

# EFFECT OF PRESSURE OR HYDROGEN ON RAPID PYROLYSIS OF OLIGOMERS' MODEL COMPOUNDS FROM RESIN AND BIOMASS TAR

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**Abstract:** Effect of reaction conditions such as hydrogen partial pressure on rapid hydrolysis of oligomers' model compounds was discussed. Supposed oligomers were partially pyrolyzed epoxy resin with biomass tar as solvent for the resin. Bisphenol-A and phenol were mainly used as model compounds in this study. Major products were benzene, methane, and phenol by rapid pyrolysis of Bisphenol-A at 973K and 1073K. Toluene was relatively minor products. More phenol produced at 973K than at 1073K. Yield of methane, which is final product by hydrolysis, increased with partial pressure of hydrogen. On the other hand, benzene and phenol was estimated to be behaved intermediate products.

## 1. Introduction

In order to recover the useful materials from glass fiber composite epoxy board such as end-of-life electronic equipments, a new process with solubilizing the epoxy resin under a mild condition by using the heavy tar derived from wood biomass was proposed [1]. In the process, solubilized and partially pyrolyzed epoxy resin with heavy biomass tar will assumed to be then reformed to lighter materials, which will be used as the circulation solvent of the process or as feedstocks. In this study, model compounds for oligomers both from epoxy resin and from biomass tar were used. Experimental study of model compounds reforming was carried out in hydrogen atmosphere. Product distributions of rapid hydrolysis were shown. The effects of reaction temperature and hydrogen partial pressure on the product yield were discussed.

## 2. Experimental

A unique batch reactor was used for rapid hydrolysis experiment which was described previously [2]. Briefly, the reactor was mainly composed of three parts, sample

feeder, reaction chamber and gas reservoir. Prior to reaction, the sample was loaded in the sample tube and was kept at room temperature. The reaction chamber filled with gas for reaction atmosphere under the condition where the reaction pressure was preheated to the reaction temperature and the sample tube was driven into preheated chamber just before the reaction started. The reaction was started with sample to be blown into the reaction chamber from the sample tube with a small amount of gas. The gas for blowing was same as reaction atmosphere which set at a slightly higher pressure than that in the chamber. After a prescribed reaction time, the gas phase of the product was moved instantaneously to the gas reservoir which was previously evacuated. Liquid phase products were captured by filter and were corrected by washing or extracting with tetrahydrofuran (THF) as a THF solution. The composition of the products was analyzed with GC-TCD, GC-FID and GC-MS. Reaction experiment was carried out at 1073K, 973K under 0MPa (100% N<sub>2</sub>), 0.9MPa (N<sub>2</sub>/H<sub>2</sub> mixed gas with ratio of 70:30 at total pressure of 3.0MPa), 3.0MPa (100% H<sub>2</sub>), 7.0MPa (100% H<sub>2</sub>) of hydrogen partial pressure. The reaction time was 80 seconds. As for model compounds, bisphenol-A and phenol were mainly used. The amount of samples for each experiment was 0.5g. Mixture of phenol and bisphenol-A was also used with the amount of 0.25g each.

### 3. Results and Discussion

#### 3.1 Major Products from each model compound

Major products from both phenol and bisphenol-A by rapid hydrolysis experiment were methane, benzene, and less amount of ethane. Significant amounts of phenol and toluene were also produced depending on the reaction conditions. Product distribution as carbon conversion of three major compounds, methane, benzene, and ethane, from phenol with varying hydrogen partial pressure at 1073K is shown in Fig.1. C<sub>2</sub>H<sub>x</sub> refers to C<sub>2</sub> hydrocarbons including ethane and ethylene, most of C<sub>2</sub>H<sub>x</sub> was ethane. Benzene produced much in the lower hydrogen partial pressure, methane produced large amount in the higher partial pressure. Methane increase linearly with partial pressure, benzene increase from 0.9MPa to 3.0MPa following by decreasing to 7.0MPa with convex upward. It is assumed that phenol mainly degraded to form benzene by deoxygenation in the lower partial pressure of hydrogen, methane was formed from benzene in the higher partial pressure. It is concluded that benzene behaved as an intermediate product which would further convert to methane, as final hydrolysis product, with more hydrogen. Product distribution of three major compounds from bisphenol-A with varying hydrogen partial pressure at 1073K is shown in Fig. 2. Overall trend of the change in product distribution with hydrogen partial pressure was similar to that from phenol as shown in Fig.1. Yield of methane and benzene from bisphenol-A were almost same level in the lower region of hydrogen partial pressure under 3.0MPa, which differed slightly to the case of phenol with larger amount of benzene production than methane.

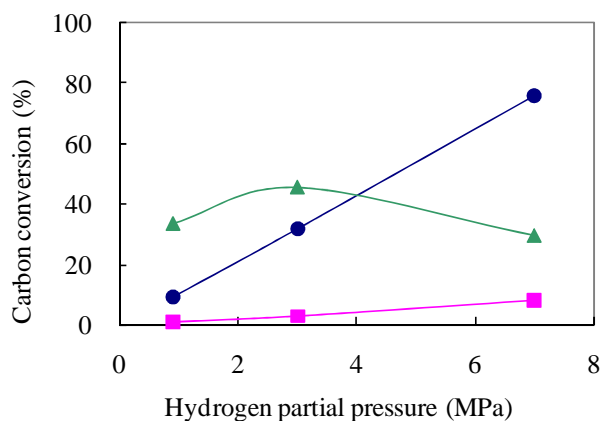


Fig. 1 Carbon conversion to major products by rapid hydrolysis at 1073K from phenol.

●: CH<sub>4</sub>, ■: C<sub>2</sub>H<sub>x</sub>, ▲: C<sub>6</sub>H<sub>6</sub>

### 3.2 Sample mixing effect on methane yield

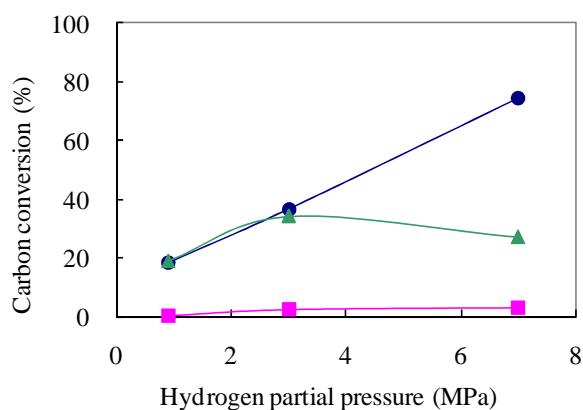


Fig. 2 Carbon conversion to major products by rapid hydrolysis at 1073K from bisphenol-A.

●: CH<sub>4</sub>, ■: C<sub>2</sub>H<sub>x</sub>, ▲: C<sub>6</sub>H<sub>6</sub>

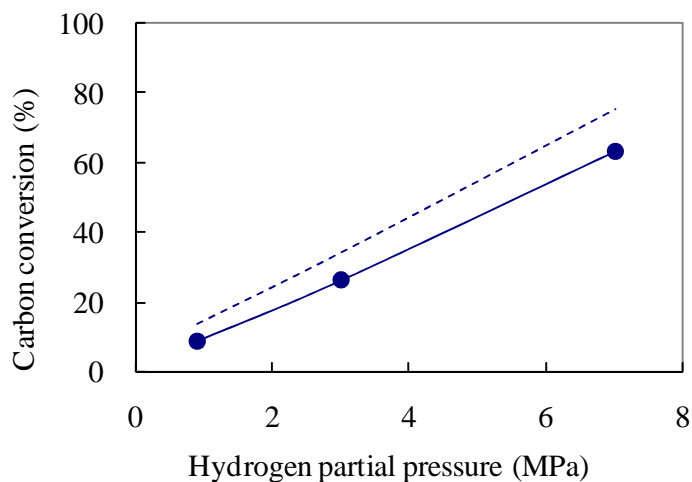


Fig. 3 Carbon conversion to methane by rapid hydrolysis at 1073K from phenol and bisphenol-A mixture. ●: mixture experiment, ---: estimated

Carbon conversion to methane from mixture of phenol and bisphenol-A at 1073K are shown in Fig. 3. The values were calculated from the results obtained from phenol and bisphenol-A respectively to estimate the methane yield from the mixture, assuming no mutual influences. The original data from them respectively have been plotted in Fig. 1 and 2. The calculated values are shown with a broken line in Fig. 3. The plotted solid line was obtained from experiment results of mixture. The methane yield from the mixture experiments seemed to be smaller than the values calculated. These phenomena are different from the observation in the mixture of phenol and paraffin hydrolysis [3] and observation also in the mixture of coal and polyethylene (PE) hydrogasification [4]. It was suggested that the enthalpy from hydrogenation of paraffin or PE, which is exothermic reaction, enhanced the endothermic step of reaction of phenol or coal. This implication of reaction mechanism was supported by observation of temperature profile inside the reaction chamber. Deviations of the temperature during rapid hydrolysis of phenol, bisphenol-A, and their mixture for the 80 seconds period are shown in Fig. 4. For all samples, the temperature dropped at the beginning of the reaction. It took about 10 seconds for the temperature to come back to the initial stage. This indicates that an endothermic reaction dominates for all samples in the early stage of the reaction. It seems consistent that the methane yield from the mixture of phenol and bisphenol-A was not increased by mixing, but rather decreased as a result.

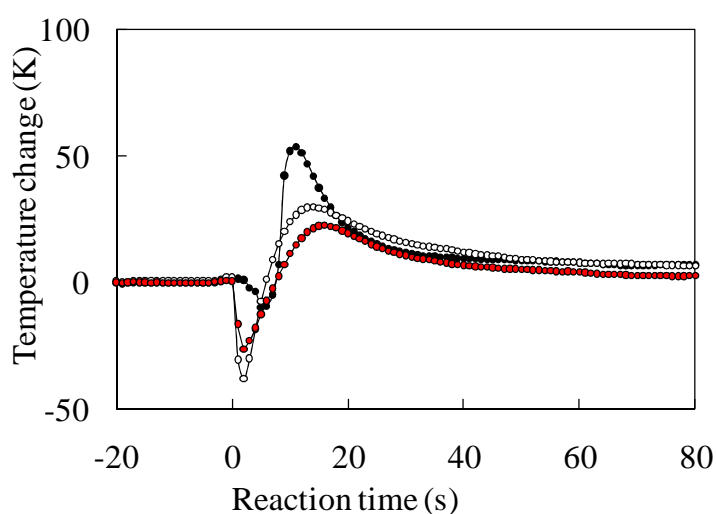


Fig. 4 Temperature change during rapid hydrolysis at 1073K of phenol (●), bisphenol-A (○), and their mixture (●).

### 3.3 Selectivity of phenol as a product from bisphenol-A

In the proposed process, epoxy tar oligomers will assumed to be reformed to feedstocks. Both phenol and toluene, which were produced from bisphenol-A as model compound of epoxy tar depending on the reaction conditions, are valuable chemicals. Carbon conversion to phenol, as a product, and toluene from bisphenol-A at 1073K are shown in Fig. 5. Both conversions to phenol and toluene seemed to have relative maximum with varying hydrogen

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partial pressure. Especially, phenol showed to have relative maximum clearly at 3.0MPa of hydrogen partial pressure, but only less than 3%. Carbon conversion to phenol and toluene from bisphenol-A at 973K are shown in Fig. 6. Both conversions showed to have relative maximum at 0.9MPa. More phenol was produced at 973K than at 1073K, comparing the Fig. 5 and Fig.6. However, toluene was produced about the same level at 973K and at 1073K. Phenol was one digit larger than toluene at 973K, which was about double as maximum ratio at 1073K. It means that there was selectivity to obtain phenol. The selectivity was higher at 973K than at 1073K. As shown in Fig. 2, benzene performed as an intermediate product. Phenol and toluene are also seems intermediate products and they may then convert to methane through benzene. Although it was shown the highest yield of phenol from bisphenol-A at 973K and 0.9MPa in the conditions which were chosen, more phenol could be obtained in higher selectivity by optimizing the reaction conditions.

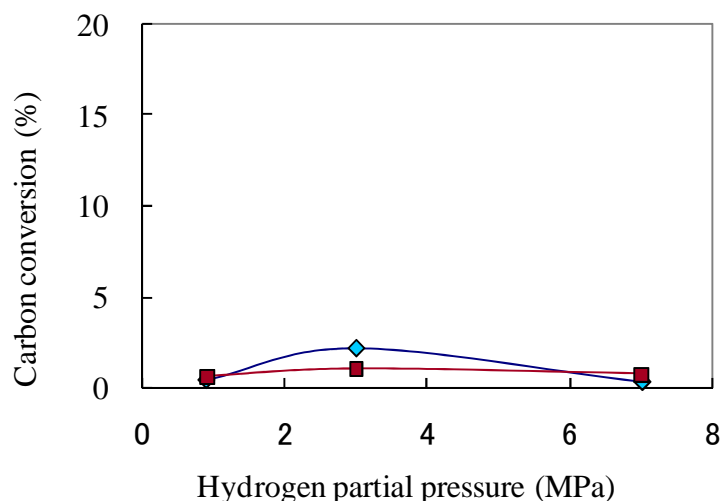


Fig. 5 Carbon conversion to products by rapid hydro-pyrolysis at 1073K from bisphenol-A mixture. ◆: phenol, ■: toluene

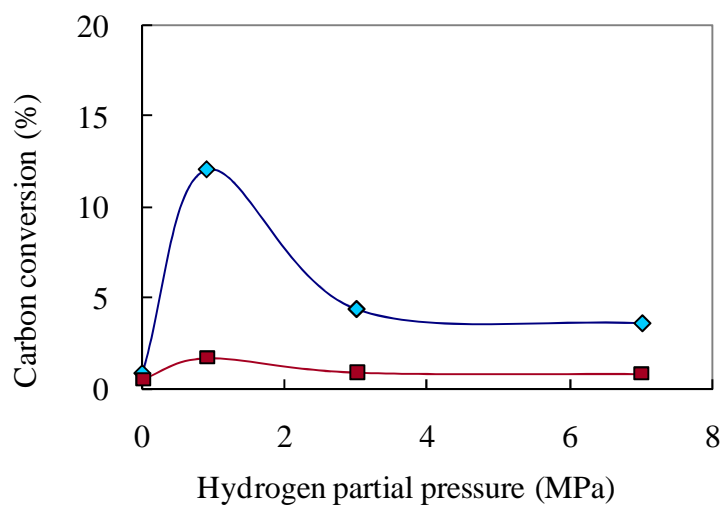


Fig. 6 Carbon conversion to products by rapid hydro-pyrolysis at 973K from bisphenol-A mixture. ◆: phenol, ■: toluene

#### 4. Conclusions

Experimental study of model compounds rapid pyrolysis was carried out in hydrogen atmosphere at 1073K and 973K. Phenol and bisphenol-A as model compounds for oligomers both from epoxy resin and from biomass tar were used. Product distributions of rapid hydrolysis were shown. The effects of reaction temperature and hydrogen partial pressure on the product yield were discussed. Major products were benzene, methane, and phenol from Bisphenol-A. Toluene was relatively minor products. More phenol produced at 973K than at 1073K. Yield of methane, which is final product by hydrolysis, increased with partial pressure of hydrogen. On the other hand, benzene and phenol was estimated to be behaved intermediate products. It was suggested that phenol could be obtained in high selectivity from tar, by optimizing the reaction conditions.

#### References

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