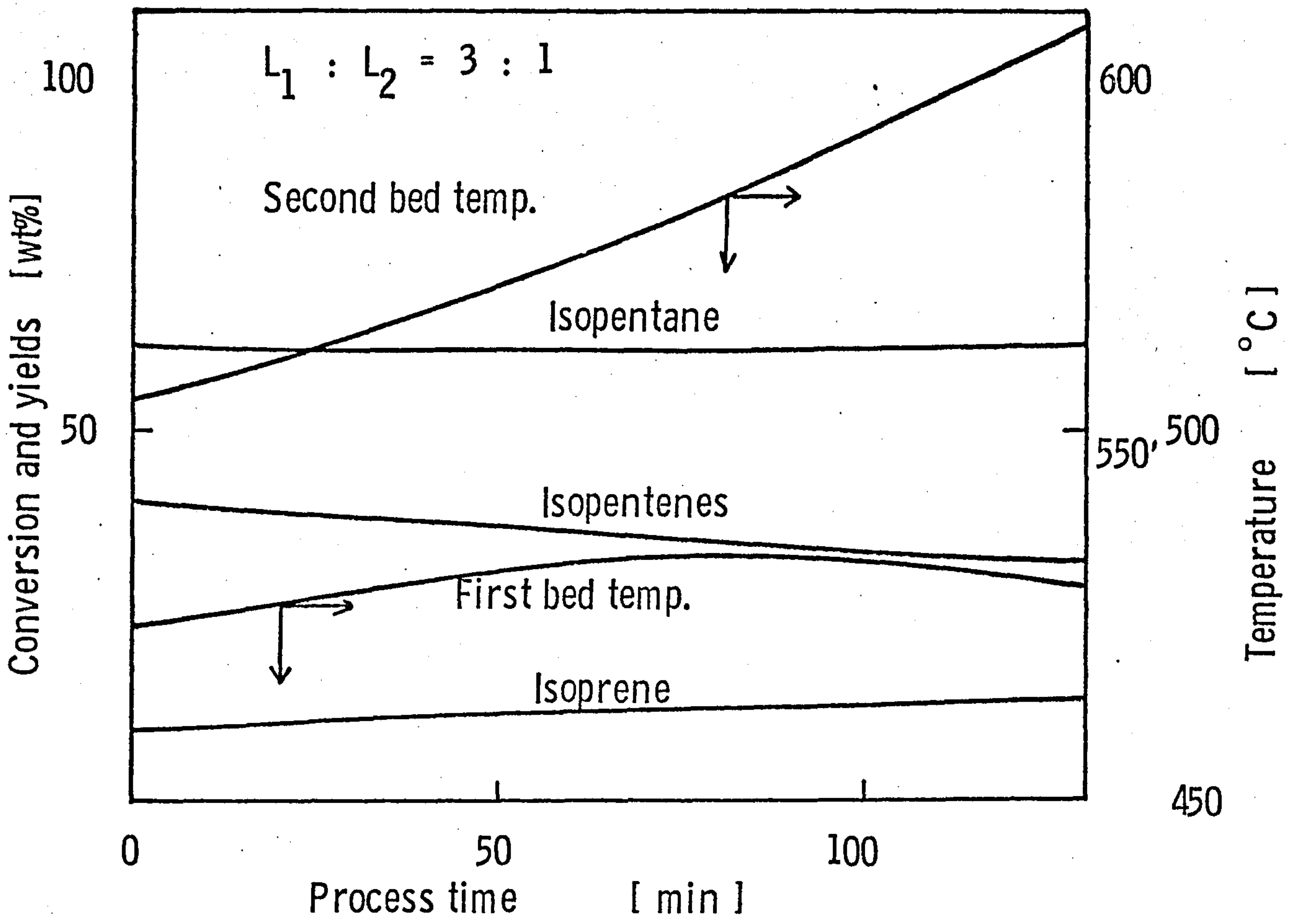


Fig.7(c) Optimal temperature control for two beds reactor
$p = 1 ; L_1 : L_2 = 3 : 1$

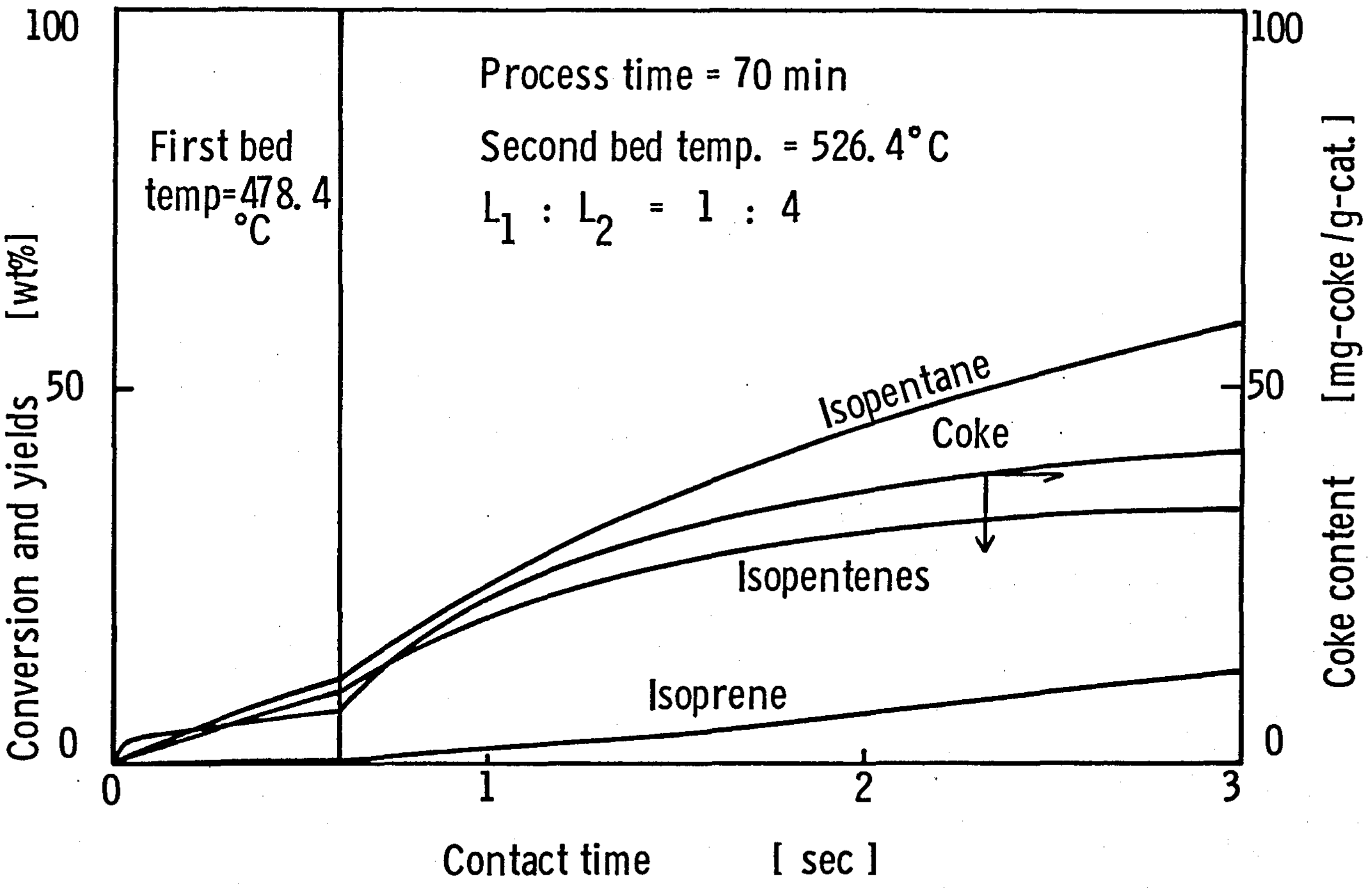


Fig. 8 Optimal temperature control for two beds reactor
Space time 3.0 sec; p= 1

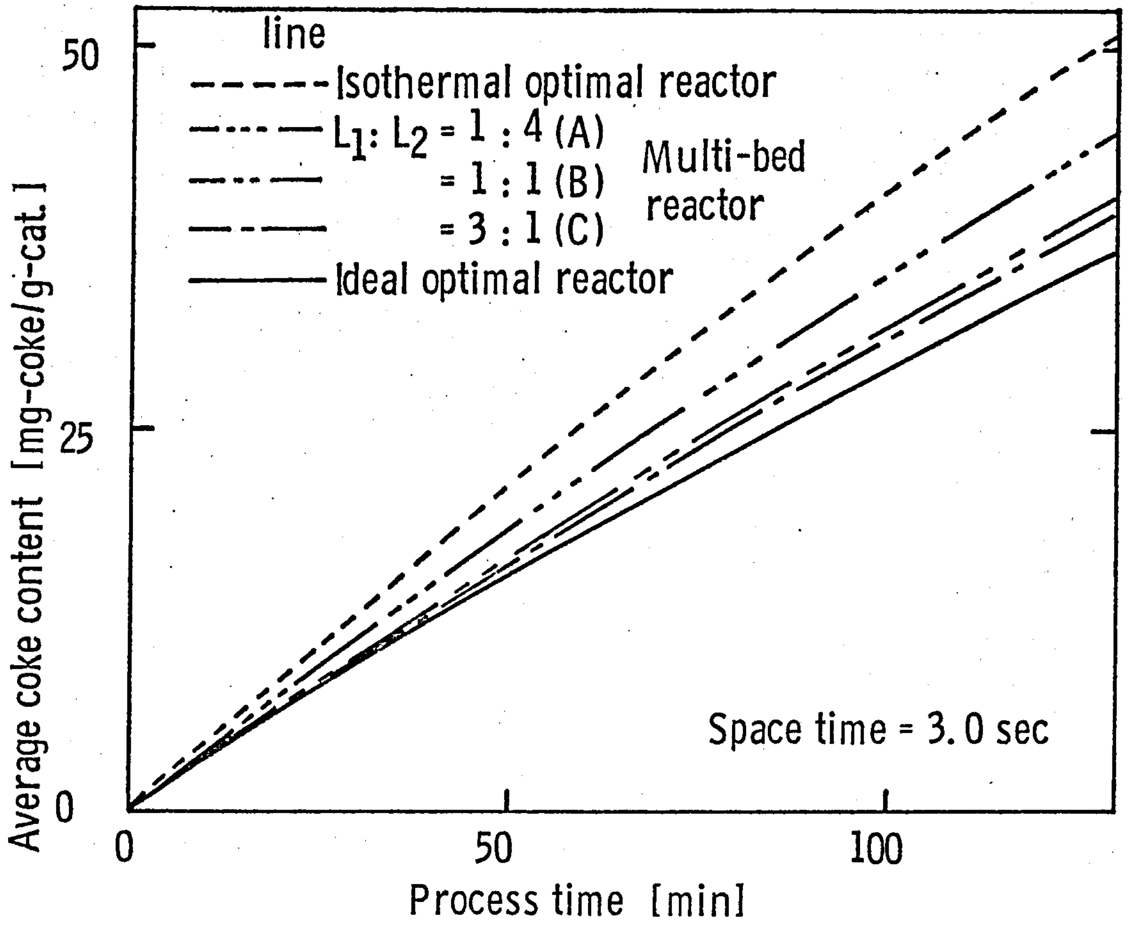


Fig. 9 Comparison of average coke content among three type of the optimal reactors

$$n_c(\theta) = \int_0^{\tau_f} n_c(\tau,\theta)\, d\tau \,/\, \tau_f \qquad (24)$$

The average coke content of the ideal optimal reactor is approximately 20% less than that of isothermal optimal reactor at the end of the process time. The multi-bed reactor (C) is almost equivalent to the ideal optimal reactor in the conversion and the average coke content, though the profiles of the coke content are different from each reactor. The isothermal optimal reactors have a rising temperature history, while the multi-bed reactors do not always have a rising temperature policy.

Conclusion

Using the algorithm the optimal temperature policy was evaluated for three kinds of reactors (ideal optimal reactor, isothermal optimal reactor and multi-bed reactor) in dehydrogenation of isopentane with deactivation by coke deposition, which was represented by a distributed parameter system. The isothermal optimal reactor has a rising temperature history. The ideal optimal reactor has rising temperature profiles in the spatial direction and the temperature at the inlet of the reactor decreases and that at the outlet increases towards the upper temperature limit as the process time proceeds. The multi-bed reactor (C) gave the best conversion of isopentane and the average catalyst activity among three types of the multi-bed reactors. The best yield of isopentenes is given by the ideal optimal reactor at space time 3.0 sec, and the conversion of isopentane is almost constant. Though the profile of the coke content is different between the ideal optimal reactor and the multi-bed reactor, the multi-bed reactor (C) shows little difference in the conversion and the average coke content. The ideal optimal reactor has approximately 20% less average coke content than the isothermal optimal reactor at the end of the process time. One interesting result is that constant conversion appears to be the optimal policy even though this system is much more complicated than the very simple ones in which it can be shown analytically that constant conversion is the best policy.

Notations

f_i = rate of i-th chemical reaction [wt%/sec]

g = rate of coke deposition [mg-coke/g-cat.min]

H = hamiltonian defined by equation (12)

I = objective functional defined by equations(10) and (11)

L = reactor length [cm]

L_i = i-th bed length [cm]

k_i = reaction rate constant [1/sec]

n_{cm} = coke content at a point m from the inlet o of the reactor [mg-coke/g-cat.]

$\bar{n}_c$ = average coke content

p = economic parameter in equation (11) [-]

r_i = rate of i-th chemical reaction [wt%/sec]

r_{nc} = rate of coke deposition [mg-coke/g-cat.min]

T = temperature [°K]

x = state variable [wt%]

Greeks

α_i = decay constant [g-cat./mg-coke]

λ,μ = adjoint variables defined by equations (13)-(16)

ν = conversion factor[mg-coke·g-feed·sec/g-cat.g-component·min]

τ = space time [sec]

ϕ_i = activity factor defined by equation (2)

θ = process time [min]

Subscripts

A = isopentane

B = isopentenes

C = isoprene

m = number of division along the reactor

n_c = coke

f = final

0 = initial

* = limit

Superscripts

\- = average

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Chapter 4

Optimal Operation of a Catalytic Reactor with Catalyst Fouling

Introduction

As shown in a previous chapter, in a catalytic reactor, the selectivity and yield of products usually decrease with catalyst decay2,4-7,14,17,19-21). The kinetics of reaction and the mechanism of deactivation have been investigated for reactor designs and optimal operation. The parameters of reaction models5,6,14,19) and optimal policy3,11,13,18) have been calculated under the assumption (quasi-steady state) that the rate of the decay or coke deposition should be negligible compared with changes of reactant in the reactor. For the optimization problem, simple reaction models have been used for the sake of the calculation, the analytical treatment and so on.

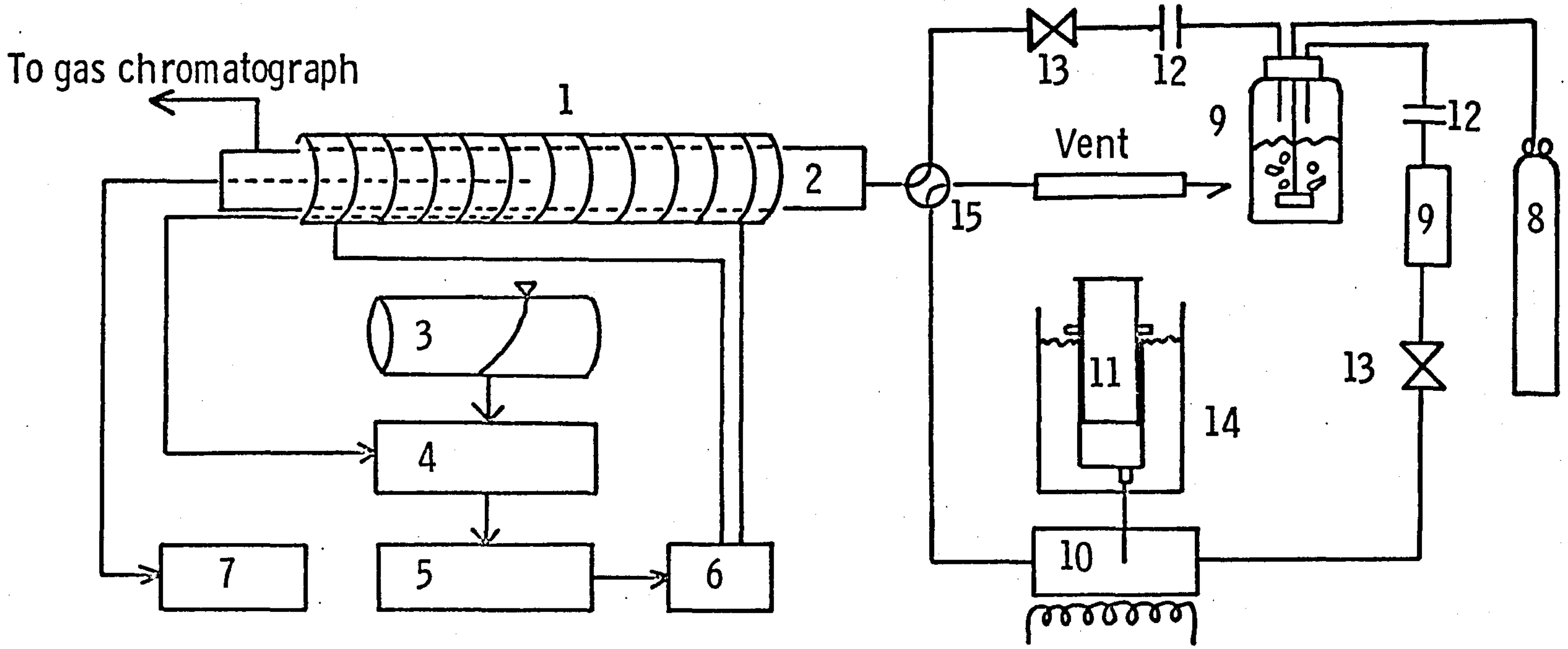
Recently Jackson9), and Ogunye and Ray15,16) derived a distributed maximum principle and presented computational algorithms for an optimal control of decaying reactors using the quasi-steady state assumption. Ogunye and Ray16) also applied their algorithm to a vinyl chloride monomer reactor and solved the problem of the optimal catalyst loading. These studies have mainly been concerned with mathematical models and computer-aid simulation. There were a few investigators1,12) who attempted optimal controls experimentally. Newberger and Kadlec12) have treated the optimal control of the saponification of diethyl adipate by using a multi-bed reactor.

In this chapter, the fouling of the dehydrogenation of isopentane was investigated. The kinetic model proposed was used and the reaction rate constants and decay constants were evaluated under the assumption. By the distributed maximum principle an optimal temperature history of an isothermal reactor with time was studied numerically. By using an isothermal reactor that was manipulated as an evaluated optimal temperature, the reaction of dehydrogenation of isopentane was examined experimentally. The observed conversion and coke content were compared with the evaluated.

1. Experimental

1.1 Dehydrogenation of isopentane

The catalysts were commercial chromia-alumina pellets (N-401A, Nikki Chem. Co.,) whose original size was 5 mmϕ×5 mm. The catalysts were crushed and sieved to 16-32 mesh and were calcined in an air stream at about 550°C for at least 3 hours. A flow diagram of the experimental apparatus is shown in Fig.1. The reactor was made of a stainless steel tube of 11 mm I.D. by 1200 mm long and the detail of the reactor is shown in Fig.2. An electric heater was used for isothermal experiments. As a heating pipe, four porcelain grooved bobbines, I.D. about 30 mm and 250 mm long, which were connected in series by a copper tube O.D. about 30 mm, were used, and on the porcelain bobbin two kanthal wires were wound in parallel at intervals of 3 mm and it was insulated with asbestos. On it another kanthal wire was wound at intervals of 5 mm, and also it was insulated with



1. Heater
2. Reactor
3. Programmer
4. P. I. D. controller
5. SCR unit
6. EFUG
7. Recorder
8. N_2 bomb
9. Dryer
10. Evaporator
11. Micro feeder
12. Flow meter
13. Micro valve
14. Ice bath
15. Four way valve

Fig. 1 Experimental equipment

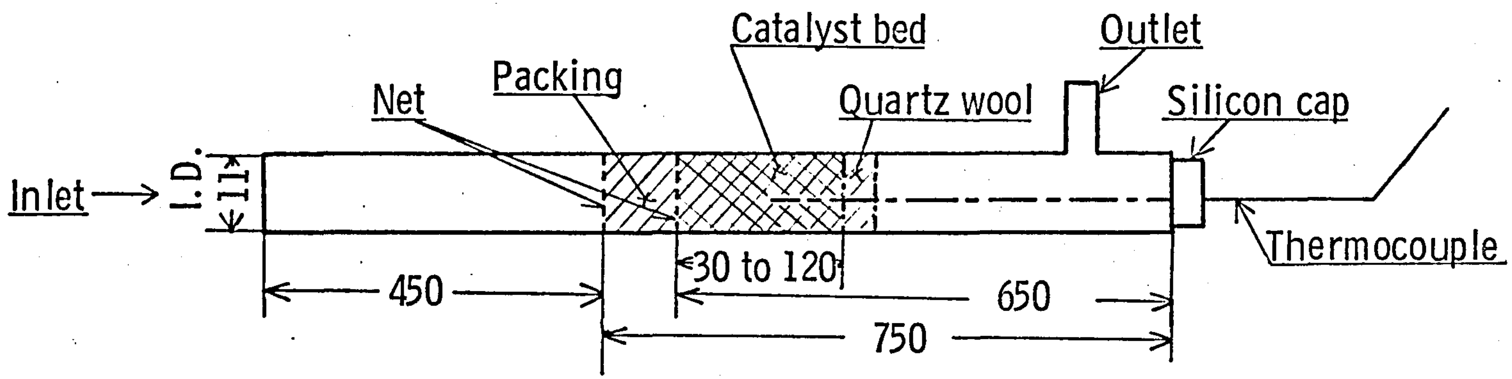


Fig. 2 Details of the reactor

asbestos. The inner wire was for a P.I.D. controller (4031-1166-A84,Yokogawa), and the outer was for a subheater. For the optimal temperature controls a programmer (PGS-2160-T11, Yokogawa) was set on the P.I.D.. An alumel-chromel thermocouple, 1 mm O.D., was positioned along the axis of the reactor to measure the temperature of the catalyst bed and another thermocouple was placed in the heater between the porcelain and the copper tube, these temperatures were recorded continuously. The reactor had a 150 mm long uniform temperature section and was kept at isothermal conditions (± 1°C) by the controller.

The reagent used was ultrapure grade isopentane. When the reactor reached a given temperature, nitrogen gas was replaced by the feed gas of a definite composition of isopentane (0.0014 mole/min) diluted with nitrogen (0.0084 mole/min). A space time was defined by Z/U_G based on the space velocity at 300°K. The total effluent from the reactor was passed through the heated (at about 50°C) gas sampler (HGS-2, Shimadzu) and analyzed on line by a gas chromatograph. The components were isopentane, isopentenes (2-methyl 2-butene, 2-methyl 1-butene, 3-methyl 1-butene) and isoprene and they were separated in a column containing 15 % β-β'-oxydipropionitrile on α-alumina.

1.2 Measurement of coke content

After a specified process time of a reaction run, the catalyst bed was divided into equal sections of about 1.0 g along the reactor. The catalyst of each section was drawn out separately by a vacuum line. The coke deposition on the catalyst was determined in a thermogravimetric balance by burning off the coke with air at about 600°C. An average coke content of the m-th section from the inlet of the reactor was denoted by $\bar{n}_{cm}$. A coke content, n_{cm}, was given as an arithmetic mean of $\bar{n}_{cm-1}$ and $\bar{n}_{cm}$.

1.3 Measurement of axial concentration profiles

As the reactor used was different from that used in the first chapter, at three temperature levels (512, 536, and 560°C), isothermal experiments were done. Typical results for the space times 0.6, 1.2 and 1.8 sec (about 6 g-cat) are shown in Figs. 3-5. Fig. 3. shows that the conversion of isopentane and the yield of isopentenes decrease rapidly and the yield of isoprene falls gradually with process time. The profiles of the conversion, the yields and coke contents along the reactor are shown in Figs. 4 and 5. Figs. 4 and 5 show that the coke contents are distributed along the reactor and the deactivation of the catalyst is not uniform through the reactor, and the reaction rate and the decay constants must be treated as a distributed parameter system.

2. Kinetic model

The effect of the reactor on the conversion and the coke

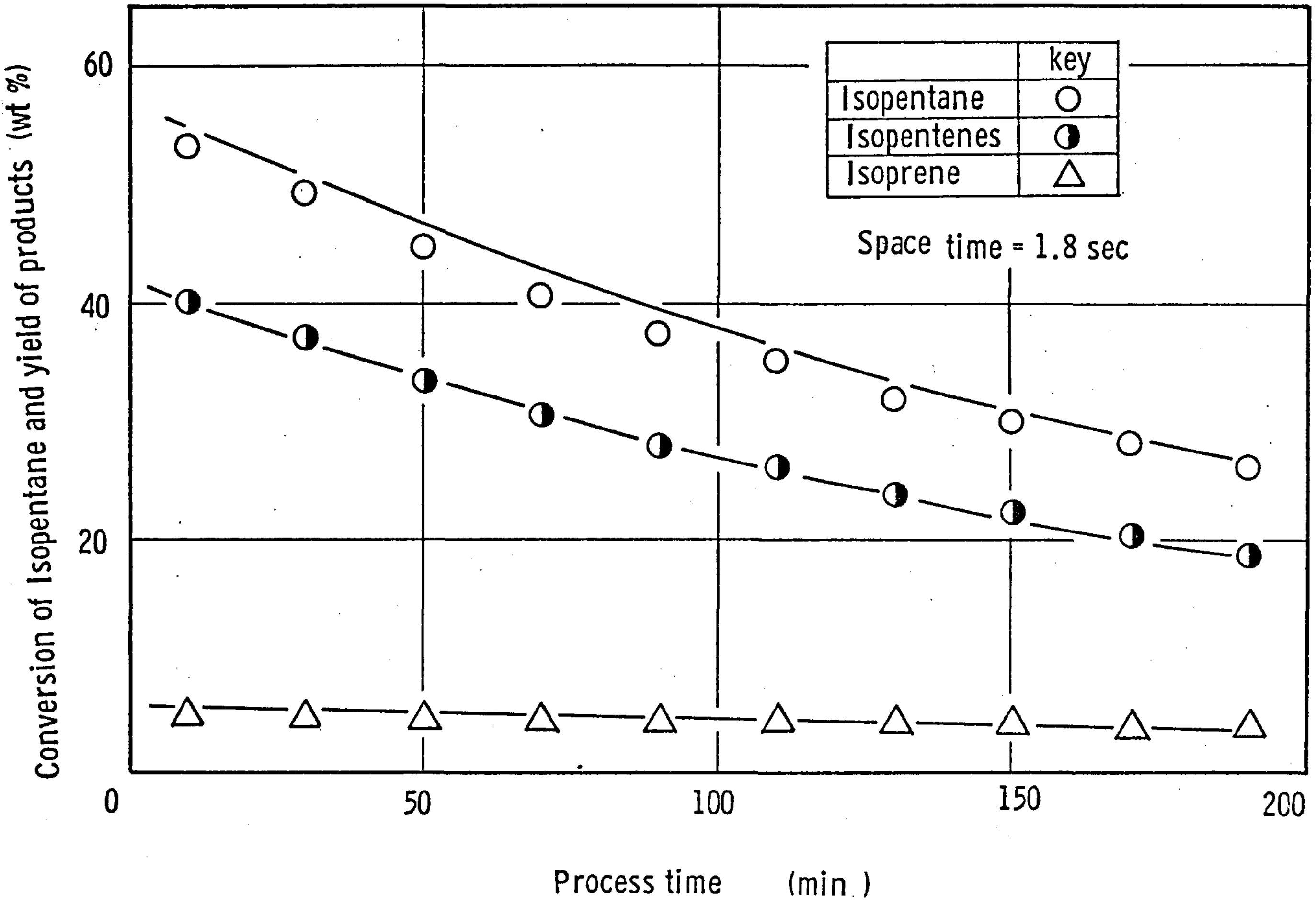


Fig. 3 Typical experimental data (isothermal operation)

Reaction temp.= 536°C

—— Calculated value

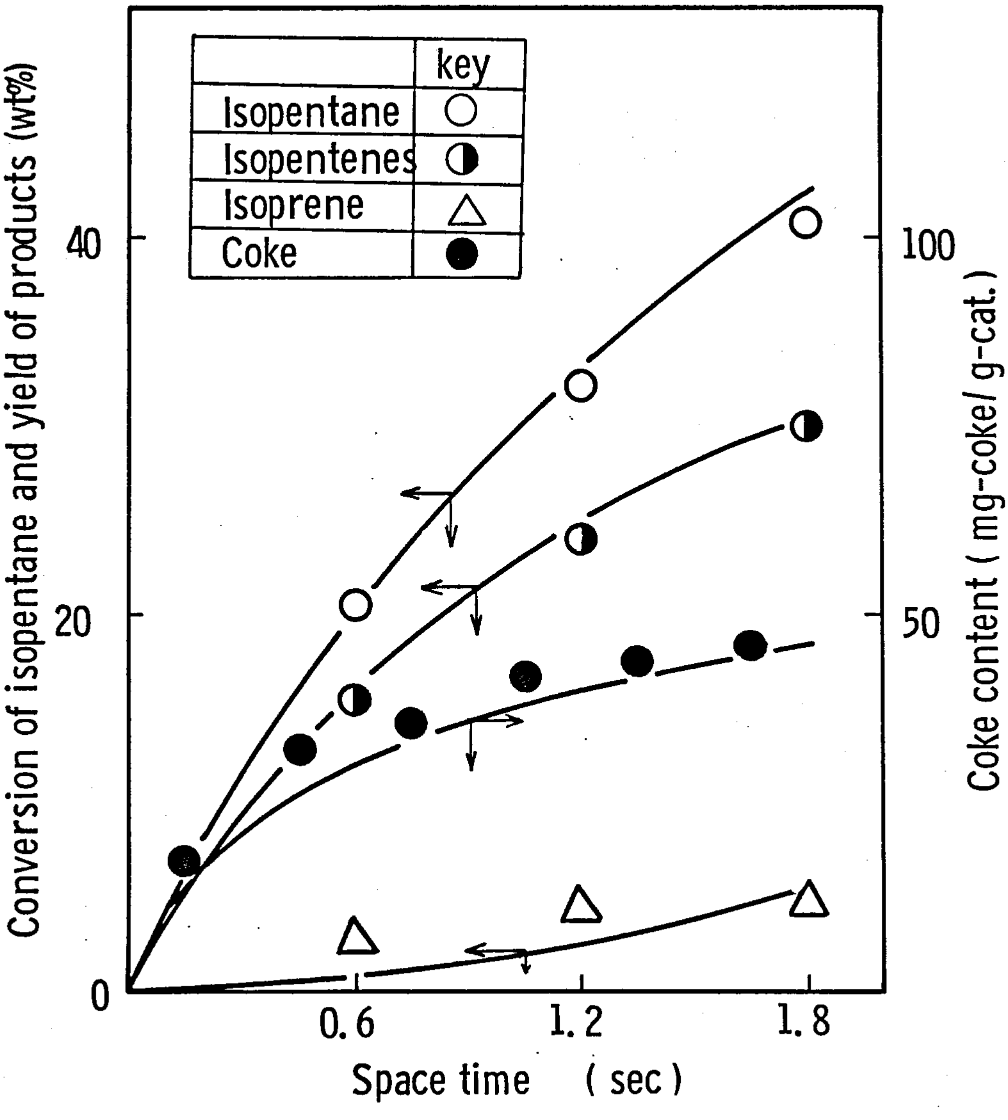


Fig. 4 Profiles of products in the reactor
(isothermal operation)
Reaction temp. = 536°C
Process time = 70 min

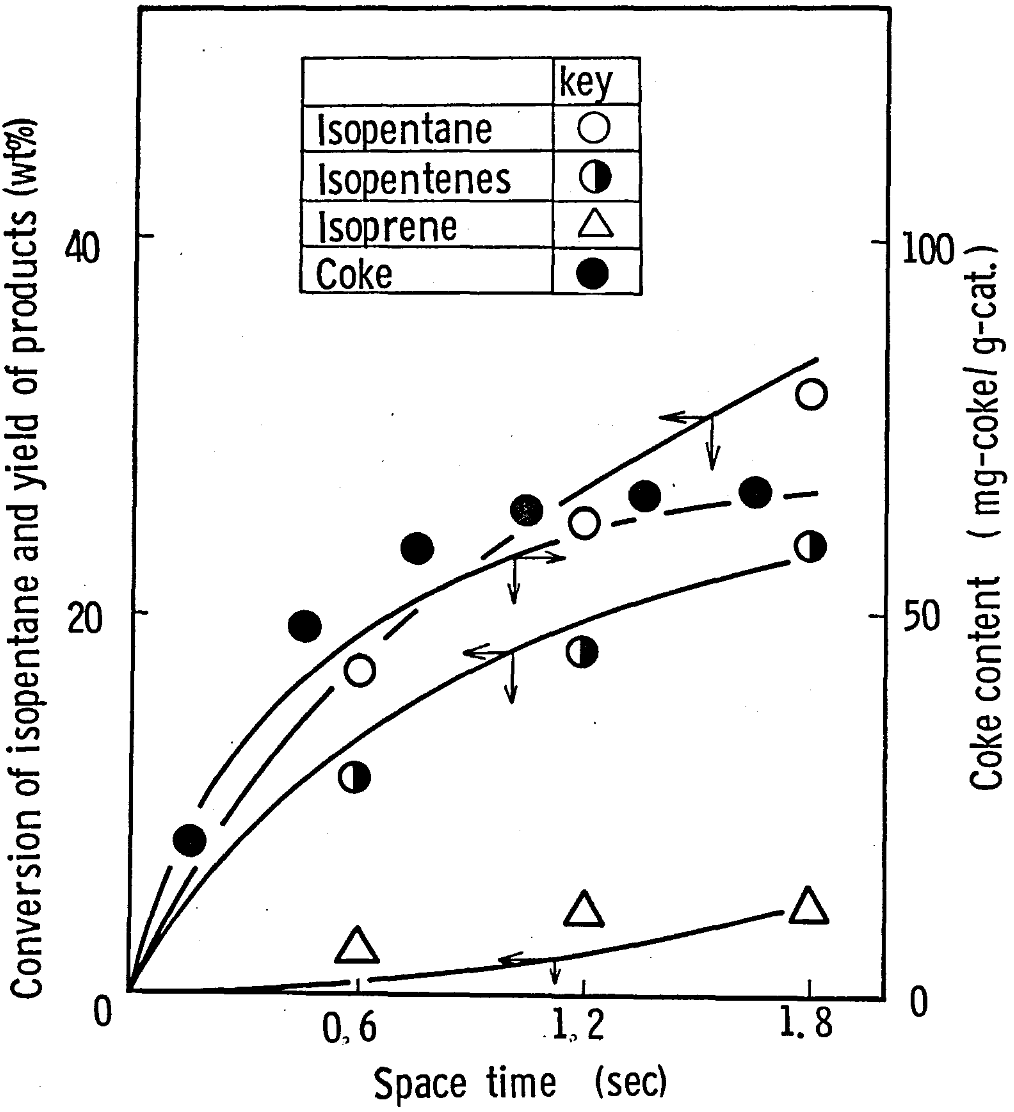
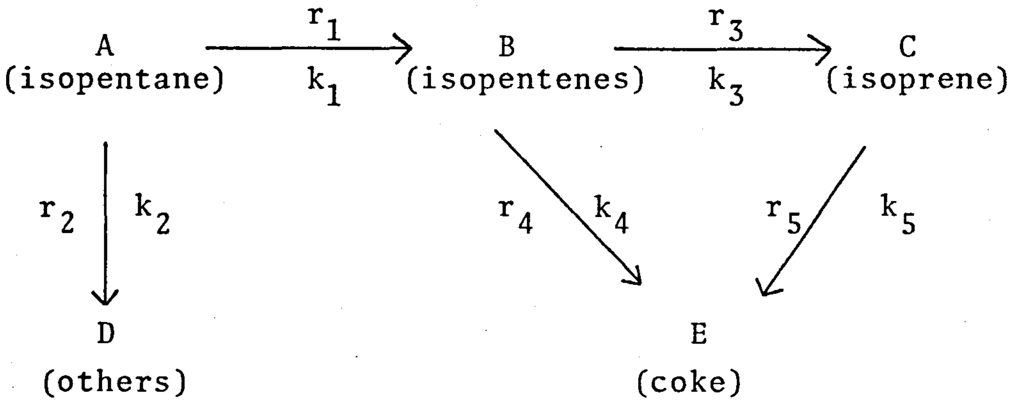


Fig. 5 Profiles of products in the reactor (isothermal operation)
Reaction temp. = 536°C
Process time = 130 min

content was examined using the same kinetic model that was shown in the first chapter.

The dehydrogenation of isopentane with chromia-alumina catalyst was used for this study of the optimal temperature policies with catalyst fouling. The following reaction model had been proposed in the first chapter as follows;



The overall disappearance of isopentane is the sum of individual step 1, 2. Each step is first order in the reactant;

$$r_A = r_1 + r_2 = - (k_1 + k_2) x_A \tag{1}$$

The overall appearance of isopentenes is given as the difference of step 1 and step 3, 4. Each step is also first order reaction;

$$r_B = r_1 - r_3 - r_4 = k_1 x_A - (k_3 + k_4) x_B \tag{2}$$

That of isoprene is given as the difference of step 3 and step 5, that is;

$$r_C = r_3 - r_5 = k_3 x_B - k_5 x_C \tag{3}$$

That of coke formation is expressed in terms of step 4 and 5;

$$r_{n_c} = r_4 + r_5 = k_4 x_B + k_5 x_C \qquad (4)$$

3. Evaluation of reaction rate and decay constants

On the basis of the assumptions that the reactor is in plug flow, and that the intraparticle and interparticle mass and heat transfer is negligible, four coupled continuity equations are derived for the reaction partners.

$$\frac{\partial x_A}{\partial \theta} + U_G \frac{\partial x_A}{\partial z} = r_A \qquad (5)$$

$$\frac{\partial x_B}{\partial \theta} + U_G \frac{\partial x_B}{\partial z} = r_B \qquad (6)$$

$$\frac{\partial x_C}{\partial \theta} + U_G \frac{\partial x_C}{\partial z} = r_C \qquad (7)$$

$$\frac{\partial n_c}{\partial \theta} = \nu r_{n_c} \qquad (8)$$

The fact that the space time scale is much shorter than the process time scale for catalyst decay by the coke deposition suggests the assumption of the quasi-steady state is valid. So that Eqs. (5)-(8) are reduced to the following simultaneous partial differential equations;

$$\frac{\partial x_A}{\partial \tau} = - (k_1 + k_2) x_A = f_1 \qquad (9)$$

$$\frac{\partial x_B}{\partial \tau} = k_1 x_A - (k_3 + k_4) x_B = f_2 \tag{10}$$

$$\frac{\partial x_C}{\partial \tau} = k_3 x_B - k_5 x_C = f_3 \tag{11}$$

$$\frac{\partial n_C}{\partial \theta} = \nu (k_4 x_B + k_5 x_C) = g \tag{12}$$

with boundary conditions;

$$x (0,\theta) = (x_{A0}, x_{B0}, x_{C0})^T , \quad n_c (\tau,0) = n_{co} \tag{13}$$

Eqs.(9)-(12) represent a distributed parameter system, but it is impossible to obtain kinetic parameters directly. For changes of a reaction rate constant, the following relation is used[4,7,21]

$$k_i = k_{io} \phi_i \tag{14}$$

where k_{io} is an initial rate constant at zero coke content and ϕ_i is an activity factor. Several functions for the activity factor have been presented[4,7,17,19]. For the relation between coke content and the rate constants, the following function[14] was postulated,

$$\phi_i = 1 - \alpha_i n_c (\tau,\theta) \tag{15}$$

where α_i is a decay constant and n_c is the local coke content.

Eq.(15) was substituted into Eqs.(9)-(12) and they were numerically integrated by the Runge-Kutta-Gill method taking into account the coke accumulation. A set of best-fit parameters was obtained by minimizing the objective function below,

$$\psi = \sum_{j}\sum_{k}\{\sum_{i}\omega_i(\hat{x}_{ijk} - x_{ijk})^2 + \omega_{n_c}(\hat{n}_{cjk} - n_{cjk})^2\} \quad (16)$$

where $\hat{x}_{ijk}$ and x_{ijk} are the observed and the calculated values of i-th component at space time τ_j and at process time θ_k, and $\hat{n}_{cjk}$ and n_{cjk} are those of coke content then, respectively. And ω_i and ω_{n_c} are weighting factors for i-th component and for coke, respectively. On theoretical grounds these weights should be inverses of the variances of the measurement errors[8)] and in this case suitable values were chosen by a trial and errors method. Evaluated rate and decay constants are shown in Table 1. There are four different α's, so this system is of the selective aging type[2,7)]. The decay constants for the step 3 and 4 were found to be zero.

4. Theoretical treatment of optimal control of the reaction with catalyst decay

4.1 Objective functional

An optimization problem to maximize the total amount of reaction product, isopentenes, and simultaneously to minimize the coke contents that account for the catalyst decay is treated as maximizing I,

Table 1 Reaction rate and decay constants

$k_{10} = \exp(9.95-17{,}400/RT)$	$\alpha_1 = \exp(-14.2+15{,}400/RT)$
$k_{20} = \exp(19.4-35{,}500/RT)$	$\alpha_2 = \exp(-7.95+5{,}300/RT)$
$k_{30} = \exp(9.2-17{,}500/RT)$	$\alpha_3 = 0.0$
$k_{40} = \exp(-13.8+12{,}600/RT)$	$\alpha_4 = 0.0$
$k_{50} = \exp(6.0-10{,}600/RT)$	$\alpha_5 = \exp(-20.0+24{,}400/RT)$

$\phi_i = 1 - \alpha_i n_c$; if $\alpha_i n_c > 1.0$, $\phi_i = 0.0$

$$I = \int_{0}^{\theta_f} x_B(\tau_f, \theta)\, d\theta - p \int_{0}^{\tau_f} n_C(\tau, \theta_f)\, d\tau \qquad (17)$$

where p is an economic parameter that accounts for the catalyst cost, regeneration cost, etc. The optimal control of the temperature, T, which maximizes the objective functional Eq.(17) subject to Eqs.(9)-(12) and boundary condition Eq.(13) according to maximum principles, is treated.

4.2 Maximum principle

A Hamiltonian is defined by the following function;

$$H = \sum_{i} \lambda_i f_i + \mu g \qquad (18)$$

where f_i and g are Eqs.(9)-(12), and λ_i and μ are adjoint variables defined below,

$$\frac{\partial \lambda_A}{\partial \tau} = - \frac{\partial H}{\partial x_A} \qquad (19)$$

$$\frac{\partial \lambda_B}{\partial \tau} = - \frac{\partial H}{\partial x_B} \qquad (20)$$

$$\frac{\partial \lambda_C}{\partial \tau} = - \frac{\partial H}{\partial x_C} \qquad (21)$$

$$\frac{\partial \mu}{\partial \theta} = - \frac{\partial H}{\partial n_C} \qquad (22)$$

Eqs.(19)-(22) have to satisfy the boundary conditions;

$$\begin{aligned} \lambda_A(\tau_f, \theta) &= 0.0 \\ \lambda_B(\tau_f, \theta) &= 1.0 \\ \lambda_C(\tau_f, \theta) &= 0.0 \\ \mu(\tau, \theta_f) &= p \end{aligned} \tag{23}$$

For T to be optimal when T is unconstrained, it is necessary that;

$$\frac{\partial H}{\partial T} = 0 \tag{24}$$

When T is constrained as $T_* \leq T \leq T^*$, it is necessary that Eq.(18) is to be a maximum with respect to T.

4.3 Algorithm for an optimization with fouling by coke deposition

To determine an optimal temperature, it is necessary that the simultaneous partial differential equations (9)-(12) and (19)-(22) may be solved with boundary conditions, (13) and (23), while Eq.(24) is satisfied. In the procedure the coke accumulation had to be taken into consideration and also changes of catalyst activity along the reactor was taken into account. A control vector iteration method proposed in the preceding chapter was chosen that was based on a gradient technique in spatial, z-direction and in temporal, θ-direction based on the extremal technique[10)].

4.4 The results of the theoretical optimal operation

Although the algorithm is applicable to the optimization problem with ideal temperature profile along the reactor and with optimal history in temporal direction, here the calculation of optimal operation of an isothermal catalytic reactor was worked out to enable a comparison of the calculated and the experimental values. For the optimal control of the isothermal reactor, the control variable is a reactor temperature and it only depends on process time. It is necessary to satisfy Eq.(24) through the reactor, but for the isothermal reactor, Eq.(24) will not always be satisfied because the reactor has activity distributions by coke profiles. For a decision of a convergence to optimal, Eq.(24) was modified as follows,

$$\int_0^{\tau_f} \frac{\partial H}{\partial T}\, d\tau = 0.0 \qquad (25)$$

and the reactor temperature has been corrected in the gradient method by the equation below,

$$T(\theta) = T(\theta) + \varepsilon\int_0^{\tau_f} \frac{\partial H}{\partial T(\theta)}\, d\tau \qquad (26)$$

where ε is a step size factor.

The economic parameter p in Eq.(11) was chosen 4.5, 5.5

and 7.5. The final process time θ_f, and the space time τ_f, were chosen 190 min and 1.8 sec, respectively. We supposed that at an initial process time, coke content was zero, $n_c(\tau,0) = 0.0$, that a run was started with new or completely regenerated catalysts, and pure isopentane was supplied from the inlet of the reactor, $x(0,\theta) = (1,0,0)^T$. The upper limit of the reactor temperature was kept at 900°C, because of the experimental conditions. In Figs. 6,7 and 8, the evaluated optimal temperature, the conversion and the yields were shown. The gradients of the temperature slightly increased near the end of the run. As the values of p increase, the conversion, the yields and the coke contents decrease. The changes in the coke contents along the reactor are shown in Fig. 9. The conversion and the yields along the reactor are also shown in Fig. 9.

In the Runge-Kutta-Gill method, the spatial direction was divided into 50 intervals and the time-axis was divided into 36 intervals. To determine an optimal policy required only five iterations in time-axis and it required 15 min on a NEAC 2200/700 (at Osaka Univ. Calculation Center).

5. Optimal operation of experimental reactor

Experiments of the isothermal optimal reactor have been carried out according to the evaluated optimal temperature history.

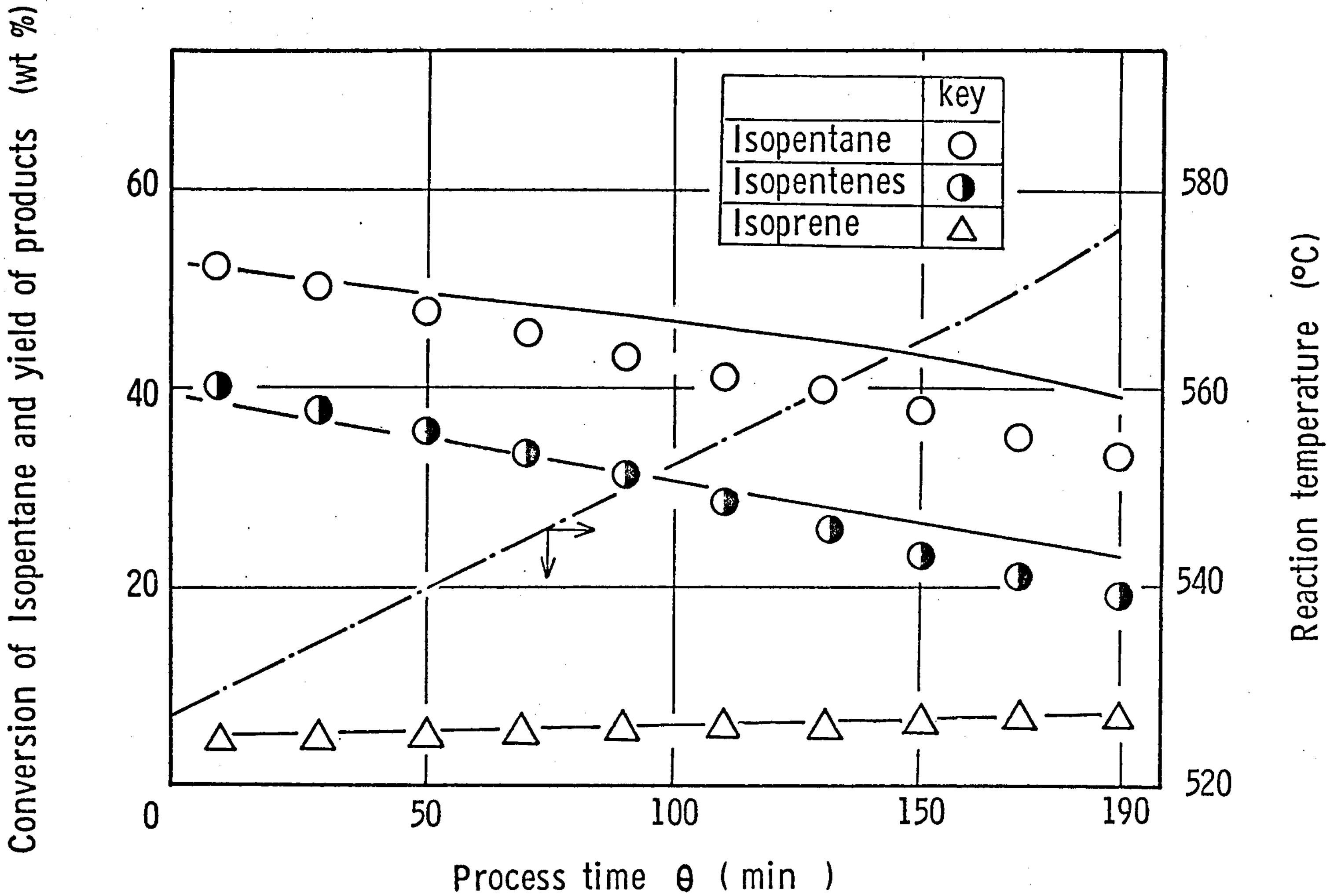


Fig. 6 Typical experimental data (Optimal control)

Space time = 1.8 sec P = 4.5

——— : Calculated value

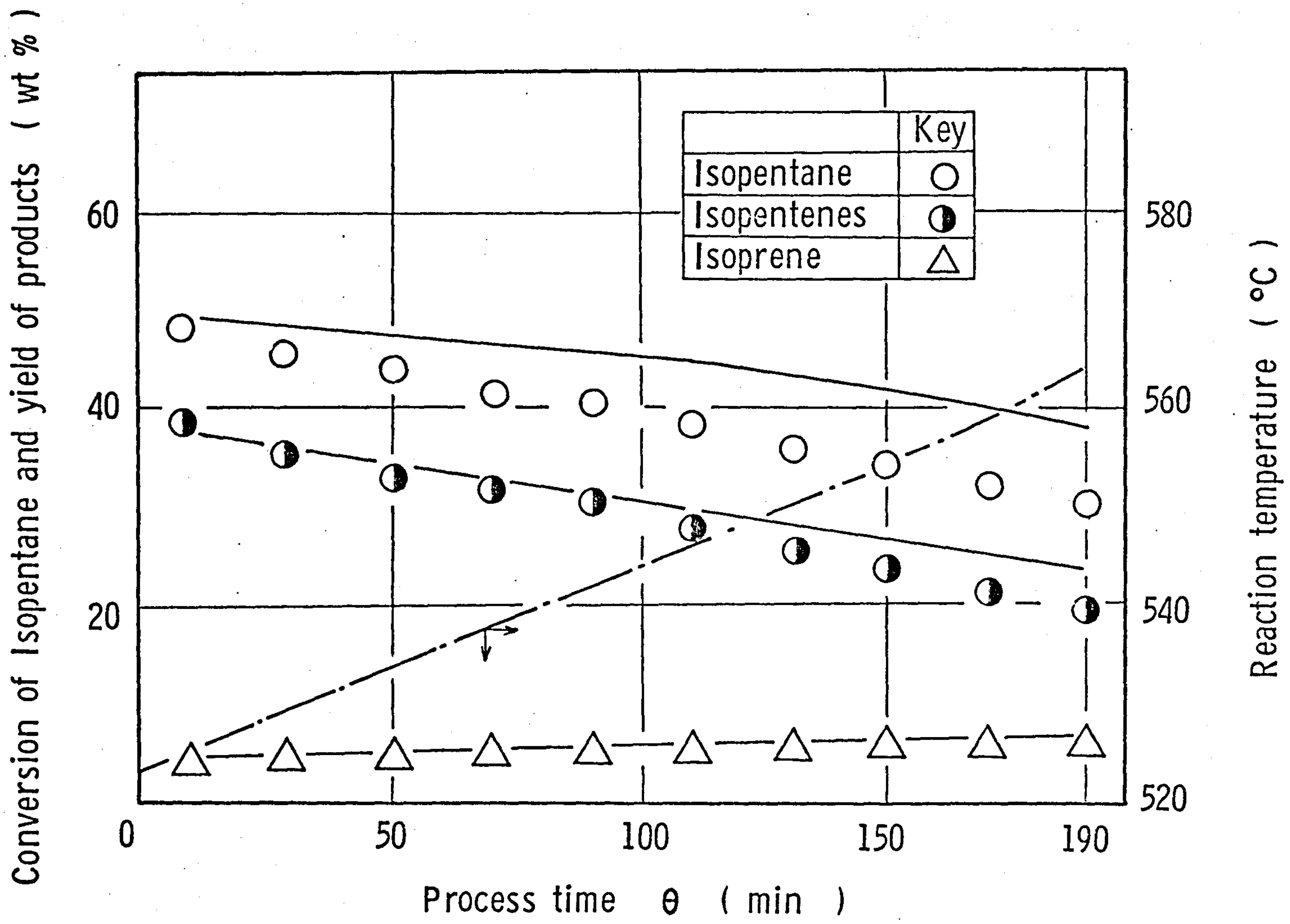


Fig. 7 Typical experimental data (Optimal control)

Space time = 1.8 sec P = 5.5

———— : Calculated value

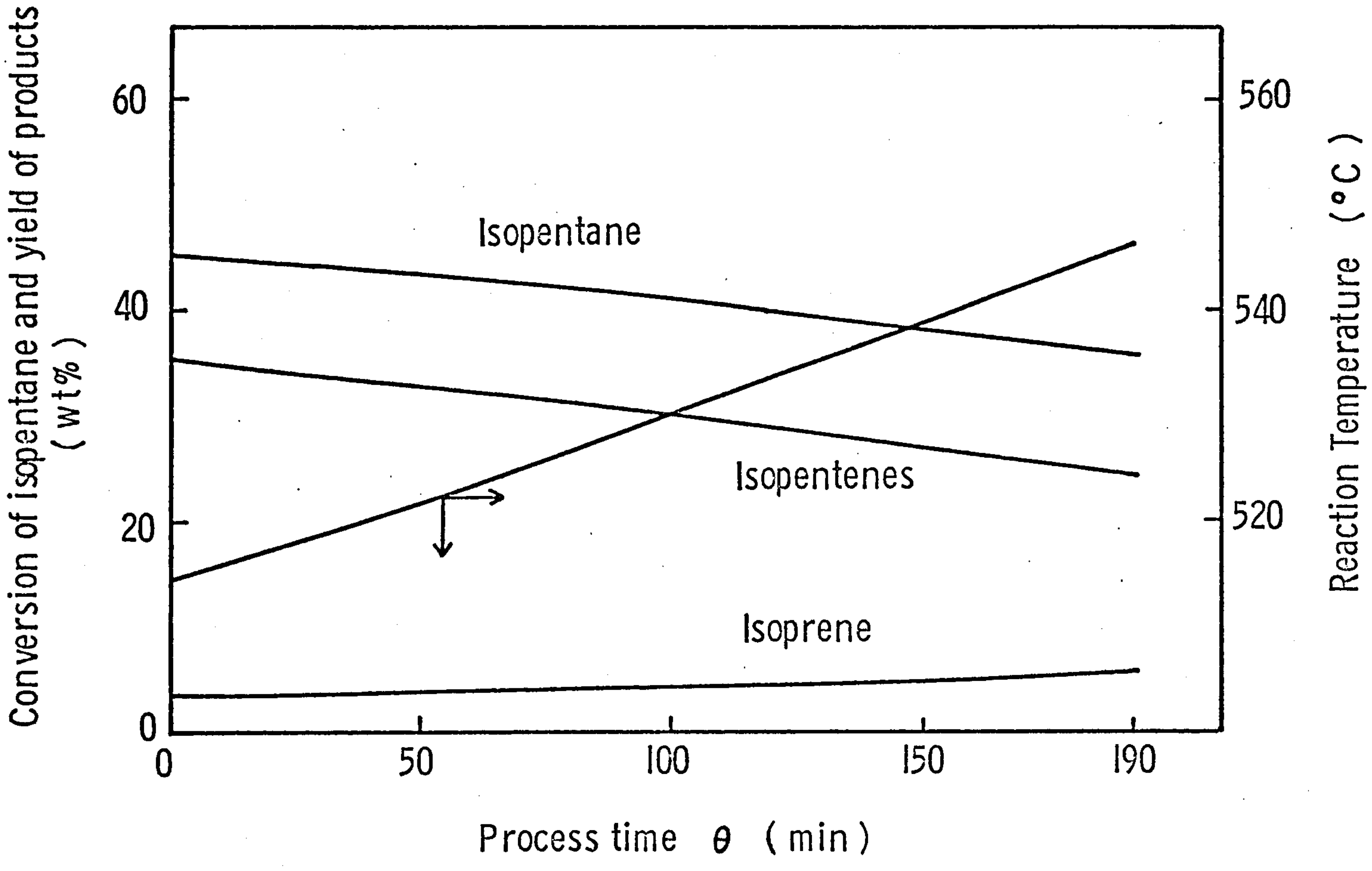


Fig. 8 Optimal control
Space time = 1.8 sec p = 7.5
——— Calculated value

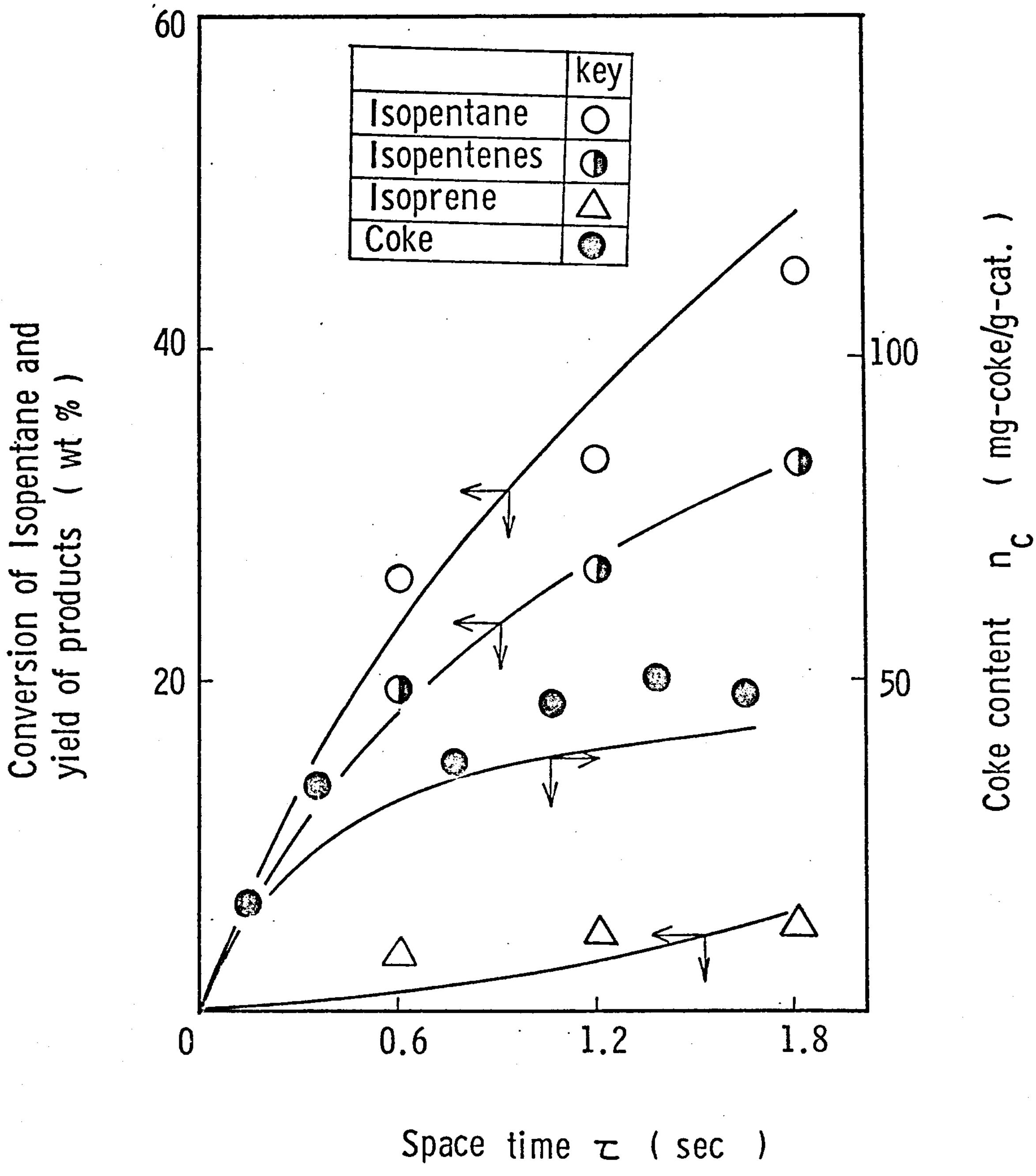
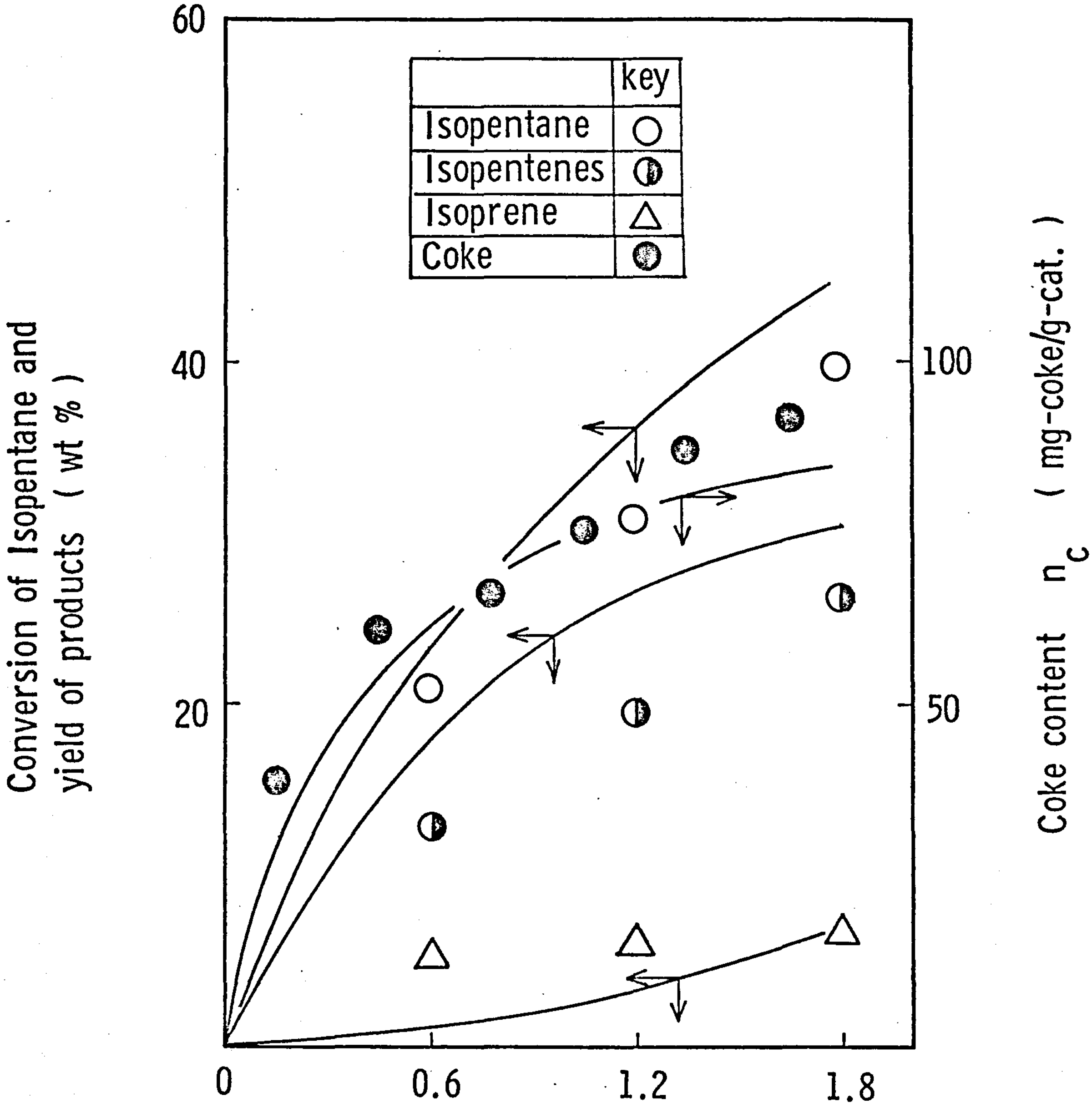


Fig. 9a Profiles of products in a reactor
(Optimal control) p=4.5
Process time = 70 min



Space time τ (sec)

Fig.9b Profiles of products in a reactor (Optimal control) p=4.5

Process time = 130 min

On preliminary experiments differences in the temperature between the heater and the catalyst bed were examined. The calibrated temperature profiles were written on resistance sheets of the programmer. The reactor temperature was manipulated by the programmer controller and was controlled by the P.I.D. within ± 2°C from the optimal. The reaction products were analyzed by the previous method and the observed conversion and the yield of the reactor vs. process times were shown in Figs. 6 and 7, and the profiles of the reactants and the coke contents along the reactor are shown in Fig. 9 at the specified process times.

Some differences were found between the observed and the calculated values near the end of the process time. It was partly owing to fluctuations of the temperature controlled from the optimal profile, and to that the system had a very complicated process of coke deposition.

Conclusions

The dehydrogenation of isopentane was experimentally carried out at three isothermal levels of temperature, and the reaction rate and decay constants were evaluated as a distributed parameter system. The deactivation kinetic was of the selective aging type. From the kinetic model, isothermal optimal policies were obtained numerically by a distributed maximum principle. On the basis of the evaluated optimal policies, the dehydrogenation of isopentane was carried out experimentally. The observed profiles agreed with the calculated ones fairly well. It was verified that the kinetic model obtained from isothermal experiments was useful for predicting unsteady operation and isothermal optimal control policies.

Notation

f_i = rate of i-th chemical reaction [wt%/sec]

g = rate of coke deposition [mg-coke/g-cat.min]

H = hamiltonian defined by equation (18)

I = objective functional defined by equation (17)

k_i = reaction rate constant [1/sec]

$\bar{k}_i$ = lumped reaction rate constant [1/sec]

n_{cm} = coke content at a point m from the inlet of the reactor [mg-coke/g-cat.]

$\bar{n}_c$ = average coke content [mg-coke/g-cat.]

p = economic parameter in equation (17) [-]

r_i = rate of i-th chemical reaction [wt%/sec]

$\hat{r}_{n_c}$ = observed coke deposition rate [mg-coke/g-cat.min]

T = temperature [°K]

x = state variable [wt%]

$\hat{x}$ = observed yield and conversion [wt%]

U_G = linear velocity of reactant [cm/sec]

z = distance along reactor length [cm]

Greek letter

α_i = decay constant [g-cat./mg-coke]

λ μ = adjoint variables defined by equations (19)-(22)

ν = conversion factor [mg-coke g-feed sec/g-cat.g-component min]

τ = space time [sec]

ϕ_i = activity function defined by equation (15)

ψ_i = objective function defined by equation (16)

θ = process time [min]

ω_i = weighting factor [-]

Subscripts

A = isopentane

B = isopentenes

C = isoprene

m = number of division along the reactor

n_c = coke

f = final time

o = initial time

* = limit

Superscripts

\- = average

^ = observed

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Summary

This thesis is carried out to clarify the reaction kinetics and deactivation mechanism of the reaction subject to catalyst decay, and sequently using the results to investigate the problem of the optimal temperature control.

In the first chapter, a reaction kinetics and deactivation mechanism are studied for isopentane dehydrogenation over chromia-alumina catalyst. A kinetic model in which isopentane dehydrogenation takes place in a consecutive reaction (isopentane → isopentenes → isoprene) and coke formation is via both isopentenes and isoprene is proposed on the basis of the experimental results. The catalyst activity is found to be propotional to coke content and the decrease of the kinetic parameter is expressed by a linear function of the point coke content which represents activity profile in the reactor. The kinetic parameters are determined by a non-linear least square method in a distributed parameter system. Applicablity of the reaction kinetic model is confirmed by the comparison of a wide range of experimental results with the calculated values.

In the second chapter, the effects of the intraparticle diffusion on the conversion and coke content in the reactor are investigated using several catalyst sizes. During the reaction coke content in the catalyst pellet increases uniformly. The observed effective diffusivity is found to be a linear function of the point coke content. The apparent diffusivity is determined by minimizing the variences between the observed conver-

sion and the calculated, using a hill climbing method. The difference between the apparent and the observed diffusivity is recognized. Effects of the catalyst size on the conversion and coke content profile in the fixed-bed reactor are explained by the proposed model.

In the third chapter, an algorithm is presented for calculation of optimal policy of the reaction subject to catalyst decay. The problem of the optimal temperature control of the reaction is investigated for three kinds of reactors, that are an isothermal, a non-isothermal and a multi-bed reactors using the kinetic model and the parameters obtained in the first chapter. One interesting result is that constant conversion might be the optimal policy even though this system is much more complicated than the very simple ones in which it can be shown analytically that constant conversion is the best policy.

In the fourth chapter, the optimal operation of the reactor with deactivation is studied experimentally using isopentane dehydrogenation. The optimal isothermal policy for the system is a rising temperature operation with process time i.e., unsteady state operation. The reactor temperature is manipulating as the calculated optimal policy. The observed conversion and coke content in the reactor agree fairly well with the calculated, which concludes that the kinetic model obtained from isothermal experiments is useful for predicting unsteady operation and optimal control policies.

The present results are applicable substantially to any type of catalytic reactor with deactivation.

Publication List

Chapter 1

(1) Kinetics of Isopentane Dehydrogenation on Chromia-Alumina Catalyst with Catalyst Fouling
Noda, H., S. Tone and T. Otake : J. Chem. Eng. Japan, 7, (2) 110 (1974)

Chapter 2

(2) Isopentane Dehydrogenation with Chromia-Alumina Catalyst — Effects of Intraparticle Diffusion on Catalyst Fouling—
Noda, H., M. Ozaki, S. Tone and T. Otake : Bull. Japan Petrol. Inst., 17, (1975) (in press)

Chapter 3

(3) Optimal Controls of Catalytic Tubular Reactors with Catalyst Deactivation by Coke Deposition — Applied to Isopentane Dehydrogenation —
Noda, H., S. Tone and T. Otake : J. Chem. Eng. Japan (submitted)

Chapter 4

(4) Optimal Operation of a Catalytic Tubular Reactor with Fouling Catalyst by Coke Deposition
Noda, H., S. Kanehara, S. Tone and T. Otake : Chem. Eng. Sci., (in press)