

## Instrumentation of High Temperature and Pressure Reaction System with Continuous Flow and Its Hyphenation to a Liquid Chromatograph

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A continuous flow-type hydrothermal reaction system, in which both temperature and pressure were rapidly and dynamically controlled, was constructed. It is called a real time high temperature and pressure reaction system (RT-HighTP). The RT-HighTP was hyphenated with liquid chromatograph (RT-HighTP-LC) to achieve prompt analysis of the reaction products. The RT-HighTP system produced stable pressure under the supercritical and subcritical phases (%RSD < 3%). The RT-HighTP-LC was able to change the hydrothermal condition rapidly. The hydrothermal products under four conditions were analyzed within 70 min. Further, the hydrothermal products of lignin was easily taken out using the sample collecting loop and analyzed by an external instrument of GC/MS.

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### Introduction

The unique properties of supercritical fluid attract many scientists and its theory and applications have been investigated well.<sup>1-5</sup> In particular, the hydrothermal reaction is widely noticed because of its possibility of reducing the environmental load as one example of the green chemistry. The hydrothermal reactors can be broadly divided into two categories, *i.e.*, batch and continuous flow types. In the case of batch type reactor, a sealed-reactor containing a sample solution is heated up and the vaporized solvent (*e.g.* water) increases the pressure in the reactor, which is controlled by its inner volume and the amount of vaporized solvent. In the case of a continuous flow type reactor, the pressure is controlled by the backpressure system such as a needle-valve. However, the needle-valve sometimes clogs causing trouble. To improve this disadvantage, we used an extra pump to control the backpressure.<sup>6</sup> Namely, the continuous flow hydrothermal reaction system using two pumps was constructed and this system can dynamically and rapidly control the hydrothermal condition. We named our proposed system as the real time high temperature and pressure reaction system (RT-HighTP). Furthermore, the RT-HighTP was hyphenated with a liquid chromatograph to achieve prompt analysis. The good performance of the hydrothermal reactor-liquid chromatograph (RT-HighTP-LC) concerning the high throughput reaction-analysis was demonstrated.

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### Experimental

#### Apparatus

A schematic diagram of an apparatus used in this experiment is shown in Fig. 1. The apparatus was composed of a hydrothermal reaction part (painted with gray) and an analysis part (painted with white). The hydrothermal reaction and the analysis parts were hyphenated *via* a rotary valve for sample injection (valve B, painted with black). The hydrothermal part was composed of two pumps (LC-10AT, Shimadzu, Kyoto, Japan), an oven (GC-8A, Shimadzu), three rotary valves (Model

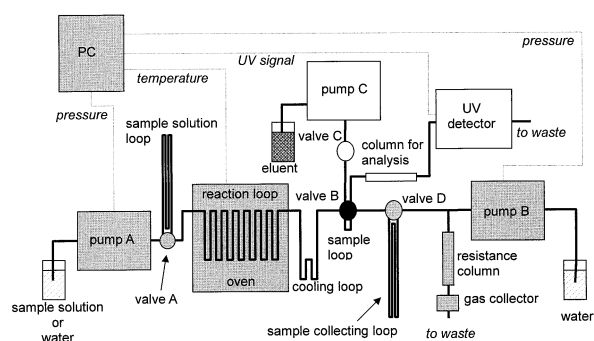


Fig. 1 Schematic diagram for high temperature and pressure reaction system with continuous flow hyphenated with liquid chromatograph (RT-HighTP-LC).

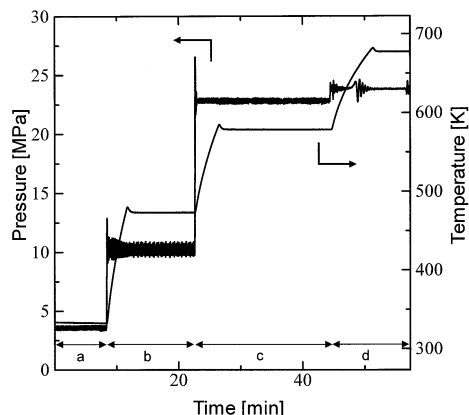


Fig. 2 Variations of pressure and temperature under various hydrothermal conditions. Flow rate of pump A: 0.20 mL/min. Details of four hydrothermal conditions (a to d) are listed in Table 1.

7000, Rheodyne, CA, USA), a reaction loop (stainless-steel tubing, i.d. 0.5 mm, length 10 m), a sample supply tube (stainless-steel tubing, i.d. 0.8 mm, length 5 m), a sample collection loop (stainless-steel tubing, i.d. 0.8 mm, length 5 m), a sample injection loop (stainless-steel tubing, volume 20  $\mu$ L), a resistance column, and a gas collector. The analysis part (liquid chromatograph) was composed of a pump (LC-10AD, Shimadzu), a column (ODS-W, i.d. 2 mm, length 150 mm, Chemco, Osaka, Japan), and an ultra violet detector (SPD-10AVP, Shimadzu). The signals concerning UV absorbance, pump pressures, and oven temperature were recorded with a PC using an A/D converter (K8DL-G16, Omron, Tokyo) with 10 Hz.

#### Procedures

The sample solution for the hydrothermal reaction can be supplied to the reaction loop by two methods. One is a continuous supply, in which the sample solution is stored in the reservoir connected with pump A and is supplied to the reaction loop continuously. In the other method, a sample solution is filled into the sample solution loop connected with valve A, and distilled water is supplied using pump A continuously. The switching of valve A starts the transfer of the sample solution by the flow of distilled water, and the sample solution plug is supplied to the reaction loop.

The reaction temperature, period, and pressure were controlled by the oven, pump A, and pump B, respectively. The reaction period was controlled by the flow rate of pump A, *i.e.*, high flow rate can reduce the reaction period. Pump B controlled the pressure in the reaction tubing by supplying distilled water with constant pressure mode. Namely, pump B is used for the dynamic backpressure system. The water to control the pressure was drained through the resistance column.

The sample solution that has passed through the reaction loop is allowed to fill both the sample loop and the sample collecting loop equipped with valves B and D, respectively. The solution in the sample loop can be directly injected to the liquid chromatograph. Valve C is used to inject the standard sample for the LC. The sample collecting loop for valve D is filled with distilled water before collecting the sample solution. When the collecting loop was filled with the gas, the destructive pressure variation was induced. The sample solution in the sample collecting loop is flushed out by the air and stored at  $-20^{\circ}\text{C}$  before use.

Table 1 Variation in pressure under various hydrothermal conditions

Condition ID	Temperature/ K	Pressure/ MPa	Variation/ MPa	Phase
a	333	3.5	0.3 (8.6%)	Liquid
b	473	10.0	1.3 (13.0%)	Liquid
c	578	22.5	0.6 (2.7%)	Subcritical
d	677	23.5	0.1 (0.4%)	Supercritical

## Results and Discussion

#### Stability of the pressure under various conditions

The stability of the pressure in the reaction loop (pressure indicated at pump B) under various conditions was measured (Fig. 2). Distilled water was used as the test solution. The temperature, pressure, and pressure variation under the stable condition obtained from Fig. 2 are listed in Table 1. The variation in the pressure was less than 1 MPa except under the condition-b. In particular, the pressure under supercritical condition (condition-d) was quite stable. The pressure variation under the condition-b is larger than that under the other conditions, and this instability of the pressure around the hydrothermal condition-b (473 K, 10.0 MPa) was well reproduced. However, the reason for this instable pressure is still not clear. Figure 2 shows the significant pressure variation around 47 min (condition-d). This variation in the pressure may be caused by the phase transition to the supercritical phase. Our RT-HighTP produced four hydrothermal conditions within 60 min and needed only less than 10 min to alter the condition to another.

#### Analysis of hydrothermal products

Methylbenzoate was hydrolyzed and analyzed using the RT-HighTP-LC with four hydrothermal conditions. The hydrothermal conditions for the hydrolysis of methylbenzoate are the same as those in Table 1. As shown in Fig. 3, only methylbenzoate (MB) was detected for condition-a. Namely, methylbenzoate was not hydrolyzed under the condition-a. Under the hydrothermal conditions (b, c, and d), methylbenzoate was partially hydrolyzed to benzoic acid (BA). The hydrolysis of methylbenzoate was suppressed under the supercritical condition (condition-d), whereas that was enhanced under the subcritical condition (condition-c) compared with condition-b (liquid). The suppression was due to the decrease in the ionic product of water ( $K_w$ ) under the supercritical condition. The hydrothermal hydrolysis and the analysis of its products under four conditions were performed within 70 min. The RT-HighTP-LC system was suitable for rapid analysis of the hydrothermal products obtained under various conditions.

Our RT-HighTP-LC system can control the reaction period by the flow rate of pump A. Figure 4 shows the relationship between flow rate (top axis) and the hydrolysis ratio of methylbenzoate. As the *x*-axis, the reciprocal of the flow rate ( $1/V$ ), which is proportional to the reaction period, was used. On the assumption that the density of supercritical water (condition-d) is approximately one-third of that of the standard state water, the value of 10 at *x*-axis is regarded as the reaction period of approximately 6.5 min. As shown in Fig. 4, the low flow rate (long reaction period) clearly enhanced the hydrolysis of methylbenzoate.

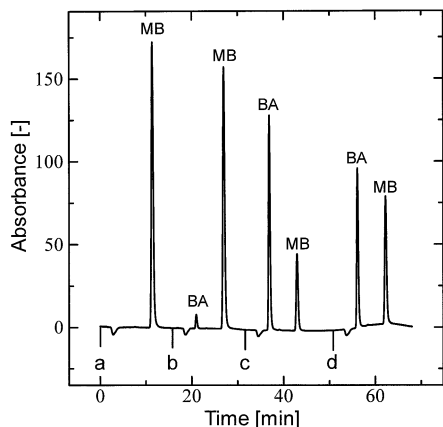


Fig. 3 Rapid analysis of hydrolyzed methylbenzoate under various hydrothermal conditions using hyphenated LC. Peaks for MB and BA are methylbenzoate and benzoic acid, respectively. The characters of a to d under the chromatogram corresponding to each hydrothermal condition, which are the same as in Fig. 2, and their injection times. Chromatographic conditions are as follows: column, ODS (i.d. 1 mm, length 150 mm); eluent, methanol/water (40/60, v/v); flow rate, 0.1 mL/min; detection, UV 254 nm.

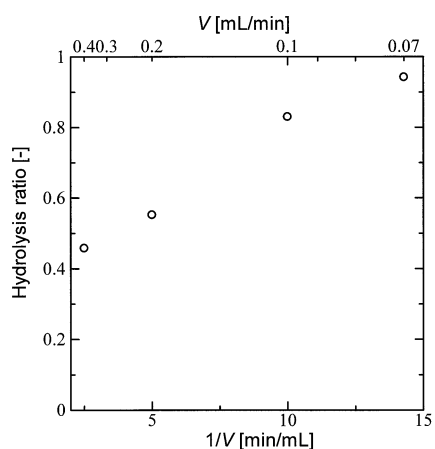


Fig. 4 Relationship between flow rate (reaction period) and hydrolysis ratio of methylbenzoate under supercritical condition (677 K, 23.5 MPa). Experimental conditions except the flow rate are the same as those in Fig. 3.

The RT-HighTP-LC can perform online analysis of the hydrothermal products as demonstrated in Fig. 3. In addition,

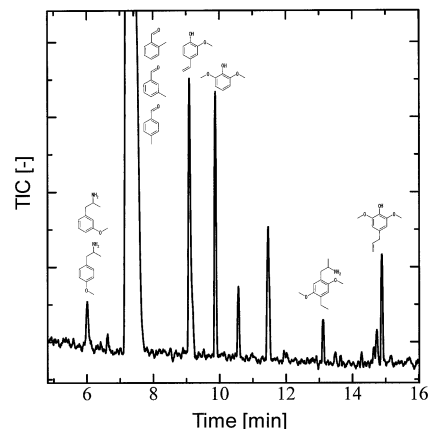


Fig. 5 GC/MS chromatogram of hydrothermal products of lignin. Hydrothermal conditions: 22.5 MPa, 573 K, 0.2 mL/min. GC conditions: column, CBP1 (i.d. 25  $\mu$ m, 25 m, Shimadzu); temperature program, initial 50°C/5 min, 10°C/min, final until 200°C.

the RT-HighTP-LC can take out the hydrothermal products using the sample collecting loop equipped with valve D to perform offline analysis using external analytical instruments. As one instance, the lignin was treated under the supercritical condition, and the hydrothermal products was analyzed by GC/MS (GC-17A/GCMS-QP5050, Shimadzu). Figure 5 shows the chromatogram of hydrothermal products of lignin, in which six peaks were identified. The RT-HighTP system was easily combined with both online and offline analyses.

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