On-line Analysis of Catalytic Reaction Products Using a High-Pressure Tandem Micro-reactor GC/MS

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When a GC/MS system is coupled with a pressurized reactor, the separation efficiency and the retention time are directly affected by the reactor pressure. To keep the GC column flow rate constant irrespective of the reaction pressure, a restrictor capillary tube and an open split interface are attached between the GC injection port and the head of a GC separation column. The capability of the attached modules is demonstrated for the on-line GC/MS analysis of catalytic reaction products of a bio-oil model sample (guaiacol), produced under a pressure of 1 to 3 MPa.

Keywords On-line GC/MS analysis, catalytic fast pyrolysis, hydrodeoxygenation, guaiacol, tandem micro-reactor, restrictor capillary tube

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Introduction

The catalytic fast pyrolysis (CFP) of biomass and waste plastics in an oxygen-free inert environment has attracted much attention throughout the past two decades, because the process is one of the most economically feasible methods to depolymerize constituents of biomass and waste plastics.1–4 The depolymerized species, i.e., pyrolyzates, can be catalytically converted to gaseous and liquid products that are further upgraded to fuels and value-added chemicals.5–6 CFP has been widely studied using various reactor systems, including a single stage reactor7–9 and a tandem reactor combined with GC/MS or a gas sampling bag and cold-trap condensers.10,11 When using a single reactor system, the feedstock and a catalyst are mixed; this mixture is heated in the reactor at the desired temperature under a pre-selected atmosphere.12 In a tandem reactor system in which two independently temperature-controlled reactors are connected in series, the feedstock is pyrolyzed in the 1st reactor and the pyrolysis vapors flow to the 2nd reactor, which contains a catalyst bed.12,13 The pyrolysis vapors are catalytically converted to value-added chemicals in the 2nd reactor. The former and the latter processes are referred to as in-situ and ex-situ catalytic pyrolysis, respectively. In a recent review,11 a detailed comparison between in-situ and ex-situ CFP was described; it is pointed out that the major disadvantage of in-situ CFP is a fixed temperature for both the pyrolysis and catalytic reaction, and this may not be the optimum for the catalyst performances. In contrast, ex-situ CFP, where catalysts are separated from the pyrolyzer, has attracted much attention, since it allows independent control of the pyrolysis and catalytic reaction conditions, such as the temperatures and atmospheres.14,15

The CFP of biomass has been studied under various reaction conditions with different temperatures and pressures.16–18 Liquid fuels, i.e., bio-oils, produced from the fast pyrolysis of lignocellulosic biomass, have a high content of water and oxygen, which cause some undesirable properties, such as poor chemical and thermal stabilities. To reduce the oxygen content in bio-oils, catalytic hydoredeoxygenation (HDO) has been carried out at high pressure under hydrogen atmosphere.16,17 In the case of on-line analysis of products formed in a pressurized reactor interfaced with a GC instrument, the GC column flow rate is directly affected by the reactor pressure, which results in different retention times of the separated products from those obtained under a standard condition. In this study, mass flow controllers and back-pressure regulators were introduced in a tandem micro-reactor system to control the gas flow rate and the reactor pressure. In addition, a restrictor capillary tube is attached between the GC injection port and the head of a GC separation column to maintain a constant column pressure irrespective of the reactor pressure; then, the effect of the size of the restrictor capillary tube on the GC separation is examined.

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On-line GC/MS analysis of catalytically converted products is also demonstrated under different reactor temperatures and pressures using guaiacol (2-methoxyphenol) as a bio-oil model sample.

**Experimental**

**Reagents and chemicals**

Guaiacol of analytical grade was obtained from Sigma-Aldrich (Seoul, Korea) and used without further purification. As for Pt/HY catalyst, Pt was incorporated on the proton-exchanged Y zeolite support (HY; Si/Al = 40), which was obtained from Zeolyst International (Conshohocken, PA, USA). The Pt content was 0.5 wt% and the catalyst was calcined at 500°C for 3 h before use. The detailed preparation and characterization procedures of Pt/HY catalyst were described previously.\(^{18}\)

**Apparatus**

**Reactor for catalytic fast pyrolysis.** The details of the tandem micro-reactor (Rx-3050TR, Frontier Laboratories Ltd., Koriyama, Japan) were described in our previous studies.\(^{19,20}\) In brief, the tandem micro-reactor is composed of two vertical-type continuous-flow tubular reactors connected in series, which is directly interfaced to a GC split injection port, as shown in Fig. 1, right side. Both reactors can be controlled independently in the temperature range of 40 to 900°C under isothermal (1°C increment) or non-isothermal (1 - 200°C/min) conditions. The 1st reactor is used for the pyrolysis of samples. A solid, liquid or solid-liquid mixture sample is put in a deactivated stainless-steel sample cup, and the sample cup is free-fallen into the preheated furnace of the 1st reactor. The sample is vaporized at a selected temperature and the pyrolysis vapors are swept by a carrier gas to the 2nd reactor. In the 2nd reactor, a quartz reactor tube (i.d., 3 mm; o.d., 4 mm; length of catalyst bed, 40 mm) packed with a catalyst is set and the pyrolysis vapors are catalytically upgraded at a desired temperature. The catalytically upgraded products formed in the 2nd reactor are separated by a UA-5 GC column (30 m, 0.25 μm film thickness; Frontier Laboratories Ltd.) after cryo-focusing at liquid nitrogen temperature by a MicroJet Cryo Trap (MJT-1030E, Frontier Laboratories Ltd.) and detected by a MS detector.

**Design of a flow control system for pressurized catalytic reaction.** A newly developed flow control system for a pressurized catalytic reaction is also schematically shown in Fig. 1, left side. The carrier gas flow is controlled by the mass-flow controller, MFC1, and the reactor pressure is controlled by a back-pressure regulator, BP1, downstream of the reactors. A by-pass pre-pressurization module is added parallel to the MFC1, which is used to quickly pressurize the reactors. As the pressure of the reactors reaches near to a set point, the pre-pressurization line is closed by 3-way valves, and the desired pressure is maintained by BP1. Additional reactant gas can be introduced between the 1st and 2nd reactors, and its gas flow is controlled by the mass-flow controller, MFC2. This gas line can also be used as a split vent to control the amount of pyrolysis vapors that are swept from the 1st to 2nd reactor. The head pressure of the GC separation column should be independent of the pressure of the reactors, and a constant flow rate of the carrier gas should be kept in the GC separation column to identify separate products based on the retention time and to obtain sufficient separation efficiency. To meet this demand, a restrictor capillary tube is placed between the GC injection port and the GC separation column in combination with an open split interface,\(^{21}\) whose pressure is controlled by the back-pressure.
The combination of a flow controller and a back-pressure regulator allows the tandem micro-reactor to be operated at a constant pressure and a constant gas flow passing through the catalytic reactor and the GC separation column. Restrictor capillary tubes (R1, R2, and R3) are used to control the pressures of any gas flow within a proper range.

**Results and Discussion**

**Optimization of the restrictor capillary tube to control the head pressure of the separation column**

When CFP experiments are done under high pressure, the pressure of the reactors is directly related to the head pressure of the GC column, and the retention time will decrease as increasing the reactor pressure. To obtain sufficient GC separation efficiency, and to identify the reaction products based on the retention time, it is necessary to keep a constant carrier gas flow at the head of the GC column. The constant flow rate of the carrier gas can be maintained by attaching a restrictor capillary tube and an open split interface to the inlet of the GC column in combination with the use of BP2, as shown in Fig. 1.

The carrier-gas flow rate depends also on the GC oven temperature due to the temperature dependency of the gas viscosity. The relationship between the vent flow rates at BP1 and BP2 and the GC oven temperature under various pressures was examined by using restrictor capillary tubes whose length was varied to explore the optimum length. The restrictor capillary tubes were deactivated stainless tubes (i.d., 0.05 mm; length, 40, 60, 80 or 100 cm); the total flow rate and the column flow rate of the carrier gas were set as 100 and 1 mL/min, respectively. The results are given in Figs. 2 and 3, respectively, for He and H2 carrier gases with varying the reactor pressure from 1 to 3.5 MPa. In each figure, the upper and lower curves represent the flow rates at BP1 and BP2, respectively. As shown in Figs. 2 and 3, a gradual increase and decrease in the vent flow rate were observed for BP1 and BP2, respectively. These
gradual changes in the vent flow rate indicate that BP1 and BP2 properly regulate the pressure at the inlet of the GC column against any changes in the reactor pressure and the GC oven temperature. Changes in the vent flow rate are more gradual for a He carrier gas compared to a H2 carrier gas, as shown in Figs. 2 and 3, which can be ascribed to the higher viscosity of He than that of H2.22 The longer restrictor capillary tubes (80 and 100 cm) do not show sufficient regulation for He carrier gas, especially under low reactor pressures (1 and 2 MPa), as shown in Fig. 2. From these results, the appropriate length of the restrictor capillary tube is in the range of 40 to 60 cm to control the column flow rate properly for both the He and H2 carrier gases.

Catalytic conversion of guaiacol over Pt/HY catalyst under H2 atmosphere

To examine the effectiveness of the restrictor capillary tube for locking the GC retention time under varied temperatures and pressures, the catalytic HDO reaction of guaiacol over 0.5 wt% Pt/HY catalyst (Si/Al = 40) was examined under a mixed H2/He atmosphere using a restrictor capillary tube (i.d., 0.05 mm; length, 50 cm). Guaiacol is one of the representative model compounds of bio-oils obtained from the fast pyrolysis of biomass.14,18,23 The upgrading of bio-oils has attracted much attention to obtain value-added chemicals by HDO, which has been carried out at high hydrogen pressure (1–5 MPa) using fixed-bed reactors.24,25

First, the effect of the reaction temperature on the catalytic conversion of guaiacol was examined under a mixed H2/He carrier gas at 1 MPa by varying the reaction temperature from 200 to 300°C; the results are given in Fig. 4. Each peak in Fig. 4 was assigned based on the retention time and its mass spectrum. Compared to the reaction without a catalyst (Fig. 4, A), the increase in the amount of catalytically converted products can be easily recognized in the gas chromatograms (Fig. 4, B to D). The main product is cyclohexane (peak c); it can be easily seen that the conversion is maximized at 250°C. Other peaks are assigned to be methanol and water (peak a), methyl cyclopentane (peak b), methyl cyclohexane (peak d), phenol (peak e), and unreacted guaiacol (peak f). The production of these compounds was also reported previously based on the catalytic HDO reaction of guaiacol over the same 0.5 wt%Pt/HY catalyst using a batch reactor under the reaction conditions of 250°C and 4 MPa;18 it was suggested that the catalytic reaction of guaiacol proceeded by HDO of oxygenated substituents, followed by hydrogenation of the aromatic ring.

Next, the effect of the reaction pressure on the catalytic conversion of guaiacol was examined at 250°C by varying the reaction pressure from 1 to 3 MPa; the results are given in Fig. 5. It can also be seen that the peak intensity of cyclohexane with catalyst does not change much irrespective of the reaction pressure (Fig. 5, B to D). Such a tendency of the pressure effect was previously reported based on the HDO reaction of guaiacol using Ni-based catalysts, where only a slight effect was observed in the pressure range of 0.17 to 1.5 MPa.26 In conclusion, as can be seen in Figs. 4 and 5, that the retention time of each peak in the chromatograms of the catalytic reaction products is unaffected by changing the temperature and

![Fig. 3 Relationship between the vent flow rates at BP1 (upper curve) and BP2 (lower curve) and GC oven temperature for the H2 carrier gas. Length of a restrictor capillary tube: (a) 100, (b) 80, (c) 60, (d) 40 cm. Pressure: (●) 1, ( ○ ) 2, (□) 3, ( △) 3.5 MPa. Column pressure, 34 kPa; flow rate, 1 mL/min; total flow rate, 100 mL/min; split ratio, 1/100; column, UA*-5-30M-0.25F.](image-url)
pressure of the reactors; also, the identification of products can be easily done by using the retention time and mass spectra.

It can be said that the use of a proper restrictor capillary tube in the tandem micro-reactor system coupled to GC/MS is quite effective for on-line analysis and screening of both catalysts and the experimental conditions under different reaction pressures in catalytic fast pyrolysis.

References