Thermal Reactions of Toluene by Use of a Clusius-Dickel Type Thermal Diffusion Column as a Reactor

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Thermal reactions of toluene were investigated in the temperature range from 1290 to 1410 K under atmospheric pressure in a Clusius–Dickel type thermal diffusion column. The main product of the reaction was benzene, the selectivity of which increased with the rise of reaction temperature, reaching over 50% under most of the reaction conditions studied. The reactions of toluene were characterized by two features; the high selectivity of benzene, and a remarkable change in the selectivity of benzene and bibenzyl with the change of toluene conversion. These two features should be attributable to the thermal diffusion and convection, which caused the hydrogen evolved during the reaction to concentrate around the heater, and subjected toluene to hydrogenolysis without adding hydrogen as a reactant. The experimental results with regard to the change in benzene selectivity can be explained qualitatively by the theories developed for the separation column.

Half a century ago, Clusius and Dickel invented a powerful separation column based on thermal diffusion and thermal convection.1) A few years later, Hirota applied this separation column for the formation of oily aromatic hydrocarbons and hydrogen from methane.2–4) His success in getting the oil in a high yield could be accounted for by the prevention of the recombination reaction by the instant separation of produced hydrogen from hydrocarbon residues owing to thermal diffusion effect caused by the temperature gradient. However, his works, which ought to be regarded as one of the earliest examples of application of a thermal diffusion column as a reactor, had been left unnoticed until very recently. Studies in the field of chemical engineering have centered on the Clusius–Dickel type diffusion column as a separator with regard to the effect of such important factors on separation as 1) the diameter of a column, 2) the length of a column, 3) the temperature difference between the heater and the cold wall of a column, 4) flow rate, and 5) the composition of a mixture. However, almost no attention had been paid to the diffusion column as a reactor until Yamaguchi (one of the authors) re-examined and modified Hirota's process in 1988, confirming the conversion of methane to C_2 compounds.5)

The thermal reactions of simple aromatic hydrocarbons in a temperature gradient system have been investigated in this laboratory.6–9) In the previous paper,8) we reported the formation of bibenzyl in a high selectivity by the dehydrogenative coupling of toluene in a reactor (so called a batch type reactor) which had a significant temperature gradient. The present paper deals with the thermal reactions of toluene in another type of reactor with a temperature gradient, i.e. a Clusius–Dickel type thermal diffusion column, and discusses the results from the viewpoint of the diameter of the column and the flow rate.

Experimental

The reactor used in this experiment, usually referred to as a Clusius–Dickel type thermal diffusion column, is schematically shown in Fig. 1. In brief, the reactor consists of a Pyrex glass-made Liebig condenser (60 cm in length, and 10, 20, 30, or 50 mm in inner diameter) and a heater made of a nickel chromium steel wire (42 cm in length and 1.0 mm in diameter) mounted at the axis of the condenser. The inlet of toluene were placed at the level 2 cm lower from the top of the heater. The reactions were carried out under atmospheric pressure, in the temperature range from 1290 to 1410 K. The air in the reactor was first replaced by nitrogen and cooling water was supplied. The power of the heater was then turned on. The temperature of the heater was measured by a radiation pyrometer (Minolta IR-120) and set at a desired reaction temperature before the toluene feeding. Toluene was charged downward parallel to the heater at a constant rate, and the

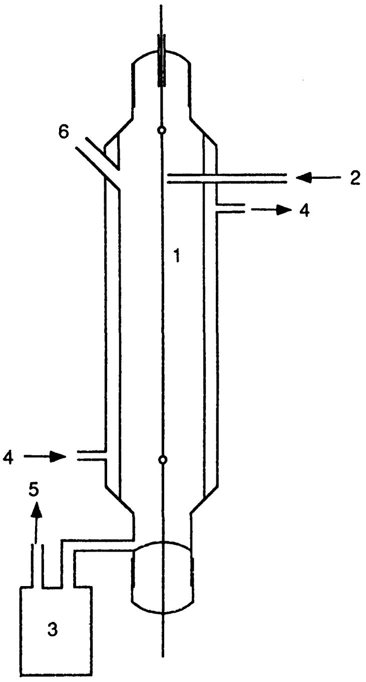

Fig. 1. Clusius–Dickel type thermal diffusion column. 1: Heater, 2: Toluene, 3: Liquid products, 4: Cooling water, 5: Gaseous products, 6: Closed.

surface temperature of the heater was adjusted to the desired temperature. During the reaction the heater was kept at the temperature by controlling the voltage and the currency of the electric current. The duration was usually 2 h. The reaction products were identified by GC-MS and GC-IR analysis by using authentic samples. Liquid products were sampled every 30 min and analyzed by gas chromatography. The result of the sample for the last 30 min was usually employed for each run. Resulting gaseous products during the duration were also collected for gas chromatographic analysis.

Results and Discussion

Reaction Products. Table 1 lists some of the results of the thermal reactions of toluene in a Clusius–Dickel type thermal diffusion column of 20 mm in diameter. The main product of the reaction was benzene, the selectivity of which increased with the rise of reaction temperature, reaching over 50% under most of the reaction conditions studied. Other major products were compounds which have one benzene ring such as ethylbenzene, xylenes, styrene, indan, and indene. Two ring aromatic compounds including biphenyls, diphenyl methanes, and bibenzyl were also produced in fairly large selectivities. Although benzene was obtained in a large selectivity, very little amount of carbon was deposited either on the surface of the heater or of the reactor. This is one of the advantages with a temperature gradient reactor.[5,6]

The thermal reactions of toluene in the diffusion column was characterized by the high selectivity of benzene of more than 50% and the low selectivity of bibenzyl of below 5% in most of the reactions when the conversion of toluene was large. This is in contrast to the result of the pyrolysis of toluene carried out at 970 K in a conventional tubular reactor, in which the selectivity of benzene and bibenzyl was 39 and 15%, respectively, when toluene conversion was as much as 6.5%.[11]

Another characteristics of the reaction was a remarkable change in the selectivity of benzene and bibenzyl with the conversion of toluene. High conversion of toluene resulted in the high benzene selectivity, and the low bibenzyl selectivity. On the other hand, the benzene selectivity declined and the bibenzyl selectivity increased as the toluene conversion decreased.

The formation of the major reaction products can be explained in the following manner. The $C_6H_5CH_2$–H bond has a bond dissociation energy of 355 kJ mol^{-1}, while that for the C_6H_5–CH_3 bond is 397 kJ mol^{-1}. For the aromatic carbon–hydrogen bond, the bond dissociation energy is approximately 440 kJ mol^{-1}. It has been well established that the fission of a carbon–hydrogen bond of the methyl group of toluene, the bond dissociation energy of which is the lowest of the three, is relatively easy to give atomic hydrogen and benzyl radical. The major elementary reactions involved in the thermal reactions of toluene are expressed by equa-

Table 1. The Thermal Reactions of Toluene in a Clusius–Dickel Type Thermal Diffusion Column (Diameter: 20 mm)

Reaction temperature/K	1390	1310	1340	1370	1390	1390	1390
Flow rate/mol h^{-1}	0.05	0.10	0.10	0.10	0.10	0.20	0.30
Conversion/%	22.0	1.0	2.4	7.2	11.1	5.0	2.8
Weight selectivity of liquid products/%							
Benzene	46.6	29.0	42.0	50.7	53.9	53.9	54.5
Ethylbenzene	4.2	8.0	7.8	7.3	4.5	6.3	7.3
Xylenes	3.9	5.3	6.4	5.9	4.6	5.8	6.0
Styrene	6.6	Tr[a]	3.8	6.6	6.6	6.5	6.2
Indan	1.2	0.5	0.5	1.4	1.4	1.4	1.2
Indene	4.7	1.5	1.6	4.1	5.3	4.6	4.0
Naphthalene	2.7	Tr	Tr	1.4	2.5	2.1	1.5
Biphenyl	2.5	0.2	0.5	1.1	1.5	1.0	0.7
Methylbiphenyls	5.1	0.9	3.2	3.2	3.4	3.1	3.0
Dimethylbiphenyls	6.1	5.1	6.0	3.6	3.6	1.8	3.3
Diphenylmethane	1.7	1.3	1.6	1.2	1.4	0.9	1.1
Phenyltolylmethanes	1.9	5.4	5.1	2.7	2.8	2.1	2.7
Bibenzyl	2.4	41.9	18.3	3.8	1.6	2.5	3.6
Stilbene	0.3	Tr	0.2	0.3	0.2	0.3	0.3
Phenanthrene	1.0	Tr	0.5	0.6	0.7	0.8	0.7
Anthracene	0.8	Tr	0.4	0.4	0.6	0.6	0.6
Others	8.3	0.9	2.1	5.7	5.4	6.3	3.3
Yield of gaseous product/ml h^{-1}	—[b]	12	29	91	142	—	—
Composition of gaseous product/mol%							
H_2	—	55.4	35.0	24.3	18.2	—	—
CH_4	—	43.6	63.3	73.4	79.2	—	—
Others	—	1.0	1.6	2.3	2.6	—	—

a) Trace. b) Not measured.

tions 1 to 6,[10] although there is still some controversy as to the details.

$$C_6H_5CH_3 \rightleftarrows C_6H_5CH_2\cdot + H\cdot \quad (1)$$

$$H\cdot + C_6H_5CH_3 \rightleftarrows H_2 + C_6H_5CH_2\cdot \quad (2)$$

$$H\cdot + C_6H_5CH_3 \rightleftarrows C_6H_6 + CH_3\cdot \quad (3)$$

$$CH_3\cdot + H_2 \rightarrow CH_4 + H\cdot \quad (4)$$

$$CH_3\cdot + C_6H_5CH_3 \rightleftarrows CH_4 + C_6H_5CH_2\cdot \quad (5)$$

$$2\,C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2CH_2C_6H_5 \quad (6)$$

Thermal diffusion does not afford special reactions. It is effective only in the separation of the components, changing the ratio of each elementary reaction. Therefore, the formation of benzene and bibenzyl can be accounted for by these equations in a thermal diffusion column as well as in a reactor without a significant temperature gradient. However, radicals formed by fission of the C_6H_5–CH_3 bond and an aromatic carbon–hydrogen bond should also be taken into account, especially in the reactions in this paper which were carried out at relatively high temperatures. The importance of these radicals is proposed by some researchers.[11,12] The most of the reaction products which have two benzene rings can be accounted for by these radicals and benzyl radical.

Gaseous products comprised mainly methane and hydrogen with a small amount of ethane, ethylene, Propane, and butanes. The selectivity of methane was more than 60% of the gaseous products for the most runs. These results contrasted sharply with those of the conventional fast flow pyrolysis in which methane occupied about 40% of the gaseous products.[13] These results were also inconsistent with those of our previous work in a batch type reactor with a temperature gradient, in which the methane selectivity of about 40% was obtained.[8] The high selectivity of methane and benzene suggests that the hydrogenolysis occurs in the thermal reaction of toluene in a diffusion column.

The Effect of Thermal Diffusion and Convection. The thermal reactions of toluene in a diffusion column are characterized by the high selectivity of benzene in the reactions with the high conversion of toluene. Another characteristics of the reaction is a remarkable change in the selectivity of benzene and bibenzyl.

These two features should be attributable to the thermal diffusion and convection. Thermal diffusion arises when a mixture is subjected to a temperature gradient making the partial separation of the components, promoted by convection synergistically. In this process, the component of low molecular weight concentrates in the hot region. The major factors in this process are 1) the diameter of a column, 2) the length of a column, 3) the temperature difference between the heater and the cold wall of a column, and 4) the flow rate of a mixture. In the thermal diffusion reactor of our experiment, molecular hydrogen or atomic hydrogen, evolved in the course of reactions, are separated and concentrated on the surface of the heater due to thermal diffusion effect. This process is further accelerated by convection. They could retard the formation of benzyl radical (Eq. 2), and promote the production of benzene by hydrogenolysis of toluene (Eq. 3), resulting in the high selectivity of benzene and low selectivity of bibenzyl. In other words, in the thermal diffusion column, toluene appears to have undergone hydrogenolysis due to the concentration of hydrogen, without supplying hydrogen as a reactant. Therefore, the selectivity of benzene is an indicator of hydrogenolysis of toluene and the degree of hydrogen concentration on the surface of the heater. Accordingly, it can be said basically that the higher is the toluene conversion, the more is the hydrogen formation with the higher selectivity of benzene. On the other hand, when the toluene conversion is low, hydrogen is not produced enough to carry out hydrogenolysis of toluene and benzyl radicals give bibenzyl by combination reaction (Eq. 6). The analysis of the gaseous products also supports the consumption of hydrogen and the formation of methane. Furthermore, when toluene was charged with hydrogen (feed rate of hydrogen was 0.04 mol h^{-1}) to the same reactor of 20mm in diameter at the rate of 0.1 mol h^{-1} at 1300 K, the selectivity of benzene was as high as 98% even with the low toluene conversion of 1.8%. This increase in benzene selectivity by the addition of hydrogen can explain the role of hydrogen in the thermal reactions of toluene in the separation column.

The Influence of Major Reaction Factors. Temperature: The influence of temperature on the toluene conversion, benzene selectivity and bibenzyl selectivity is

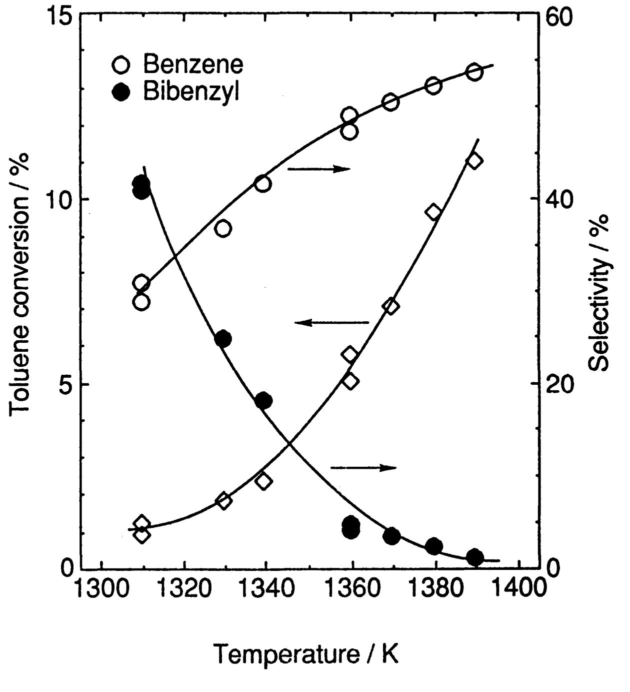

Fig. 2. The influence of temperature on the toluene conversion, and bibenzyl and benzene selectivities. Feed rate: 0.10 mol h^{-1}, Inner diameter: 20 mm.

shown in Fig. 2 for the reactor with 20 mm diameter. The rise of reaction temperature resulted in an increased toluene conversion accompanied by the increase in benzene selectivity and the decrease in bibenzyl selectivity. The change in selectivity of the two products was remarkable. The same tendency was observed for other thermal diffusion columns with an inner diameter of 10, 30, or 50 mm.

Thermal diffusion and convection should be mainly responsible for the remarkable change in the selectivity of benzene and bibenzyl with the temperature. The rise in reaction temperature brings about increasing toluene conversion, resulting in more production of hydrogen, which is concentrated on the heater by thermal diffusion and convection to be consumed for hydrogenolysis of toluene.

Flow Rate: The influence of the feed rate on the bibenzyl and benzene selectivities (reaction temperature 1390 K) is shown in Fig. 3 for the thermal diffusion column with an inner diameter of 20 mm. The toluene conversion at a constant temperature is proportional to the reciprocal of the feed rate for the same reactor. The selectivity of benzene was almost constant regardless of the feed rate except for the rate of 0.05 mol h^{-1}. These results can be explained in the following manner. According to Clusius and Dickel,[1)] the velocity of convection and that of thermal diffusion must be balanced appropriately to carry out the separation effectively. If the former is much larger than the latter, the mixture is disturbed before reaching satisfactory separation by thermal diffusion. On the other hand, if the former is far smaller than the latter, the fully separated mixture by thermal diffusion is reversed by ordinary diffusion due to concentration gradient. If the column length is constant, the convection velocity should be primarily affected by the flow rate. Therefore, the flow rate must be set in a certain range to make suitable convection which accelerates the separation. Unlike a diffusion column in which only separation is made, the method has not been established yet to calculate a suitable range of flow rate specifically in a diffusion column in which chemical reactions occur. In spite of this difficulty, it can be said that the flow rate of 0.05 mol h^{-1} is not enough for convection compared with other flow rates.

Inner Diameter of Column: The relationship between the toluene conversion and the selectivity of benzene is shown in Fig 4. The selectivity of benzene increased with the raise of toluene conversion for any diffusion column. However, the selectivity of benzene at the same conversion was increased in accordance with the column diameter in the following order; 20 mm<30 mm<50 mm<10 mm. Clusius and Dickel suggested from the separation of nitrogen and oxygen in the air that the equilibrium concentration after the separation is reversely proportional to the fourth power of the diameter.[1)] They further proposed the minimum diameter of 0.8 cm for the separation of nitrogen and oxygen to be carried out effectively from theoretical studies using the diffusion equation.[1)] Here again, it is difficult to calculate actually the minimum diameter for the thermal reactions of toluene in a diffusion column, because no chemical engineering methods have been established to calculate the dimensions of a diffusion

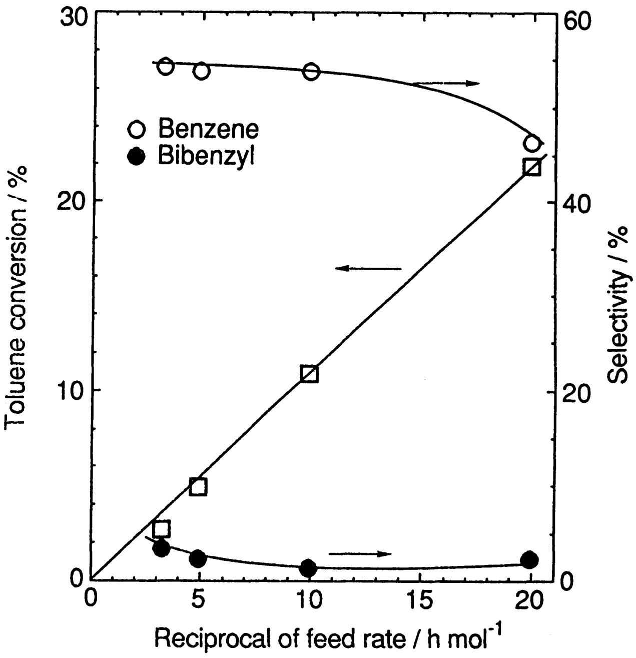

Fig. 3. The influence of feed rate on the toluene conversion, and bibenzyl and benzene selectivities. Temperature: 1390 K, Inner diameter: 20 mm.

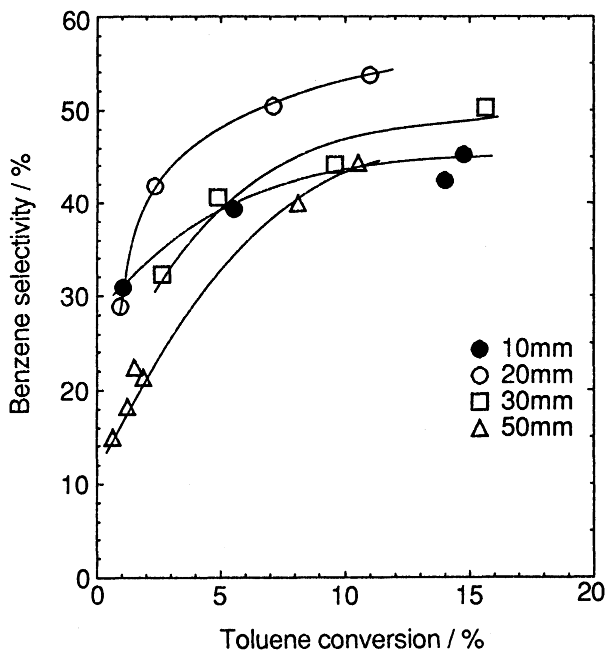

Fig. 4. The influence of inner diameter of a diffusion column. Feed rate: 0.10 mol h^{-1}.

column in which chemical reactions are carried out. However, these explanations support that the minimum diameter should also exist for the thermal reactions of toluene, and the selectivity of benzene, which was an indicator of the hydrogen concentration in the hot region, varied in the order mentioned above.

Conclusions

Thermal reactions of toluene in a Clusius–Dickel type thermal diffusion column were characterized by two features; the high selectivity of benzene which increased with the rise of reaction temperature, reaching over 50% under most of the reaction conditions, and a remarkable change in the selectivity of benzene and bibenzyl with the toluene conversion. These two features should be attributable to the thermal diffusion and convection, which caused the hydrogen evolved in the reaction to concentrate around the heater, and subjected toluene to hydrogenolysis without adding hydrogen as a reactant. Although the theories, which handle thermal diffusion in a column accompanied by chemical reactions, have not yet been established, the experimental results can be explained qualitatively by the theories developed for the separation column.

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