

Dechlorination and Degradation of Polyvinylchloride in Solvents

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PVC resin was decomposed in t-decalin at 400°C and 440°C for 60 min under 4.0 MPa initial pressure of nitrogen. Yields of oil and residue were 24.6%, 9.1% at 440°C and 23.8%, 10.2% at 400°C respectively. Relatively higher oil yields and lower residue yields than that on conventional pyrolysis of PVC imply that solvent have role to prevent condensation on the degradation of PVC even if the solvent do not have enough hydrogen donating property. At the presence of copper, yield of chlorinated solvent and products increased in t-decalin at 400°C. However, chlorine content of oil decreased with sodium hydroxide. Copper chloride (CuCl₂) is considered to be a catalyst for chlorine transfer under these reaction systems.

Introduction

PVC have been used widely as well as other three major plastics, polyethylene (PE), polypropylene (PP), and polystyrene (PS). However, PVC can not be used as a feed of chemical recycling or energy recovery with other plastics due to the production of hydrogen chloride that corrode reactor on decomposition. Particularly, PVC is pointed out to be one of the main chlorine sources for production of dioxins in waste incineration plant. Therefore, development of safe and useful recycling technology for PVC is very important for conservation of global environment and natural resources.

Liquid-phase-cracking is effective method to obtain liquid products from waste plastics as well as coal. Recently, we have shown possibility of conversion of PVC to useful chemicals (1). Particularly, significant high yield of oil was observed liquid-phase-cracking of PVC using hydrogen donor solvent such as tetralin (2). However, lower hydrogen donating solvent, waste motor oil or light cycle oil, is considered to be used in practical process. In this work, liquid-phase-cracking of PVC was carried in t-decalin to study conversion of PVC to low molecular products with low chlorine using a poor hydrogen donor solvent.

Experimental

PVC (Aldrich, Mw=129000) resin (24.0 g) and tetralin or t-decalin (50.0 g) were charged into a 200 ml magnetic stirred autoclave made of hastelloy C. Experiments were carried out at 400°C or 440°C for 60 min under an initial pressure of 4.0 MPa of

nitrogen gas. In some experiments, copper powder (12.2 g) or sodium hydroxide powder (15.6g) were added. Gas products were collected into a Teflon gas bag through two gas-washing-bottles filled with water and analyzed by GC. Liquid product was separated to oil (Oil & water) and vacuum residue (VR) by vacuum distillation under 2 torr at 330°C for 60 min. Solid products were washed by tetrahydrofuran (THF) and dried for one day at 110°C under vacuum. Chlorine contents of oils were analyzed by GC with atomic emission detector (AED, Hewlett Packard 5921). 1-Chlorohexane and 2-chloronaphthalene were used as an internal standard for quantitative measurement.

Results and discussion

Products distributions from PVC on pyrolysis, liquid-phase-cracking in tetralin, and in decalin at 440°C are shown in Fig.1. In the pyrolysis of PVC without solvent, yields of oil and residue were 11.2% and 33.1% respectively. In liquid-phase-cracking of PVC, yields of oil and residue were 36.3%, 1.8% in tetralin and 24.6%, 9.1% in t-decalin respectively. Relative lower residue yield observed in the case of t-decalin imply that not only hydrogen donation from solvent but also solvent have a role to prevent condensation of PVC.

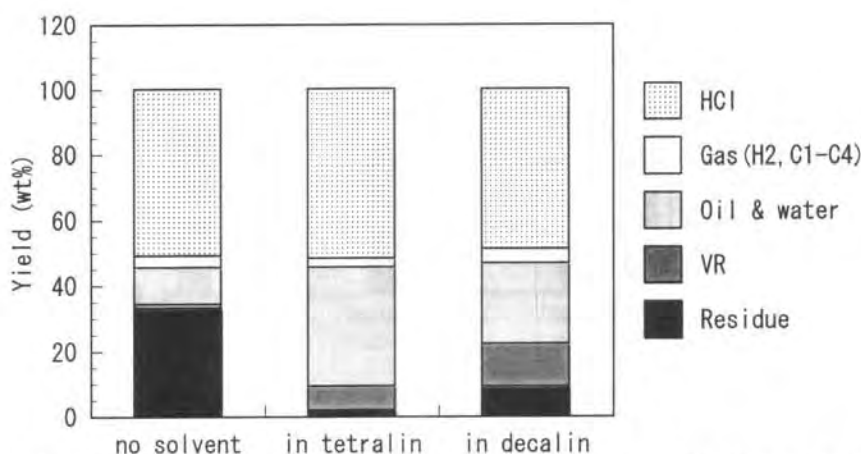


Fig.1 Products distribution from PVC on pyrolysis, liquid-phase cracking in tetralin, t-decalin at 440°C for 60 min.

Products distributions from PVC in t-decalin with copper powder and sodium hydroxide powder at 440°C were shown in Fig.2. At the presence of copper, oil yield from PVC increased and that of hydrogen chloride decreased. The results imply that a part of hydrogen chloride react with copper and convert to the residue as copper chloride. In the case of liquid-phase-cracking with sodium hydroxide, production of hydrogen chloride gas was not observed. Oil yield with sodium hydroxide was almost equal to the sum of that of oil without sodium hydroxide and that of water produced from sodium hydroxide and hydrogen chloride. Increment of yield of residue is corresponding to that of sodium chloride production.

Products distributions from PVC in t-decalin at 400°C were shown in Fig.3. Almost equal oil yields at 400°C to that at 440°C imply that t-decalin dilute PVC and prevent condensation reaction of polyene produced from PVC by removal hydrogen chloride, because t-decalin is inert under this reaction condition.

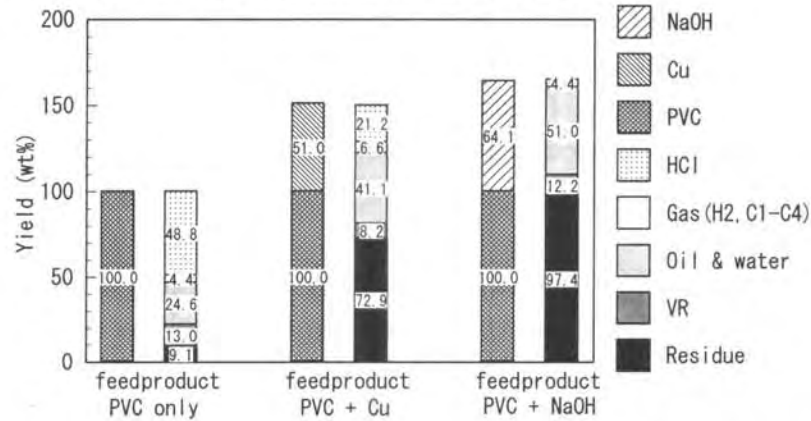


Fig.2 Effect of additives on products distribution in liquid-phase-cracking of PVC at 440°C for 60 min.

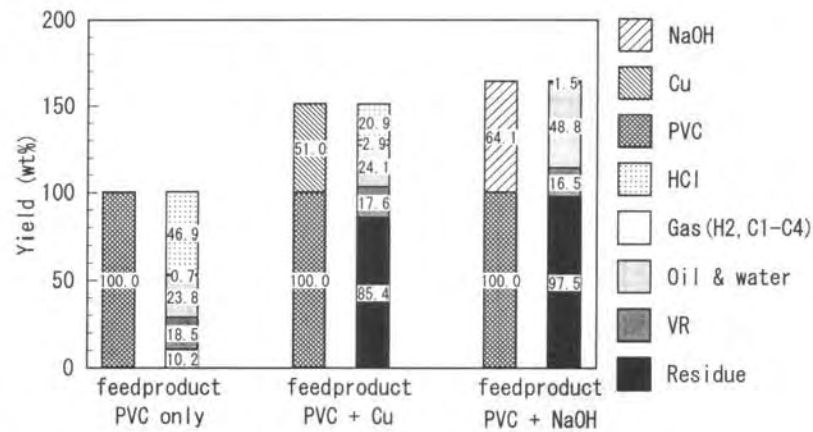


Fig.3 Effect of additives on products distribution in liquid-phase-cracking of PVC at 400°C for 60 min.

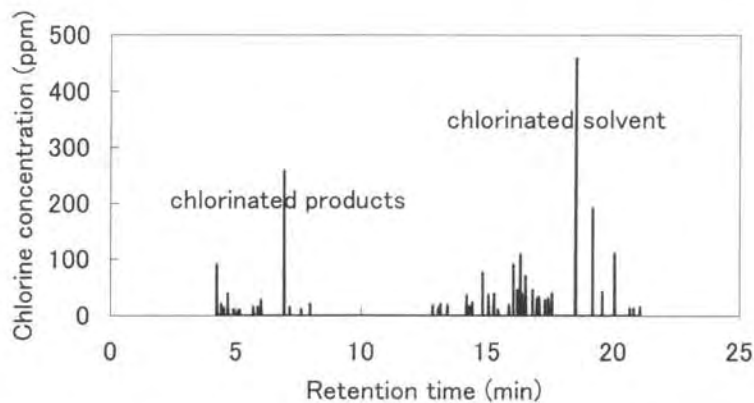


Fig.4 AED spectra of oil produced from liquid-phase-cracking of PVC in t-decalin at 440 °C for 60 min

AED spectra of the oil produced from liquid-phase-cracking of PVC in t-decalin at 440°C for 60 min are shown in Fig.4. To understand reaction behavior of the chlorine compounds, the spectra were divided to chlorinated products and chlorinated solvent by retention time. Effects of additive for chlorinated products and chlorinated solvent were shown in Fig.5. In the tetralin, chlorinated products increased with copper and decreased with sodium hydroxide. However, chlorinated solvent decreased at 440°C and increased with copper at 400°C in t-decalin. In both temperatures, chlorine content decreased with sodium hydroxide. Chlorinated solvent and products were produced from tetralin and decalin in the presence of copper chloride (CuCl_2) without PVC under this reaction condition. However, the chlorinated compounds were not obtained with other copper chloride (CuCl). These experimental results imply that copper chloride (CuCl_2) was estimated to be a catalyst for chlorine transfer under these reaction systems.

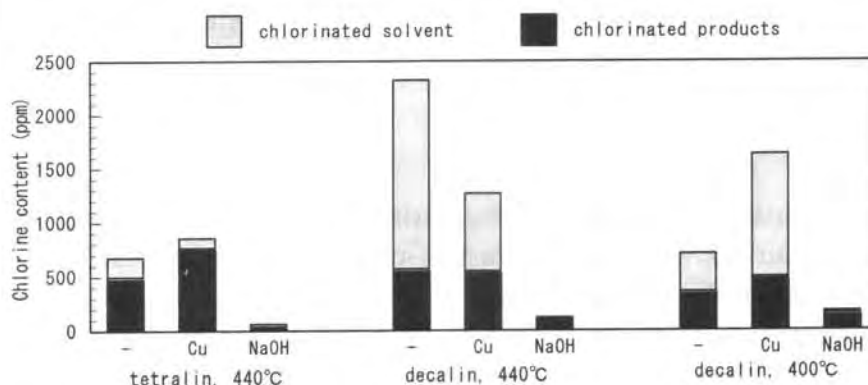


Fig.5 Effects of additives on chlorine concentration of oil produced from liquid-phase-cracking of PVC

Conclusions

In the liquid-phase-cracking of PVC in t-decalin at 400°C with sodium hydroxide, lower chlorine content oil was produced. The experimental results show that not only hydrogen donation and but also dilution by solvent are important on liquid-phase-cracking of PVC. Chlorine content of oil from PVC in t-decalin was higher than that in tetralin. However, additive of chlorine capture, such as sodium hydroxide, help to reduce chlorine content of oil from PVC in t-decalin as low as that of oil produced from PVC on liquid-phase-cracking in tetralin.

References

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2. T. Kamo, Y. Sato, "Liquid-Phase-cracking of Polyvinyl Chloride (PVC), Role of Solvent on Decomposition of PVC and Removal of Chlorine", Preprint ACS meeting, 42(4), 1014(1997).