

# Recovery of Indan Derivatives from Polystyrene Waste

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## Synopsis

The recovery of indan derivatives from polystyrene waste for the purpose of efficient utilization of plastic wastes was studied. An attempt was made to construct the apparatus, in which thermal decomposition of polystyrene and catalytic reaction of its decomposition products over silica-alumina catalyst could be controlled continuously at the same time. The reaction temperature for thermal decomposition of polystyrene in the upper part of a reactor tube was 420°C, while that for catalytic reaction of the thermal decomposition products in the bottom of a reactor tube was 300°C. These results indicated that the composition of thermal decomposition products of polystyrene could be controlled by the use of a flow reactor. The indan derivatives recovered were two 1-methyl-3-phenylindans, one 1-methyl-1-phenylindan, and 1-phenylindan. The yields of these indan derivatives were 20% of the weight of the liquid products recovered. On the basis of the results obtained in the present work, the most suitable reaction conditions to recover indan derivatives from polystyrene waste is discussed.

## INTRODUCTION

Although numerous studies on thermal decomposition of polystyrene have been reported,<sup>1</sup> the study to keep the composition of decomposition products of polystyrene under control has not been carried out yet. If practical problems for efficient utilization of plastic wastes were not evolved, it is doubtful that the investigation keeping the composition of products obtained from pyrolysis of polymers under control would be necessary. The pyrolysis of plastic wastes containing polystyrene has so far been carried out for recovering fuel oils. However, since the economical utility value of fuel oils recovered from pyrolysis of plastic wastes is low, attempts to apply this pyrolysis practically have been unsuccessful.<sup>2,3</sup> Thus, the products recovered from pyrolysis of plastic wastes should be reused maximally. Further, it would be more important to increase the utility value of the products.

In the present study, an attempt was made to construct the apparatus, in which thermal decomposition of polystyrene and the catalytic reaction of its decomposition products over silica-alumina catalyst could be controlled continuously at the same time in order to recover indan derivatives from polystyrene. Though the products obtained from pyrolysis of polystyrene usually consist of a monomer (styrene), a dimer (2,4-diphenyl-1-butene), a trimer (2,4,6-triphenyl-1-hexene), waxlike compounds (4–10 monomer units), and degraded polystyrene (30–80 monomer units),<sup>4</sup> we require the products consisting of only monomer and dimer because the indan derivatives are formed from monomer and dimer in the presence of acid catalysts.<sup>5,6</sup> Therefore, it is the most important to keep the

composition of products obtained from pyrolysis of polystyrene under control. Trimer, waxlike compounds, and degraded polystyrene also speed up the formation of coke on the surface of catalyst. In particular, vigorous coking reaction was observed in the catalytic reaction of degraded polystyrene over silica-alumina catalyst.<sup>7</sup>

From the reasons described above, it is necessary to select reaction conditions under which the yields of trimer, waxlike compounds, and degraded polystyrene decrease and the yields of monomer and dimer increases. Thus, trimer, waxlike compounds, and degraded polystyrene are negative constituents in the present work. The purpose of our study is to keep the composition of thermal decomposition products of polystyrene under control and to discuss the most suitable reaction conditions to recover indan derivatives from polystyrene.

## EXPERIMENTAL

*Sample:* Two polystyrenes were used: One was an article on the market, and the other was a crushed polystyrene obtained from the injection molding waste. However, since the experimental results of both samples were almost the same, the data in this work showed only those obtained from the commercial sample. The commercial sample was supplied from Asahi Dow Co., Ltd., and contained no additives. The number average molecular weight was  $8.3 \times 10^4$  and specific gravity, 1.067. It was used directly without purification in all experiments.

*Catalyst:* A silica-alumina catalyst used was IS catalyst (13 wt % of alumina) supplied from Catalysts and Chemicals Ind. Co. The catalyst was crushed into 20–40 mesh particles and calcinated in a stream of air at 540°C for 3 h before use. The catalyst had a broad acid strength distribution curve, and its acidic property was reported in the preceding paper.<sup>6</sup>

*Apparatus:* All experiments were carried out by the use of a fixed bed flow reactor, as shown in Figure 1. The reactor consisted of two sections: One is for the thermal decomposition of polystyrene, in which it was packed with Raschig rings; the other is for the catalytic reaction of thermal decomposition products of polystyrene, in which it was packed with catalyst. The former was situated at the upper part and the latter at the bottom part of the reactor tube.

The reactor tube was heated by five electric furnaces and its temperature was controlled within  $\pm 2^\circ\text{C}$ . Figure 2 shows the temperature distribution curve in

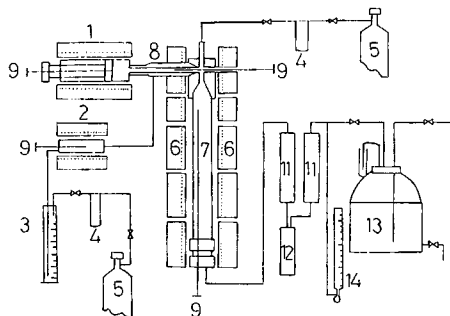


Fig. 1. Flow diagram of experimental apparatus: (1) melter; (2) steam generator; (3) mess cylinder; (4) manometer; (5) He bomb; (6) electric furnace; (7) reactor tube; (8) feeding nozzle; (9) thermocouple; (10) carrier gas inlet; (11) cooler; (12) trap; (13) gas holder; (14) soap film flow meter.

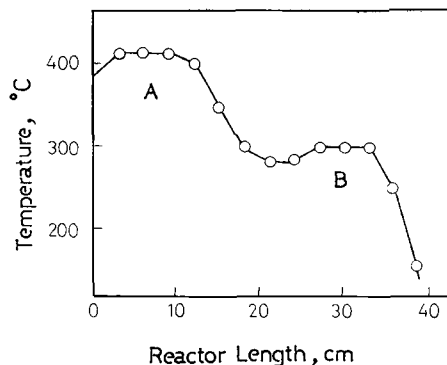


Fig. 2. Temperature distribution in a reactor tube: (A) a section of thermal decomposition of polystyrene; (B) a section of catalytic reaction of thermal decomposition products of polystyrene.

the reactor tube. In the present work, the thermal decomposition of polystyrene was carried out at 420°C, while the catalytic reaction of its decomposition products was done at 300°C.

Just before the reaction, approximately 20 g of polystyrene were placed in sample melting section (1) and allowed to melt at 180°C. The melted sample was fed into the section for thermal decomposition in the reactor tube at a rate of 140 mg/min. Its decomposition products, while flowing toward the bottom of the reactor tube (7), continued to undergo the catalytic reaction over silica-alumina catalyst. Subsequently, the final reaction products were discharged from the bottom of the reactor tube. Liquid products at room temperature were collected in a cooled trap (12) beneath the reactor tube, and gaseous products were placed in a gas holder (13).

*Analysis:* The instruments used for identifying products were the same as used in the preceding work.<sup>8</sup> Gas chromatography was carried out for the separation of the liquid products. The separation was effected by the use of a column (3 mm × 3000 mm) of 15% Apiezon grease L supported on Chromosorb WAW (60–80 mesh). Gaseous products at room temperature were also analyzed by gas chromatography. However, the amount of gaseous products was below 0.5 wt % of total products, and propane was a main product. Consequently, these gaseous products were not important for the present work.

## RESULTS AND DISCUSSION

### Thermal Decomposition of Polystyrene

It was reported in the preceding paper<sup>4</sup> that thermal decomposition products of polystyrene obtained by the use of a flow reactor consisted of a monomer, a dimer, a trimer, waxlike compounds, and degraded polystyrene. Reaction temperature and residence time are important factors for keeping the reaction under control in a flow reactor system. As shown in Table I, the yields of the monomer and byproducts increased with an increase in reaction temperature, while the yield of the trimer decreased remarkably. It is estimated that thermally labile trimer decomposes easily to form monomer and byproducts with increase in the reaction temperature. The effect of residence time on product

TABLE I  
Data on Thermal Decomposition of Polystyrene

Conditions	Sekiguchi <sup>4</sup>				Present work
	350	400	450	450	
Reaction temperature (°C)	350	400	450	450	420
Residence time (s)	4	4	4	8	16
Process time (min)	72	72	72	72	144
Wt % of polystyrene supplied					
Gaseous products	—	—	0.1	0.1	—
Liquid products	84.2	87.1	90.2	91.0	90.2
Toluene	—	—	0.7	1.5	0.8
Ethylbenzene	—	—	0.2	0.8	0.1
Styrene	35.4	50.1	58.5	62.6	62.4
$\alpha$ -Methylstyrene	—	—	1.7	1.9	0.8
Diphenylmethane	—	—	0.5	1.9	0.6
1,2-Diphenylethane	—	—	0.5	1.5	0.8
1,3-Diphenylpropane	—	—	0.6	3.0	0.5
Dimer	12.3	9.5	8.8	3.3	10.3
1,3-Diphenyl-2-butene	—	—	1.5	4.5	1.4
Trimer	24.9	18.2	5.3	0.7	9.2
Isomeric trimer	—	—	1.4	—	2.1
Waxlike compounds	11.6	9.3	10.5	9.3	1.2
Reactor residue <sup>a</sup> and weight loss	15.8	12.9	9.7	8.9	9.8

<sup>a</sup> Degraded polystyrene.

distribution as shown in Table I indicates a similar tendency as that for the reaction temperature described before. That is, it is anticipated that the yield of the trimer will consist of trace amounts at higher temperatures and longer residence times. However, since we do not wish to decrease the yield of the dimer, it is necessary to select the reaction conditions under which only the yields of the trimer, waxlike compounds, and so on decrease. Thus, the difference in thermal stabilities of the dimer and trimer has to be clarified at first.

Table II shows the data concerning thermal decomposition of the dimer and trimer. The trimer decomposes more easily than the dimer. Its conversion is

TABLE II  
Data on Thermal Decomposition of Dimer and Trimer

Reaction temperature (°C)	Dimer		Trimer
	450	475	475
Residence time (s)	4.5	1.0	1.0
Conversion (%)	4.8	2.9	66.6
Products (mol/100 mol feed)			
Toluene	0.5	0.3	3.4
Styrene	2.4	1.1	65.8
$\alpha$ -Methylstyrene	0.6	0.5	8.7
Unknown 1	—	—	3.0
1,2-Diphenylethane	1.6	1.0	10.5
1,3-Diphenylpropane	—	—	2.4
Unknown 2	0.1	0.1	1.0
Dimer	—	—	29.6
2,5-Diphenyl-1,5-hexadiene	1.4	0.9	12.5
High-boiling-point products	—	—	4.1

greater by about 20 times than that of the dimer under the same conditions. Styrene monomer and dimer are also formed during the thermal decomposition of the trimer. Since detailed data on the thermal decomposition of the dimer have already been reported,<sup>8</sup> Table II shows only a part of them. Consequently, dimer was almost stable below 450°C. Thus, if we choose the reaction conditions under which the trimer decomposes but the dimer does not in the thermal decomposition of polystyrene, it is to be expected that the yields of the monomer and dimer increase. Hence, the reaction temperature for the thermal decomposition of polystyrene must be controlled below 450°C.

In the present work, polystyrene decomposed at 420°C, while the residence time was as long as possible in order to increase the conversion of the trimer formed. Actually, the experiments were carried out by packing the section for the catalytic reaction in the reactor tube with Raschig rings instead of a catalyst. Table I shows the results. The monomer was 62.4%, dimer 10.3%, trimer 9.2%, and waxlike compounds 1.2% of the weight of polystyrene. These results indicate that the yields of the monomer and dimer increase compared with the results reported in the preceding paper.<sup>4</sup> That is, the composition of thermal decomposition products can be controlled by the use of a flow reactor. The thermal decomposition products obtained by controlling the reaction conditions consist of mainly monomer, dimer, and trimer. Byproducts such as toluene,  $\alpha$ -methylstyrene, 1,2-diphenylethane, 1,3-diphenylpropane were also formed, but their yields below about 1% of the weight of polystyrene.

### Catalytic Reaction Products

The experiments were carried out continuously by packing the catalyst in a section of the catalytic reaction situated at the bottom of a reactor tube. The products recovered in the trap (12), as shown in Figure 1, were separated into three fractions by gas chromatography. The detailed data on them are shown in Table IV.

The products in fractions I, II, and III were identified by the generally available instruments, as described in the experimental section. Consequently, fraction I consisted of monophenyl compounds such as alkylbenzenes, alkenylbenzenes, and so on. Fraction II consisted of diphenyl compounds and their derivatives. Four indan derivatives were main products in this fraction II. Their identical results are as follows:

(1) 1-Phenylindan:

MS:  $M^+$ , 194

$^1\text{H}$ -nmr ( $^{\text{CDCl}_3}$ ): 2.10 (1H,  $-\text{C}\text{H}$ —, multiplet), 2.61 (1H,  $-\text{C}\text{H}$ —, multiplet), 2.98 (2H,  $-\text{CH}_2-$ , multiplet), 4.31 (1H,  $-\text{CH}-$ , triplet), 7.20, 7.24 (9H).

(2) 1-Methyl-1-phenylindan:

MS:  $M^+$ , 208

The  $^1\text{H}$ -nmr spectrum was identical with that of 1-methyl-1-phenylindan.<sup>6</sup>

(3) 1-Methyl-3-phenylindans:

There were two stereo isomers. One of them was observed  $M^+$  ion (208) in the mass spectrum and its  $^1\text{H}$ -nmr spectrum was as follows:

$^1\text{H}$ -nmr ( $^{\text{CDCl}_3}$ ): 1.39 (3H,  $-\text{CH}_3$ , doublet), 1.65 (1H,  $-\text{C}\text{H}$ —, multiplet),

2.72 (1 H,  $-\text{CH}^{\oplus}-$ , multiplet), 3.18 (1H,  $-\text{CH}-$ , multiplet), 4.23 (1H,  $-\text{CH}-$ , multiplet), 7.26 (9H).

The other was identical with that of 1-methyl-3-phenylindan in the mass spectrum.<sup>9</sup> The IR spectra were also identical with those of 1-methyl-3-phenylindans.<sup>10</sup> At the end fraction III consisted of a vast number of constituents, but each yield of the products in this fraction was below 1% of the weight of polystyrene. Though each of them was not identified, the total yield of them is shown in Table IV.

As shown in Table I, thermal decomposition products under the present experimental conditions consisted of monomer, dimer, and trimer. After these products formed in the section for thermal decomposition of polystyrene, then passed to the bottom of the reactor tube, here the catalytic reactions of these products took place over silica-alumina catalyst. Therefore, it is necessary to clarify each catalytic reaction product of styrene, dimer, and trimer over silica-alumina catalyst.

The catalytic reaction of styrene over silica-alumina catalyst has been reported by Greensfelder and Voge,<sup>11</sup> but little has been reported on those of the dimer and trimer. Thus, each catalytic reaction of styrene monomer, dimer, and trimer, respectively, over silica-alumina catalyst was carried out. Though the detailed data for the catalytic reaction of the dimer has already been reported in the preceding paper,<sup>6</sup> a part of them is also shown in Table III. It was already reported that 1-methyl-1-phenylindan is formed selectively from the dimer. The reaction mechanism was shown in the following equation:

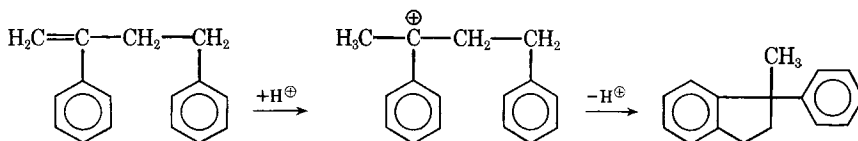


TABLE III  
Data on Catalytic Reactions of Styrene, Dimer, and Trimer over Silica-Alumina Catalyst<sup>a</sup>

Sample contact time (g-cat-s/g-mol-feed)	Styrene		Dimer		Trimer	
	$4.9 \times 10^4$	$17.1 \times 10^4$	$4.4 \times 10^4$	$17.5 \times 10^4$	$5.0 \times 10^4$	$20 \times 10^4$
Conversion (%)	63.4	92.0	96.8	99.1	98.5	99.9
Products (mol/100 mol feed)						
Benzene	2.6	7.9	11.5	27.0	8.8	22.3
Toluene	0.3	0.5	—	—	—	—
Ethylbenzene	14.7	34.1	2.6	2.8	5.4	13.2
Isopropylbenzene	—	—	3.0	3.8	30.0	49.7
$\alpha$ -Methylstyrene	—	—	—	—	11.7	0.8
Other low-boiling-point products	1.5	5.1	11.2	28.4	10.1	39.8
1-Phenylindan	—	—	—	—	48.2	20.5
1-Methyl-1-phenylindan	—	—	68.7	50.6	—	—
1-Methyl-3-phenylindans	8.1	5.1	—	—	—	—
1,3-Diphenyl-1-butene	1.1	0.7	1.3	1.1	—	—
Other dimer products	2.0	2.8	5.8	1.6	14.2	5.3
High-boiling-point products	6.0	8.1	3.9	6.9	32.1	33.1

<sup>a</sup> Reaction conditions: Temp = 300°C; Process time = 19 min; N<sub>2</sub>/sample, 18.

TABLE IV  
Effect of Contact Time on Products Yield

Contact time (g-cat-s/g-mol-feed)	$5 \times 10^4$	$10 \times 10^4$	$20 \times 10^4$	$30 \times 10^4$
Wt % of polystyrene supplied				
Gaseous products	0.2	0.3	0.4	0.5
Liquid products	77.7	67.8	67.3	66.9
Fraction I <sup>a</sup>				
Benzene	0.3	0.4	0.9	1.4
Toluene	0.8	0.6	0.7	0.8
Ethylbenzene	5.7	9.3	14.5	18.3
Styrene	43.6	22.8	16.9	10.1
Isopropylbenzene	0.4	0.8	1.2	1.6
$\alpha$ -Methylstyrene	1.7	1.0	0.8	0.5
Unknown 1	0.3	0.5	0.9	1.5
Unknown 2	0.2	0.5	0.9	1.8
Unknown 3	0.6	0.9	1.3	1.6
Fraction II <sup>b</sup>				
1-Phenylindan	3.0	2.2	2.4	2.2
1-Methyl-1-phenylindan	4.1	5.9	6.2	6.0
1-Methyl-3-phenylindans	4.8	6.8	6.5	6.7
Diphenyl compound 1	1.1	0.8	1.1	0.9
Diphenyl compound 2	0.9	0.8	0.8	0.6
Diphenyl compound 3	2.0	0.9	1.0	0.9
Fraction III <sup>c</sup>				
High-boiling-point products	8.2	13.6	11.2	11.6

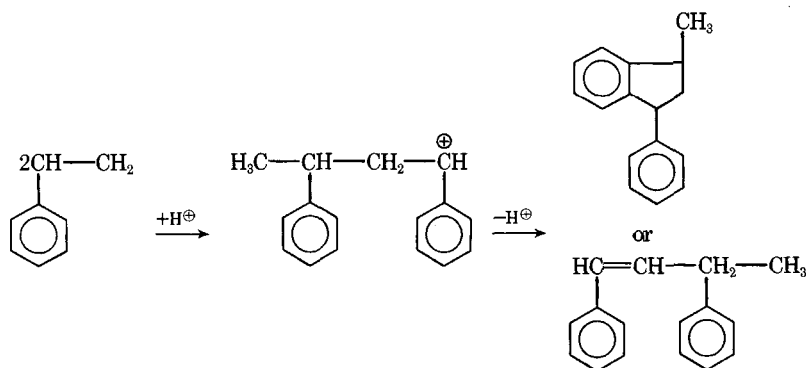
<sup>a</sup> In this fraction, there were a few unidentified constituents, but their yields were below about 1% of the weight of polystyrene.

<sup>b</sup> A few unidentified constituents were considered to be diphenyl compounds, but the unconverted quantity of dimer was not confirmed in this fraction II.

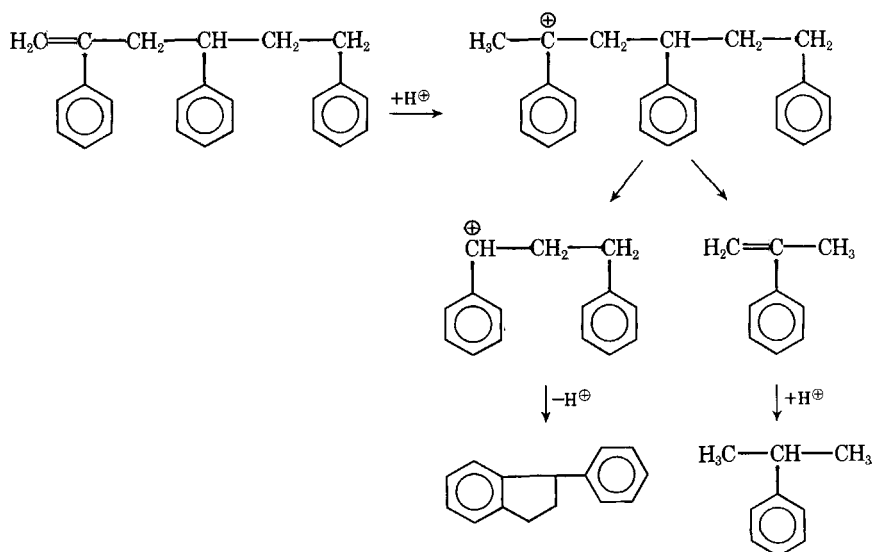
<sup>c</sup> This fraction consisted of high-boiling-point products which were detected after fraction II by gas chromatography.

Further, it was found that two 1-methyl-3-phenylindans were formed from styrene and a 1-phenylindan from the trimer, as can be seen from Table III. Since the yield of styrene monomer in the thermal decomposition products of polystyrene was the highest as shown in Table I, large amounts of its catalytic reaction products would be recovered in the present work. Consequently, the catalytic reaction of styrene monomer over silica-alumina catalyst should be studied in detail. The reaction temperature at which Greensfelder and Voge performed experiments<sup>11</sup> was higher than that in the present work. Main products were ethylbenzene and coke. In the present work, two 1-methyl-3-phenylindans and a 1,3-diphenyl-1-butene were formed instead of ethylbenzene and coke. 1-Methyl-3-phenylindans and 1,3-diphenyl-1-butene are styrene dimers. Therefore, the hydrogenation and dimerization of the styrene monomer were observed to be the main reactions. One of the main reactions is the hydrogenation of styrene to form ethylbenzene. It is estimated that coke is deposited on the surface of catalyst to an appreciable extent. However, the total yields of styrene dimers and high-boiling-point products were higher than that of ethylbenzene at  $4.9 \times 10^4$  g-cat-s/g-mol-feed, as can be seen from Table III. It seems most probable that the reaction, of forming heavy oily products containing its dimerization products, is the main reaction rather than its hydrogenation. As the reaction temperature was so high in the experiments carried out

by Greensfelder and Voge,<sup>11</sup> the secondary reactions of heavy oily products such as styrene dimers and high-boiling-point products were not considered. However, it is clear from Table III that the secondary reactions should be considered. It was confirmed that the hydrogenation and dimerization of styrene took place in the catalytic reaction of styrene over silica-alumina catalyst. The following equation is supposed for the dimerization of styrene:



On the other hand, 1-phenylindane and isopropylbenzene were main products in the catalytic reaction of the trimer, as shown in Table III. It is estimated that they are formed as follows:



Also, it was found that appreciably more high-boiling-point products were formed than the dimer and styrene monomer.



### Effect of Process Time

The liquid products recovered in trap (12), as shown in Figure 1, were separated roughly into three fractions. Changes in the yields of these fractions are very important for understanding the results obtained in the present work. In Figure 3, the relationship between process time and each yield of fractions is shown. Each yield kept constant after about 30 min. The yield of fraction I was high in the earlier stage of the reaction. Each constituent formed in fraction II and fraction III was converted into low-boiling-point products in fraction I or coke. Further, the relationship between each product in fraction I and process time is shown in Figure 4. This figure shows that the yield of ethylbenzene is very high in the earlier stage of the reaction while that of styrene is small. The styrene monomer formed is almost converted entirely into ethylbenzene. The results described above indicate that hydrogenation of styrene, cracking, and coking of products takes place predominantly in the earlier stage of the reaction.

Further, in the earlier stage of the reaction, it is estimated that the concentration of styrene monomer in the thermal decomposition products of polystyrene is higher than that shown in Table I.<sup>12</sup> Namely, all velocities, with which decomposition products evolve by the pyrolysis of polystyrene at the top of the

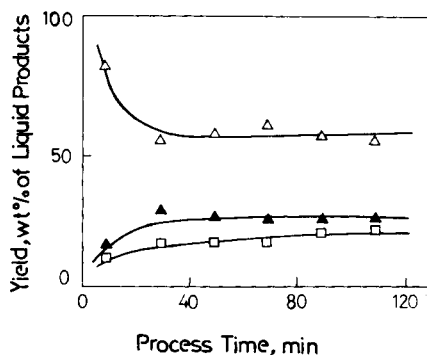


Fig. 3. Effect of process time on each yield of fractions: ( $\Delta$ ) fraction I; ( $\blacktriangle$ ) fraction II; ( $\square$ ) fraction III.

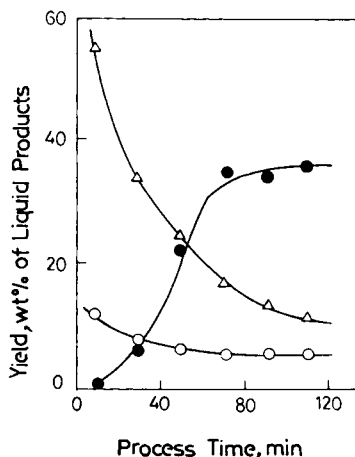


Fig. 4. Effect of process time on each yield of products in fraction I: ( $\Delta$ ) ethylbenzene; ( $\bullet$ ) styrene; ( $\circ$ ) other alkylbenzenes.

reactor tube and which were moved into the catalytic bed situated at the bottom of the reactor tube, are considered not to be equal. The movement of styrene monomer, which is gasified more easily than the dimer, trimer, etc., will be the fastest of the thermal decomposition products of polystyrene. Styrene monomer may be considered to be a constituent causing the catalytic reaction over silica-alumina catalyst at first. Consequently, in the earlier stage of the reaction so high in the activity of the catalyst, a high yield of ethylbenzene was recovered, as can be seen from Figure 4.

### Effect of Contact Time

The contact time is calculated from the following equation.

$$W/F: \text{ contact time (g-cat-s/g-mol-feed)}$$

Hence,  $W$  is the amount of catalyst used by weight (g), and  $F$  is the total amount of decomposition products evolved by pyrolysis of polystyrene per unit time (g-mol/s).  $F$  was calculated from the rate of polystyrene supplied into the reactor tube, which was constant as described in the experimental section and the composition of its decomposition products as shown in Table I.

The material balances in the present work were shown in Figure 5 and calculated from the following equation:

$$P = L + G + C + R + E$$

Here,  $P$  is the amount of polystyrene supplied (g),  $L$  is the amount of liquid products recovered (g),  $G$  is the amount of gaseous products recovered (g),  $C$  is the amount of coke deposit (g),  $R$  is the amount of reactor residue (g), and  $E$  is weight loss. The amount of coke deposit shows the increase in amount of catalyst during the reaction. Reactor residue is the total amount of constituents sticking to the reactor tube wall and Raschig rings.

In Figure 5, since the sum of reactor residue and the weight loss is considered to be constant during change in contact time, a decrease in the yield of liquid products is roughly equal to an increase in the amount of coke deposit. The relationship between each yield of fractions of liquid products and contact time is shown in Figure 6 and Table IV. The yield of fraction I is higher before  $10 \times 10^4$  g-cat-s/g-mol-feed and kept at a constant level (about 37 wt %) after  $10 \times 10^4$

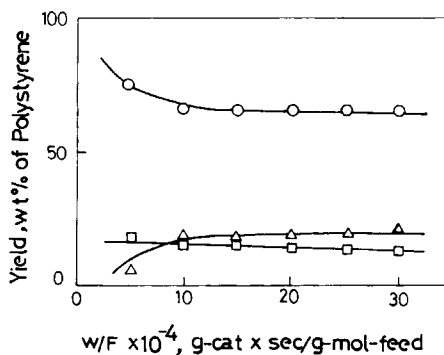


Fig. 5. Material balances in the present work: (O) liquid products; (Δ) the amount of coke deposited; (□) reactor residue + weight loss.

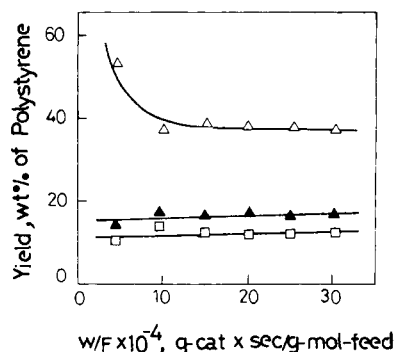


Fig. 6. Relationship between contact time and each yield of fractions: ( $\Delta$ ) fraction I; ( $\blacktriangle$ ) fraction II; ( $\square$ ) fraction III.

g-cat-s/g-mol-feed. The changes in the yield of fraction I in Figure 6 and those of liquid products in Figure 5 against contact time show a similar tendency. It is clear that the decrease in the yield of liquid products is caused by that of fraction I. Further, only the yield of the styrene monomer decreases with an increase in contact time, as can be seen from Figure 7. Thus, styrene monomer was found from the results described above to contribute to the formation of coke in the present work.

On the other hand, each yield of fractions II and III kept at a constant level (about 18 wt % and 12 wt %) with an increase in contact time, respectively. However, in the results obtained from each catalytic reaction of the styrene monomer, dimer, and trimer, each yield of indan derivatives decreases and, in contrast to this, the yields of alkylbenzenes and high-boiling-point products increases with increasing contact time, as shown in Table III. It is estimated that the cracking and coking reactions of these indan derivatives take place to a great extent with increasing contact time. The results for each catalytic reaction of the styrene monomer, dimer, and trimer are contradicted by the results shown in Figure 6 and Table IV. That is, it is supposed that these indan derivatives are formed from the constituents except from styrene monomer and dimer. The yield of indan derivatives is increased by this reaction. Though the detailed reaction mechanism is not clear at the present stage, it is satisfactory to consider

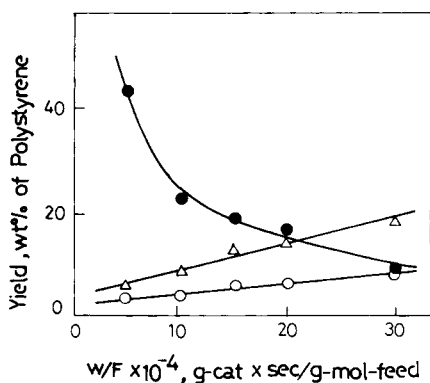


Fig. 7. Effect of contact time on each yield of products in fraction I: ( $\Delta$ ) ethylbenzene; ( $\bullet$ ) styrene; ( $\circ$ ) other alkylbenzenes.

this reaction as the secondary catalytic reaction of heavy oily products such as high-boiling-point products and reactor residue. There is such a difference in process time between the results in Table III and those in Table IV. The former was 19 min and the latter 144 min. When the process time is so long, the activity of catalyst decreases remarkably in the latter stage of the reaction. The data as described above indicate that the activity of catalyst is an important factor and, in particular, that indan derivatives are formed from heavy oily products over the catalyst poisoned by coke deposit.

On the other hand, since the degraded polystyrene is considered to make an important contribution to the formation of coke, we carried out the following experiments. That is, the thermal decomposition of polystyrene and the catalytic reaction of its decomposition products were carried out separately. Since the degraded polystyrene is reactor residue as shown in Table I and not recovered in the trap (12) of Figure 1, only the thermal decomposition of polystyrene was carried out by the use of the apparatus shown in Figure 1 and its decomposition products were recovered in the trap (12) at first. Next, the catalytic reaction of its thermal decomposition products over silica-alumina catalyst were carried out by the use of another apparatus.<sup>6</sup> If we compare the results obtained from this experiment with those shown in Table IV, it is possible to reveal the catalytic behavior of the degraded polystyrene. The results are shown in Table V. Here, the results of the catalytic reaction of thermal decomposition products indicate that the yields of ethylbenzene and high-boiling-point products increase while the amounts of indan derivatives formed and coke deposit decrease. Conse-

TABLE V  
Data on Catalytic Reaction of Thermal Decomposition Products<sup>a</sup>

Starting sample	Polystyrene	Thermal decomposition products
Wt % of feed sample		
Liquid products	66.9	78.5
Fraction I		
Benzene	1.4	5.8
Toluene	0.8	0.8
Ethylbenzene	18.3	26.0
Styrene	10.1	3.0
Isopropylbenzene	1.6	1.9
$\alpha$ -Methylstyrene	0.5	0.5
Unknown 1	1.6	2.5
Unknown 2	1.7	2.7
Unknown 3	1.6	1.3
Fraction II		
1-Phenylindan	2.2	2.4
1-Methyl-1-phenylindan	6.0	4.6
1-Methyl-3-phenylindans	6.7	4.9
Diphenyl compound 1	0.9	1.0
Diphenyl compound 2	0.9	1.2
Diphenyl compound 3	0.9	0.8
Fraction III		
High-boiling-point products	11.7	19.1
Coke deposit	21.9	13.9
Reactor residue and weight loss	10.7	7.6

<sup>a</sup> Reaction conditions: Contact time =  $25 \times 10^4$  g-cat-s/g-mol-feed; process time = 144 min.

quently, the degraded polystyrene made an important contribution to the formation of coke and the decrease in activity of catalyst. Also, it is estimated from these results that indan derivatives are formed predominantly from high-boiling-point products over the catalyst poisoned by coke deposit.

On the basis of the results described above, it is suggested for obtaining further increases in the yields of indan derivatives to carry out investigations on lines as follows:

1. Since the yield of the styrene monomer is the highest in the thermal decomposition products of polystyrene, it is necessary to select reaction conditions under which the dimerization of styrene proceeds more remarkably than its hydrogenation.

2. It should be considered that the indan derivatives are formed from high-boiling-point products formed over the catalyst poisoned by coke deposit.

3. It is anticipated that the recovery of indan derivatives becomes an advantage in terms of controlling the activity of catalyst.

## CONCLUSION

An attempt has been made to construct an apparatus in which thermal decomposition of polystyrene and catalytic reactions of its decomposition products over silica-alumina catalyst could be controlled continuously at the same time in order to recover indan derivatives directly from polystyrene. As a result, the following results and conclusions have been obtained:

1. The composition of thermal decomposition products of polystyrene has to be kept under control by the use of a flow reactor.

2. The indan derivatives recovered are two 1-methyl-3-phenylindans, one 1-methyl-1-phenylindan, and 1-phenylindan. The yields of these indan derivatives are about 20% of the weight of liquid products recovered.

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