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Glucose reactions within the heating period and the effect of heating rate on the reactions in hot compressed water

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Abstract—Glucose reactions were conducted in hot compressed water (473–773 K, 4–40 MPa) by means of a batch-type reactor. The reactions in the heating period (about for 60 s) were observed. More than 80% of the glucose was consumed in the heating period above 573 K. Gasification of glucose was promoted with increasing temperature. The effect of heating rate (from 4.2 to 15.8 K/s) on glucose conversion was also examined, and gasification of glucose was enhanced with increasing the heating rate.

Keywords: Glucose; Batch reactor; Hot compressed water; Gasification; Heating period; Heating rate

1. Introduction

Biomass conversion in hot compressed water is one of the candidates for a biomass refinery technique because biomass reactions such as the conversion of cellulose into glucose and its oligomers,[1,2] the conversion of oligomers and glucose into useful chemicals,[3–13] and the gasification of glucose into H_2 and CH_4,[14–35] effectively proceed in the media. For biomass cascade utilization, a compound from biomass has to be transformed into important chemicals. Glucose can be selectively produced from cellulosic biomass, and it becomes the starting material of the biomass refinery because glucose is the monomer unit of cellulose, which is the most abundant organic compound on the earth and is the major component of plant biomass. Thus, the conversion of glucose into chemicals will be an alternative process to petroleum chemistry and is desirable for a sustainable feedstock.

The reaction mechanism of glucose in supercritical water (SCW) was studied by Kabyemela et al.[3–6] They used a flow apparatus, almost without a heating period, to evaluate the reaction rate. As a result, the primary reactions of glucose were found to be as follows (Fig. 1): (1) glucose isomerization into fructose via keto–enol tautomerization, (2) glucose dehydration into 1,6-anhydroglucose, and (3) glucose decomposition into aldehyde and ketone via retro-aldol condensation. Further, (4) dehydration of the tautomerization intermediate and fructose produce 5-hydroxymethyl furfural (HMF). This reaction mechanism can typically be applied to the reaction that proceeds in a rapid heat–flow apparatus. Sinag et al.[10,12] and Dinjus and Kruse[36] studied glucose decomposition in SCW. They proposed a relatively simple reaction mechanism for glucose as shown in Figure 2. According to their reaction scheme, glucose converts into furfurals and acids/aldehydes in parallel. Further conversion of furfurals leads to acids/aldehydes and phenol formation. Acids and aldehydes are precursors of the gaseous compounds. Furfural formed through dehydration is shown in Figures 1 and 2. Further dehydration of furfural gives phenols. In contrast, acids and aldehydes are produced by bond-breaking reactions. This mechanism is quite simple; however, it tells us that the glucose reaction mainly proceeds via dehydration or bond breaking. The predominance of

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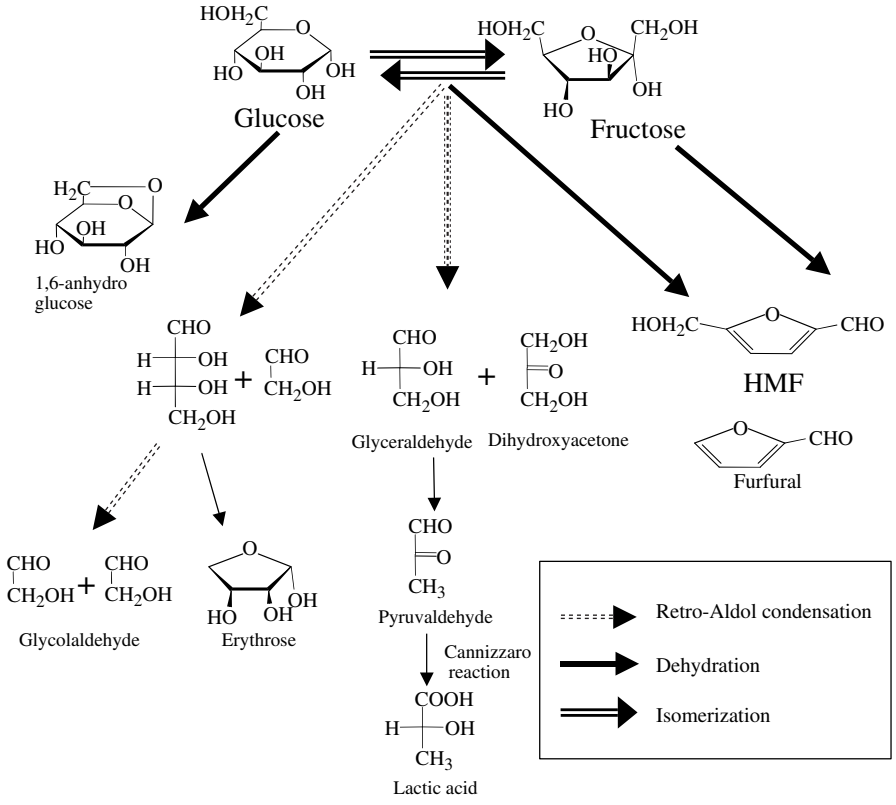

Figure 1. Primary reaction pathways of glucose in supercritical water.

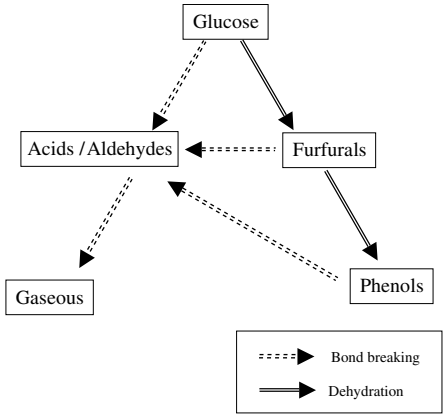

Figure 2. Simple reaction pathways of glucose reaction including secondary or higher reactions in supercritical water.

the two pathways (dehydration and bond breaking) can be estimated from the yields of the key compounds such as furfurals, acids, aldehydes, phenols, and gaseous products.

Most of the biomass is solid under ambient conditions. Therefore, understanding biomass reactions in batch and semi-batch reactors is important for the establishment of a biomass refinery process. One of the characteristics for batch and semi-batch systems is that they have a non-steady-state stage, namely heating up (this period is called 'heating period' in this study) and cool down of the reactor. There are several studies on the effect of this non-steady-state stage on the glucose and cellulose reactions.[2,13,37] Ehara and Saka[2] conducted the experiments of cellulose conversion in supercritical water with a batch and a flow apparatus. In the batch system, the heating period was only 10 s from room temperature to 653 K, and the reaction time was 2–8 s. Even at the shortest reaction time, they obtained a lot of decomposition products such as dihydroxyacetone, glycolaldehyde, levoglucosan, and so on. This means glucose reactions rapidly proceed at 653 K. They also confirmed the rapid reaction of cellulose and glucose using the flow apparatus at the reaction time below 0.5 s. From this study, the effect of the heating period on glucose reaction was not clear. Matsumura et al.[37] investigated the reaction within the heating period. They focused on the effect of heating rate (how fast the temperature of the reaction mixture increased) on gasification of glucose in supercritical water. They confirmed that higher heating rates brought higher gasification and higher cold gas efficiency. In this report, they only focused on gasification, and thus the effect of the heating period on the other glucose reactions was not shown. Sinag et al.[13] observed the effect of heating rate on the product distribution of glucose reaction in supercritical water. They conducted experiments at 1 K/min (0.0167 K/s) and 3 K/min (0.05 K/s) and reported that the acids production and gasification were enhanced