

초임계유체를 이용한 PS 분해 속도론

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Kinetics for Degradation of Polystyrene in Supercritical Fluids

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INTRODUCTION

Plastics are very useful materials but they are not disposable easily. The use of plastics as commodities continues to grow, the increasing amount of waste plastics causes serious environmental hazards. Waste plastics occupy a large volume, when buried in a landfill, due to low density; moreover, they are hardly degraded biologically in the soil. Incinerating waste plastics also generates toxic gases, and is not a viable option. These are the reasons why new technologies are needed in the waste plastic treatment. Supercritical fluids have recently been used in waste plastic treatments to address the difficulties in thermal degradation of waste plastics[1-3]. In this study, thus, the degradation of PS(Polystyrene) was performed in supercritical fluids using an autoclave batch-type reactor. n-hexane and water were employed as a supercritical solvent. The kinetic behavior of degradation of PS in supercritical fluids was discussed.

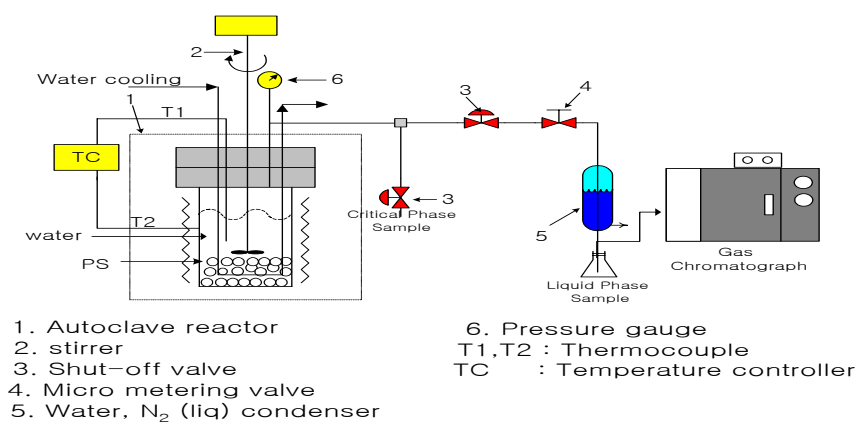


Fig. 1. Schematic diagram of experimental apparatus.

EXPERIMENTAL

All experiments for this study were carried out in a specially designed 1 liter autoclave reactor equipped with high-power heater of 4kW in order to reach the reaction temperature as quickly as possible. Fig.1 shows a schematic of experimental apparatus.

The PS used for this study was GPPS(General Purpose of Polystyrene) HF-2660 supplied by Starex in Korea. The material was in the form of pellets, approximately 3mm long and 2.5mm in diameter. The reactor was charged with 30g of PS and solvent. In order to remove the oxygen, the reactor was purged by Ar gas. The experiments were performed using n-hexane and water over the region of the critical point. We set the time as the starting point of reaction when the temperature and pressure reach the prescribed values of supercritical temperature and pressure. After the reaction completion, the products were recovered by condensing it in a glass cylinder cooled by water and liquid nitrogen. The weight of remained substance and oil product was measured respectively. The conversion of the reactant was calculated by measuring remained substance.

RESULTS AND DISCUSSION

The mechanism for the degradation of PS in supercritical n-hexane and water as well as the thermal pyrolysis of PS can be described as



The degradation of PS in supercritical n-hexane and water as well as the thermal pyrolysis is presumed to follow the first-order kinetics in the initial stage of the reaction, i.e.

$$d[\text{PS}]/dt = -k_1[\text{PS}]$$

or

$$X = 1 - \exp(-k_1t)$$

where k_1 refers to the first-order rate constant and X refers to the conversion of PS. In our experiment, the time dependencies of the conversions are shown in Fig.1. for the degradation of PS in supercritical water at 370, 380, 390 and 400°C and at 335 bar. At the four levels of reaction temperature, similiary linear relationships were got between the logarithm of unconverted fraction and the reaction time. From the slope of each straight line, the first-order rate constant was evaluated as follows: 0.095 min^{-1} at 370°C min^{-1} . The temperature dependency of the first-order rate constant is shown in Fig.1.

We expect that slopes k should depend on T as

$$k(T) = k_0 \exp(-E/RT)$$

Taking the logarithm of both sides, we obtain

$$\ln k = \ln k_0 - E/RT$$

so that a plot of $\ln k$ versus $1/T$ should give a straight line whose slope is $-E/R$. From this Arrhenius plot, the activation energy can be evaluated.

In our preceding paper[4], the time dependencies of the conversions are drawn for the degradation of PS in supercritical n-hexane at 330, 350 and 370°C and at 50 bar. The logarithms of unconverted fractions (1-X) were plotted against the reaction time. From the slope of each straight line, the first-order rate constant was evaluated respectively: 0.0111 min⁻¹ at 330°C, 0.0375 min⁻¹ at 350°C and 0.0693 min⁻¹ at 370°C. The temperature dependency of the first-order rate constant is shown in Fig.1. The activation energy can be evaluated to be 132kJ/mol.

As a reference, the first-order rate constant data for the thermal pyrolysis of PS[5] were also plotted in the same figure. From this Arrhenius plot, the activation energy can be evaluated to be 224kJ/mol, a value close to the reported one by Carniti et al. (195kJ/mol)[6].

It is apparent from Fig.1. that the first-order rate constant of degradation in supercritical water is higher than the others and it would be expected that the degradation in supercritical n-hexane can take place at lower temperatures than the thermal pyrolysis.

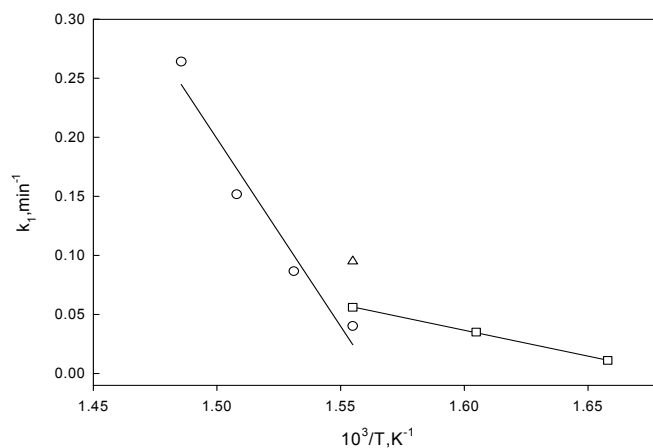


Fig.1. Temperature dependencies of first-order rate constants for the degradations of PS in supercritical n-hexane and water and for the thermal pyrolysis of PS. PS/Supercritical n-hexane ; \triangle PS/supercritical water ; \circ Thermal pyrolysis of PS

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