

## Carbon Materials-catalyzed Hydroliquefaction of Flame-retardant Plastics in Organic Solvents

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Flame-retardant plastics such as thermosetting resins and personal computer bodies could be completely liquefied in their carbon materials-catalyzed hydroliquefaction in tetralin without use of H<sub>2</sub> as a hydrogen source. Polybromodioxins and organic bromides were not contained in the product gases and oils. Active carbons with larger surface areas (1,310 ~ 3,460 m<sup>2</sup>/g) acted as superior catalysts transferring hydrogens in tetralin to plastics. The thermogravimetric analysis in nitrogen was shown to be effective in conveniently monitoring the additive effects of hydrogen donor solvents and carbon materials in the hydroliquefaction of plastics and the chemical interactions between mixed plastics.

### Introduction

The amount of waste plastics has been increasing year by year and reaches 6 million ton per year in 1996. About 40 % of waste plastics constitutes flame-retardant plastics such as thermosetting resins and the ones containing organic and/or inorganic flame-retardants. They cannot be incinerated conventionally due to their much low reactivities and formation of polybromodioxins. It is urgently necessary to develop pertinent methodologies to recycle these kinds of plastics without secondary pollution. We have already reported that flame-retardant plastics such as thermosetting resins and personal computer bodies can be completely liquefied in their carbon materials-catalyzed hydroliquefaction in hydrogen donor solvents at around 400°C [1], [2]. Moreover, the additive effect of hydrogen donors and carbon materials in this reaction and the behavior of mixed solvents could be conveniently monitored by thermogravimetric analysis in nitrogen [3]. This paper presents our approach to hydroliquefy flame-retardant plastics with carbon materials as catalysts without using H<sub>2</sub>. It will be also shown that the thermogravimetric analysis is effective in monitoring the chemical interactions between plastics, hydrogen donor solvents, and carbon materials.

### Materials and Methods

Thermosetting phenol resin (TSP), thermoplastic phenol resin (TPP), ABS resin (ABS), epoxy resin (EPO), and urea resin (URA) were commercially purchased. Desktop [WP(W)] and laptop [WP(B)] personal computer bodies were collected and grounded at < 2 mmφ. Tetralin, 1-methylnaphthalene, and 9,10-dihydroanthracene (DHA) of special reagent grades were purified by conventional methods before use. Some of the carbon materials used in this research were donated from chemical companies and the others were commercially purchased. They were dried in vacuo at 50°C for 1 h before use. Five grams of plastics, 300 mg of carbon materials, and 80 ml of solvents were put into a 200 ml Hastelloy C magnetically stirred autoclave. After being pressurized by nitrogen up to 2.0 MPa, the autoclave was heated to the

reaction temperature within 30 min, and maintained at the temperature for 0 to 3 h. After the reaction, the autoclave was cooled to room temperature in an ice water. The gaseous products were collected in a Tedlar bag through a water bubbler, and identified and quantified by GC-MS and GC, respectively. The liquid products were recovered with THF and the solids were filtered out. The filtrates were directly analyzed by GPC. The samples for the thermogravimetric analyses were prepared by thoroughly kneading plastics, hydrogen donor solvents, and carbon materials (weight ratio 10:4:1) on a agate mortar. They were put in the furnace and predeaerated in nitrogen streams of 500 ml/min. Then, the furnace temperature was raised at 20 K/min up to 1173 K in nitrogen streams of 50 ml/min.

## Results and Discussion

Additive Effect of Carbon Materials in the Hydroliquefaction of Flame-retardant Plastics. It is shown from Fig. 1 that **AC 1** is the most effective catalyst in the hydroliquefaction of **TSP**. On addition of mesocarbon microbeads **MC 3**, condensation reactions concurred with the hydroliquefaction of **TSP**. Addition of fullerene-rich soot (**FS**) increased the yields of intermediates, but the degree of **TSP** hydroliquefaction was not satisfactory.

In the hydroliquefaction of **WP(W)**, the yields of lighter fractions increased with reaction severity (Fig. 2). Polybromodioxins and other organic bromides could not be detected in the liquid products. The yields of benzene, toluene, and ethylbenzene increased with reaction time.

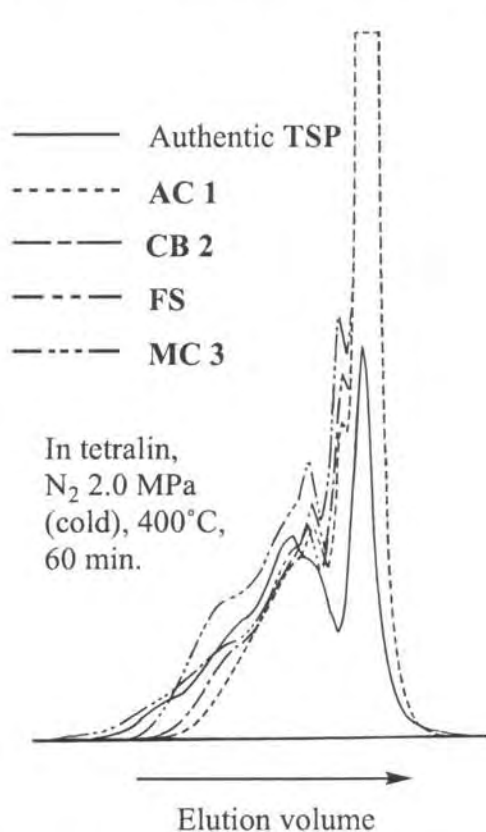


Figure 1 Additive effect of carbon materials on the GPC profiles of the products from **TSP**.

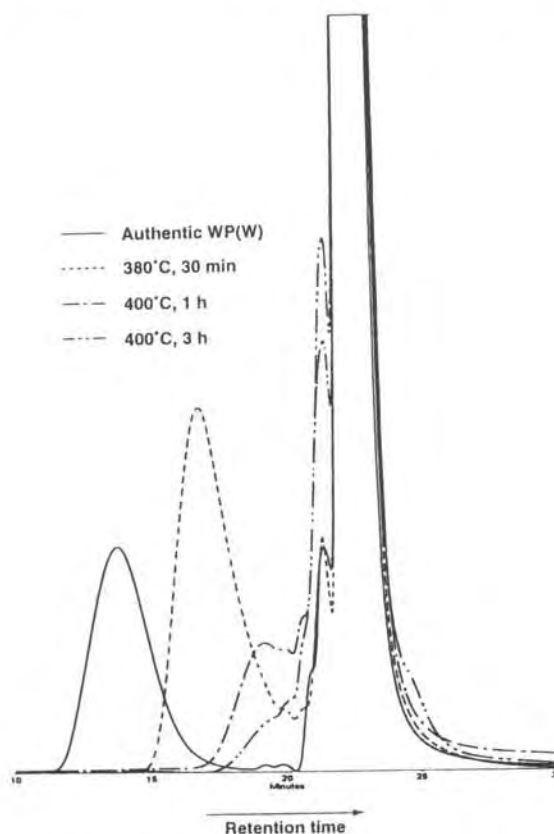


Figure 2 GPC profiles of the liquid products derived from **WP(W)**.

Additive Effect of Hydrogen Donor Solvents and Carbon Materials on the Thermogravimetric Behavior of TSP. Fig. 3 shows the additive effect of tetralin and AC 1 on the thermogravimetric behavior of TSP. Only 43 % of TSP was pyrolyzed at 1173 K, but a tenth-fold amount of AC 1 addition enhanced TSP pyrolysis. This fact indicates that the migration of hydrogen atoms inherently present in TSP is promoted by AC 1 to give the larger weight loss. Interestingly, TSP pyrolysis was further promoted for the ternary mixture of TSP, tetralin, and AC 1. The colors of the residues recovered after these analyses well reflected the difference in their thermogravimetric behavior. Those from TSP and the mixture of TSP and AC 1 were pitch black, while that from the ternary mixture was grayish white. For the samples of TSP + tetralin and TSP + tetralin + AC 1, more than 70 % of the tetralin was evaporated out during the predeaceration process. Therefore, only small amounts of tetralin hydrogens are good enough for AC 1 to catalyze the TSP pyrolysis via the hydrogen transfer from tetralin to TSP. These observations also support that the more carbons in TSP were hydrogenatively pyrolyzed. It is interesting that the corresponding additive effects of AC 1 and tetralin were observed in the hydroliquefaction of TSP and its pyrolysis in nitrogen.

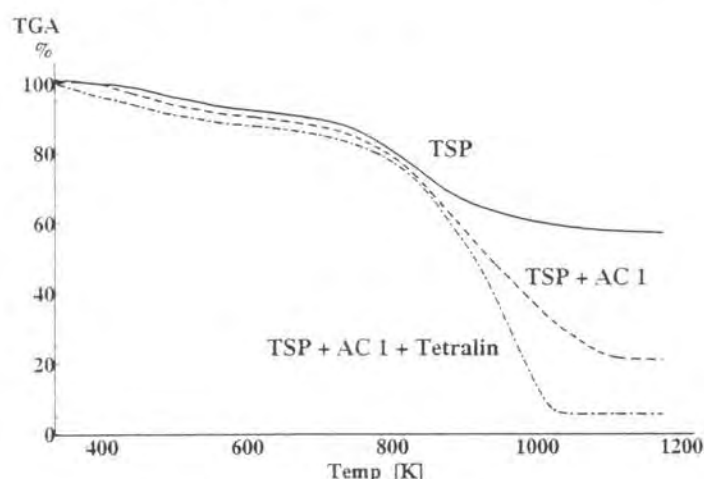


Figure 3 Additive effect of tetralin and AC 1 on the thermogravimetric behavior of TSP.

Thermogravimetric Behavior of Mixed Plastics. Since the similar additive effects of hydrogen donor solvents and carbon materials were observed in the hydroliquefaction of TSP and in its pyrolysis in nitrogen, chemical interactions between mixed plastics were also monitored by this technique. From the viewpoint of practical application of this technology, the information on the behavior of mixed plastics is indispensable. Fig. 4 shows that the final weight loss for the mixture of TSP and URA (weight ratio 1:1) was larger than expected from each of them. These findings suggest that mixing TSP and URA promotes hydrogen migration between them, resulting in the larger weight loss. On the other hand, mixing of TSP and TPP apparently retarded the pyrolysis of TPP, and almost the same thermogravimetric pattern was obtained for TSP and the mixture of TSP and TPP (Fig. 5). These findings suggest that some cross-linking network structures develop during their pyrolysis. Although this kind of intermolecular interaction could be diminished in the liquid-phase hydroliquefaction of TSP and TPP, the occurrence of retrogressive condensation reactions are expected to accompany their decomposition. In the case of the mixed samples of TSP and EPO, they decomposed

independent of each other, and no chemical interaction was apparently observed. **AC 1** accelerated the pyrolysis of **TSP** and **URA** at higher than 900 K, but its promoting effect was not observed in the pyrolysis of **TSP + TPP** or **TSP + EPO**. It has been shown that different kinds of chemical interactions occur between mixed plastics with different chemical structures.

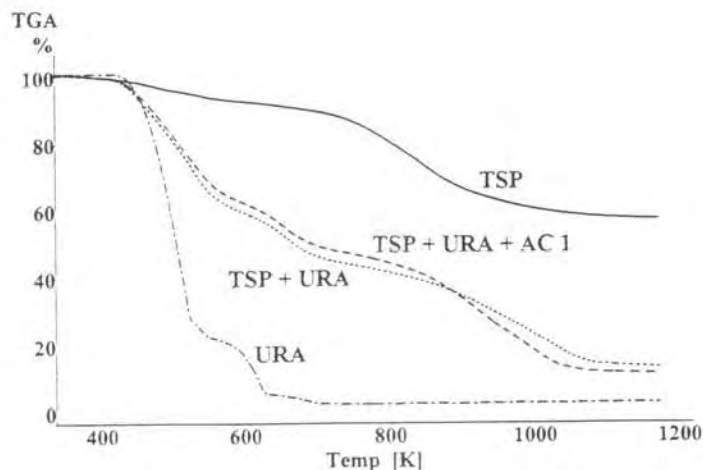


Figure 4 Thermogravimetric behavior of **TSP** and **URA**.

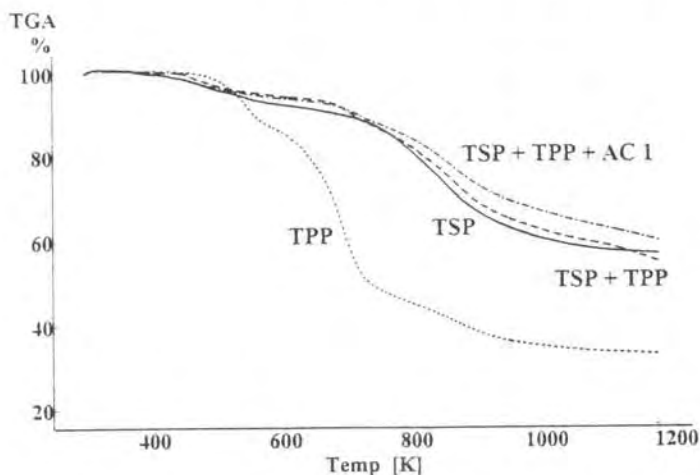


Figure 5 Thermogravimetric behavior of **TSP** and **TPP**.

### Conclusions

It has been shown that active carbons are effective in the hydroliquefaction of thermosetting resins such as **TSP** and personal computer bodies such as **WP(W)** in tetralin at 400°C. Thermogravimetric analysis in nitrogen is effective in monitoring the additive effect of hydrogen donor solvents and carbon materials in the hydroliquefaction of flame-retardant plastics, and in detecting the chemical interactions between mixed plastics.

### References

1. S. Futamura, *Kino Zairyo* 1999, **19**(6), 13-20 (Japanese).
2. S. Futamura, *New Technology Japan* 1999, **26**(12), 37.
3. S. Futamura, Proc., 8th Convention of the Japan Institute of Energy, Osaka, 1999, 111-114.