

Monomert Recycling of Thermosetting Resins

Yoshiki Sato*

National Institute for Resources and Environment,
16-3 Onogawa, Tsukuba-shi, Ibaraki-ken 305-8569 JAPAN,
e-mail : yoshiki@nire.go.jp, FAX : +81-298-58-8409

Liquid-phase cracking of thermosetting resins were studied using hydrogen-donor or non-donor solvent for chemical recycling using 200 ml autoclave at 430-450°C with 60 min of reaction time under 2.0 MPa of initial nitrogen pressure. These resins gave almost 100 wt% conversion by the use of tetralin and about 85 wt% yield of oil product with 40-74 wt% of monomer compounds such as phenol and cresols. However, cracking of these resins could not proceed at all in decalin as solvent.

The effect of polystyrene addition and hydrogen pressure on the liquid-phase cracking were also investigated. Novolak type of resin shows the enhanced conversion of 51.1 wt% and the distillable oil yield of 43.6 wt% respectively, when polystyrene is added to the reaction system. The effect of the hydrogen gas pressure more than 5MPa is obviously to enhance cracking reactivity. Conversion in the liquid-phase cracking of epoxy, ABS, urethane resin, and urethane foam was very high in the case of both tetralin and decalin.

Conversion in the liquid-phase cracking of epoxy, ABS, urethane resin, and urethane foam was very high in the case of both tetralin and decalin.

1. INTRODUCTION

About 1.6 million tons of thermosetting resins, such as phenol and epoxy resins, are produced annually for use mainly in electrical appliances and automobiles as well as heat-proof tableware and adhesive agents. However, it is well known that liquefaction of these resins by pyrolysis is impossible because of their property of hardening when heated.

In the present study, we investigated the liquid-phase cracking of thermosetting resins and some other plastics (ABS, urethane foam and resin) using hydrogen-donor or non-donor solvents¹⁾. The effect of hydrogen pressure and polystyrene addition on the liquid-phase cracking of thermosetting resins were also investigated.

2. EXPERIMENTAL

Pellet-form pure resins with no contamination were used as the reactant. Experimental runs were carried out in a 200-ml stainless steel magnedrive autoclave at 430, 440 and 450 °C under 2.0 MPa of initial nitrogen pressure and a reaction time of 60 min in the presence of either tetralin or decalin. Tetralin was used as a model for a typical hydrogen-donor solvent and decalin as a typical non-donor solvent. For the purpose of comparison, we used LCO (light cycle oil) from an FCC unit in the petroleum refinery process as an inexpensive, conventional solvent. Gaseous products and the distilled oils were subjected to gas chromatography for compositional analysis.

3.RESULTS AND DISCUSSION

(1) Phenol resins

The conversion and the product distribution from the liquid-phase cracking of novolak and resol types of phenol resins at 440 °C and 60 min under nitrogen are shown in Table 1.

Table 1. Liquid-phase cracking of phenol and epoxy resins at 440°C

Resin type	Phenol (Novolak)			Phenol (Resol)		Epoxy
	Tetralin	Tetralin	t-Decalin	Tetralin	Decalin	Tetralin
Solvent						
Catalyst	Fe ₂ O ₃	non	non	Fe ₂ O ₃	non	Fe ₂ O ₃
Conv.(wt%)	96.8	100.0	19.6	99.1	9.2	98.1
Yield of product (wt%)						
Gas	1.3	0.1	0.1	1.1	0.3	2.7
Oil	84.6	68.0	17.8	50.6	5.6	88.1
Product distribution (wt%)						
Phenol	25.7	22.2		9.8		16.7
Cresol	38.1	23.7		26.8		1.2
iso-Propylphenol						24.3
Dimethylphenol	11.8	7.5		20.4		0.6
total	75.6	53.4		57.0		42.8
VR	7.2	29.1	1.4	44.7	2.4	7.3
water	3.7	2.8	0.3	2.7	0.9	0.0

Gaseous products were very small of 1-5 wt% and consisted of mainly methane and hydrogen with traces of C₂ and C₃ hydrocarbon gases. The novolak type of phenol resin showed almost 100% conversion when tetralin was used as a solvent. When using an iron catalyst, the distillable oil yielded by vacuum distillation was fairly high at 85 wt%. The difference in the distillable oil yield between the catalytic and thermal reactions was explained by the hydrogen transfer activity of the iron catalyst. In these reactions, tetralin plays the role not only of the solvent to solubilize the resin and the product, but also as a hydrogen-donating agent. Small amounts of naphthalene was produced from tetralin and the generation of hydrogen was 0.5 wt%. Therefore 0.76 wt% of the hydrogen was consumed in the catalytic cracking of the novolak type of phenol resin to an oil product. The experimental results, obtained by the use of LCO as a solvent, showed higher conversions and the oil yields. The liquid products, as analyzed by gas chromatography, consisted of large amounts of phenols and cresols in the distillable oil, 26 wt% and 38 wt% respectively, for catalytic cracking (see Table 1). This indicates that more than 75 wt% of the alkylphenols in the distillable oil were recovered in the catalytic reaction.

In contrast, by the use of decalin, more than 80% of the resin could not be converted to oil either with or without the iron catalyst. A mixture of solid products stuck to the stirrer and the walls of the autoclave. The results observed for the use of decalin showed a reaction behavior similar to pyrolysis without any solvent.

The resol type phenol resin, which has a three-dimensional cross-linkage structure, again showed a high conversion level of more than 99 wt% in the presence of tetralin. There was not a high oil yield, however, 57 wt% of phenol compounds were found in the oil products. With decalin, the conversion was again less than 10 wt%. The differences in cracking

reactivity between the novolak and resol types of phenol resins are considered to be due to the difficulties of hydrogen transfer.

Table 2. Liquid-phase cracking of epoxy, ABS, and urethane resins

(Reaction temperature : 440°C Reaction time : 60min. Initial N₂ pressure : 2MPa)

Resin type	Epoxy			ABS	Urethane Resin	Urethane Foam
	Tetralin	Tetralin	t-decalin	t-decalin	Tetralin	Tetralin
Solvent	Tetralin	Tetralin	t-decalin	t-decalin	Tetralin	Tetralin
Catalyst	Fe ₂ O ₃	non	Fe ₂ O ₃	non	Fe ₂ O ₃	Fe ₂ O ₃
Conversion (wt%)	98.1	99.4	95.2	99.5	92.2	97.1
Product yield (wt%)						
Gas	2.7	4.3	8.6	0.5	15.6	21.8
Oil	88.1	76.0	72.1	84.3	62.1	61.4
VR	7.3	11.4	8.1	14.0	9.6	13.9
Water	0.0	7.7	6.4	0.7	4.9	0.0

(2) Effect of polystyrene addition and high pressure hydrogen

The effect of polystyrene addition to the liquid-phase cracking of novolak type of phenol resin in the presence of t-decalin under nitrogen gas were shown in Fig. 1. Polystyrene itself showed 100% conversion and 92.2 wt% of the oil yield at 440°C with 60min of reaction time under 2.0 MPa of initial nitrogen pressure. The conversion and the oil yield were enhanced drastically with the addition of polystyrene. Assuming that the polystyrene shows the same reaction behavior as it reacts alone, novolak type of resin shows 51.1 wt% conversion and 43.6 wt% of the distillable oil yield respectively, when polystyrene is added to the reaction system with phenol resin to polystyrene weight ratio of 1. In this reaction, tetralin and naphthalene, which are the dehydrogenation products from decalin, are not found so much and lots of toluene are produced. This indicates polystyrene or the produced styrene and/or ethylbenzene takes a role of hydrogen donor.

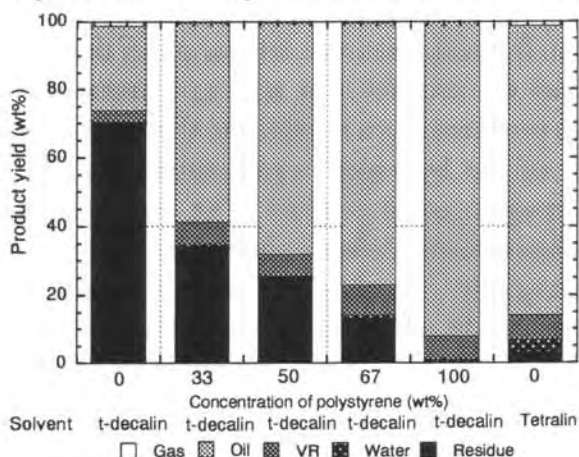


Fig. 1 Effect of Polystyrene Addition on the Liquid-Phase Cracking of Phenol Resin (React. temp : 440°C, React. time : 60min, Initial N₂ press. : 2MPa)

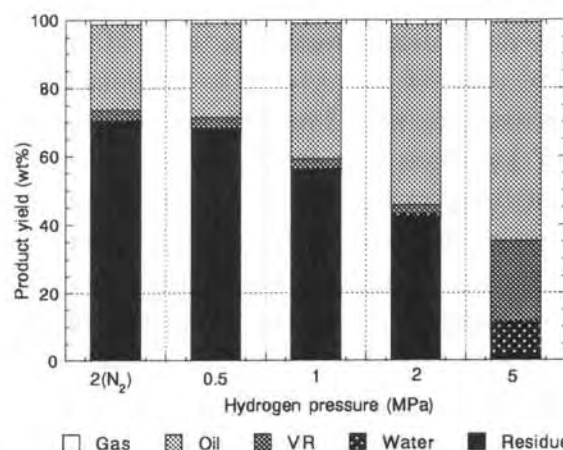


Fig. 2 Effect of Hydrogen Pressure on the Liquid-Phase Cracking of Phenol Resin in t-Decalin. (Fe₂O₃ catalyst, React temp : 440°C, React time : 60min)

The cracking of novolak type of phenol resin in the presence of t-decalin showed the increased conversion and the oil yield with the hydrogen gas pressure as shown in Fig. 2. When the hydrogen pressure increased to 5MPa, the conversion and the distillable oil yield reached to more than 95 wt% and 65 wt% respectively. The effect of the hydrogen gas pressure is obviously to enhance cracking reactivity. Liquid product, as analyzed by gas

chromatography, consisted of large amount of phenol 22.7wt% and cresols 28.3wt%. Monomer yield also increased with hydrogen pressure.

(3)Epoxy, ABS, urethane resins and urethane foam

Epoxy resin, ABS, urethane resin, and urethane foam are also known to show poor conversion to oil by pyrolysis. The results of the liquid-phase cracking of these resins at 440 °C and 60 min under nitrogen atmosphere are shown in Table 2. In the case of epoxy resin, more than 95 wt% conversion was obtained with and without catalyst as well as donor solvent. Solvent or catalyst made no significant difference in conversion. Under the former reaction conditions, 0.5 wt% of hydrogen in the tetralin was transferred to stabilize the phenol and isopropylphenol. The concentrations of monomer compounds, such as phenol and isopropylphenol, in the oil were also very high at 42.8 wt% in the catalytic reaction with tetralin (Table 1). The production ratio of phenol/isopropylphenol from the catalytic cracking with tetralin was 0.69 wt/wt, (0.99 mol/mol). This indicates that the cracking of epoxy resin proceeded stoichiometrically. On the other hand, with the catalytic reaction in decalin, the yield of monomer compounds, phenol and isopropylphenol, was only 14.4 wt%.

The liquid-phase cracking of ABS, urethane resin, and urethane foam in the presence of tetralin also represented a conversion of more than 90 wt% with a high yield of oil (Table 2). Notwithstanding the fact that t-decalin was used as a solvent instead of tetralin, it was possible for these resins, including epoxy resin, to be converted into an oil fraction whose reaction behavior was quite different from that under pyrolysis.

Conclusion

Phenol resins showed very different reaction behaviors in the liquid-phase cracking depending on the hydrogen-donor characteristics of the solvent. Both novolak and resol types of phenol resin gave almost 100 wt% conversion with the use of tetralin and high yields of monomer-size compounds. On the other hand, cracking of these resins could not proceed at all with decalin as solvent. From the points of view of another hydrogen source and hydrogen transfer compound, the high pressure hydrogen and polystyrene addition on the liquid-phase cracking of novolak type of resin shows the enhanced conversion, the distillable oil and monomer yield. Conversion in the liquid-phase cracking of epoxy, ABS, urethane resin, and urethane foam was very high in the case of both tetralin and decalin.

Acknowledgments

The authors are grateful for frequent discussions with Mr. K. Tatsumoto, Mr. M. Haneda, and Mr. M. Kameyama of Mitsui SRC Co., Ltd. We also thank Gun Ei Chemical Industry Co., Ltd., Mitsui Chemical, Inc., Sumika A & L, Inc., and Japan Urethane Industries Institute for providing plastic materials.

References

- 1) Y.Sato, Y.Kodera and T.Kamo, *Energy & Fuels*, *13*, 364-368 (1999)