Development of the batch-type and flow-type supercritical fluid biomass conversion systems

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Recently, the supercritical fluid treatment has been considered to be an attractive alternative in science and technology as chemical reaction field and the solvent for extraction. Especially, it has been proven that the cellulose was hydrolyzed in the supercritical water to the glucose in short time. Therefore, the supercritical fluid is expected as a solvent for converting biomass into the valuable substances. In our laboratory, a batch-type and two flow-type supercritical fluid biomass conversion systems were developed to study the chemical conversion of various biomass to liquid fuels and useful chemicals.

Introduction

The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. Therefore, it is expected that the chemical reactivity can be high in it. In addition, ionic product and dielectric constant of supercritical water, which are important parameters for chemical reactions, can be continuously controlled by regulating pressure and temperature. Therefore, the supercritical water can be realized from the ionic reaction field to the radical reaction field. For example, ionic product of the supercritical water can be increased by increasing pressure, then the hydrolysis reaction field, in which the cellulose is rapidly hydrolyzed to the glucose, is realized. However, glucose obtained from cellulose hydrolysis was further decomposed rapidly in supercritical water due to its critical temperature to be high [1]. Therefore, the reported yields of glucose from the supercritical water treatments of cellulose were low in general, and millisecond treatment will be required to obtain the high yield of hydrolysis products. In our laboratory, therefore, methanol was also selected as the solvent for supercritical treatment of biomass in which the critical temperature (T_c) is 239. and the critical pressure (P_c) 8.09MPa, can offer the milder conditions of the reaction than those of water (T_c=374., Pc=22.1MPa). In addition, it has been proven that the vegetable oil could be converted efficiently into biodiesel fuel by transesterification and esterification reactions in the supercritical methanol [2][3]. In our laboratory, three supercritical biomass conversion systems , a batch-type system and two flow-type systems for liquid-liquid reaction and solid-liquid reaction, have been developed to convert various biomass resources into valuable substances.

Characteristics and applications of the systems

The characteristics of the developed systems are shown in table.1. These systems should be used properly in proportion to type of the biomass and purpose of the conversion. The details of these systems are described in the following.

The batch-type supercritical fluid biomass conversion system

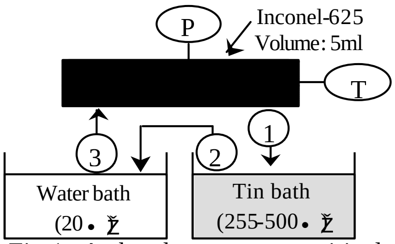

Fig.1 A batch-type supercritical biomass conversion system. (P: pressure monitor, T: temperature monitor)

The system which has a batch-type reaction vessel is shown in Fig.1. The system was developed to study the chemical conversion of the solid and liquid biomass. The reaction vessel with a 5ml volume is made of Inconel-625. This system can cover a range in pressure and temperature up to 200MPa and 500., respectively. To start a treatment, 5ml of solvent was fully fed with the biomass sample. Then the reaction vessel was quickly heated by immersing it into the tin bath preheated at an adequate temperature and maintained under supercritical conditions. After an adequate reaction time, the reaction vessel was moved into the water bath to quench the reaction. Advantages of this system are that the solid substances can be treated and that the long-time treatment over 10min can be made. However, about 10-15sec is needed for achieving the supercritical conditions. Thus, a pyrolysis of biomass occurs to some extent in this interval. Besides, the pressure which depends on the temperature of the solvent is uncontrollable, unless the inert gas is used to control in the reaction vessel. This system has been applied for the chemical conversion of wood flour, avicel, starch, chitin, rapeseed oil and so on. For example, over 90% of wood flour was decomposed and liquefied in methanol after 30 min supercritical treatment at 350.-43MPa [4]. In addition, the rapeseed oil was converted into biodiesel by methyl esters formation in the supercritical methanol [2].

The flow-type system for the liquid-liquid reaction Fig.2 shows the schematic diagram of the system which was developed for treatment of liquid and liquid. Major sections of the system consist of pump stations, preheaters, supercritical treatment tube which is constructed from Hustalloy C276 with 1250cm in length and 1.2mm in inner diameter, cooling system and separatory tank. The flow rates of the pumps and the pressure of the system can be controlled up to 10 ml/min and 50MPa, respectively. Before a treatment, the system was pressurized up to set point over the critical pressure of the solvent. Subsequently, the solvent which was preheated over the critical temperature was mixed with the biomass sample in the solvent at the entrance of the treatment tube. The biomass sample in the solvent was also preheated up to an adequate temperature in which the sample was stable, for example, about 100-150.. By this method, it is possible to expose the biomass sample in the supercritical fluid within 1sec. The sample in the solvent was conveyed through the treatment tube in which the temperature was kept to be an adequate temperature (>T_c) by the salt bath. The treatment time can be accurately controlled by controlling the flow rate of the pumps. To quench the reaction, the reactant was immediately cooled by the circulating water and ethanol. Advantages of this system are that the controllability and its accuracy of the treatment time, pressure and temperature are achieved. In addition, the continuous treatment of the sample, which is an advantage for the industrialization, is possible. However, a large quantity of the solvent is required for a treatment compared with the batch-type system. The disadvantage of this system is a limitation of the solid sample size less than 10.m, or only for liquid biomass. This system has been applied to the supercritical methanol treatment of the rapeseed oil for biodiesel fuel production as in the batch-type system[3].

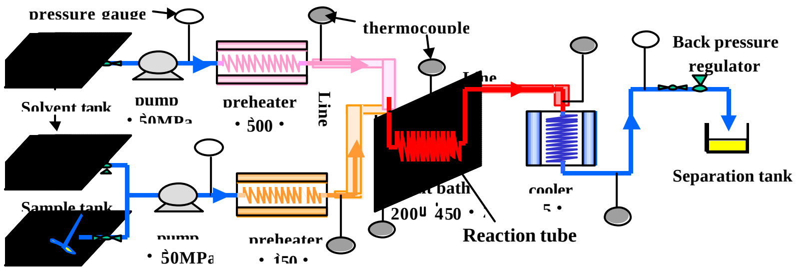

Fig.2. A flow-type system for the liquid-liquid reaction.

The flow-type system for the solid-liquid reaction This flow-type system was newly developed in order to enable the treatment of the solid biomass larger than 10.m in size. The slurry circulatory system with a high-pressure circulating pump was employed to keep stirring the slurryed sample in the solvent in order to prevent the precipitation of the sample. The slurryed sample was injected into the treatment tube by the slurry injector with the solvent of the supercritical state to start a treatment. This flow-type system has two treatment tubes, one is the 1cm length which is used when the reaction time is very short, another is 7m length which is used when the reaction time is longer. In case of using the 1cm tube, to quench the reaction immediately, the amount of solvent was injected into the reactant coming out from the tube. This flow-type system has been applied to study the chemical conversion of wood flour and avicel [5].

Table.1 Characteristics of the developed supercritical biomass conversion systems.

	Batch-type	Flow-type	
		liquid-liquid	Solid-liquid
Temperature [.]	255-500	200-450	200-450
Pressure [MPa]	1-280	1-50	1-45
Treatment time	>1sec	1sec-10min	1sec-10min
Sample	liquid and solid	liquid	solid (slurry)
Quantity of solvent	appropriate	large	large

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