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Catalytic gasification of mannose for hydrogen production in near- and super-critical water

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ABSTRACT

Hydrothermal decomposition of mannose (8 wt.%) in near- and super-critical water was investigated at 500–700 °C and 20.0–42.5 MPa with a reaction time of 1 h in the absence and presence of alkali catalyst (K_2CO_3). Gaseous products, aqueous products, and residue were observed in the batch reactor. The produced gases were carbon dioxide, methane, hydrogen, carbon monoxide, and C_2–C_4 hydrocarbons. The effect of operating parameters (temperature and pressure) on the product distribution was examined in the absence and presence of potassium carbonate. The gaseous product yields were compared with the theoretical equilibrium values that are estimated by Gibbs free energy minimization. In the absence of catalyst, the hydrogen yield was 5.82 mol H_2/mol mannose at 700 °C and 20.0 MPa. At this condition, theoretical equilibrium yield of hydrogen was found as 5.78 mol H_2/mol mannose which was very close to the experimental value and addition of K_2CO_3 increased the hydrogen yield to 10.34 mol H_2/mol mannose. The hydrogen yield increased with increasing temperature and decreasing pressure. Acetic acid was the major component of the aqueous product in gasification of mannose.

1. Introduction

Supercritical water (SCW) behaves like a non-aqueous fluid dissolving nonpolar compounds. Many of organic compounds, (alkanes and aromatics) and gases are completely dissolved in supercritical water, resulting in a single phase [1]. However, the solubility of inorganic compounds decreases sharply at supercritical conditions of water [2]. Reactions in SCW proceed by free-radical or ionic mechanisms depending on temperature and pressure. Ionic reactions prevail at sub-critical temperature and very high pressures (high density) while free-radical reactions dominate at high temperatures (low density) [3].

Supercritical water gasification (SCWG) is a novel technology for the conversion of the wet biomass and waste streams to hydrogen or methane-rich gas and valuable aqueous product assessable as chemical feedstock. Drying process is eliminated in SCWG and water content of biomass is beneficial as being reaction medium, catalyst and organic solvent at supercritical conditions. Lu et al. were gasified wet biomasses such as wood, sawdust, rice straw and shell, corn cob and stalk, wheat and sorghum stalks in supercritical water. Corn cob, wheat and sorghum stalks were easily gasified than other biomasses selected. The difference in distribution of gaseous and liquid product was explained by varying biomass composition [4]. Biomass mainly composed of cellulose, hemicellulose, lignin, and extractives. The chemical structure of lignin is not well known and hemicellulose is a very complex compound due to changing ratios of its monomers depending on the plant type. Studies on supercritical water gasification of biomass were performed with model compounds to highlight the reaction mechanisms and understand the attitude of the main constituents in the gasification process. Many researchers intensified their research on glucose, which is a monomer of cellulose [5,6]. Sinag and co-workers [6–8] proposed the reaction mechanisms for glucose decomposition in supercritical water. Determining the yields of the intermediate compounds' provides information on which reaction pathways (dehydration or bond breaking) dominate at the operating conditions. Dehydration reactions take place during conversion of glucose to phenols through furfurals. Phenols and furfurals can also degrade into acid/aldehydes which can further decompose to gaseous products through bond breaking reactions.

Hemicellulose composed of pentoses (usually xylose and arabinose) and hexoses (galactose, glucose, and mannose). Compared with cellulose, hemicellulose is more amorphous and it is easier to hydrolyze into its monomer sugars. There are only few

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Nomenclature

C_i	concentration of component 'i' in the gas product (vol.%)
n_i	number of carbon atoms of component 'i' in the gas product
m	weight of mannose in feed (g)
M	molar mass of carbon (g mol^{-1})
P	pressure (Pa or MPa)
R	universal gas constant, 8.3143 J mol^{-1} K^{-1}
T	temperature (K)
V	volume of gas product under ambient conditions (L)
$\bar{V}$	volume of aqueous product under ambient conditions (L)
w	carbon content of mannose (wt.%)
TOC_{aq}	total organic carbon content of the aqueous product (g L^{-1})
TOC_{RE}	total organic carbon content of the residue (wt.%)
K	weight of residue (g)

studies on model compounds of hemicellulose. Srokol et al. studied the hydrothermal treatment (340 °C, 27.5 MPa, 25–204 s) of dilute (50 mM) solutions of glucose and some other monosaccharides (fructose, mannose, galactose and arabinose) to obtain more insight about the reaction paths [9]. Yu et al. reported that the decomposition product distribution of 6-carbon sugars is not considerably different while quantitative variation was obtained due to difference in the structure of sugars and degradation rates. The decomposition products of arabinose are mainly glycolaldehyde and 2-furaldehyde, which are also same as the main products of xylose decomposition [10].

High yields of hydrogen and low amounts of solid residue (char and tar) can be obtained by using catalysts in SCWG. Common types of catalysts that have been used in SCWG are the metal catalysts [6,11], alkali catalysts [6], and carbon based catalysts [12–14]. The effects of heating rate and catalyst (K_2CO_3 and Raney Nickel) on SCWG (500 °C, 30 MPa and 1 h of reaction time) of glucose were investigated in a batch reactor. They found that the relative yields of H_2 doubled with addition of K_2CO_3 and the relative yields of CH_4 increased in the presence of nickel [6].

The reactor types have great effect on product distribution in SCW. The gasification products are exposed to long residence time in the batch-type reactor and therefore the glucose easily decomposes to oil and char [15,16]. In flow-type reactor system, heating, treating, and cooling times are shorter so the degradation of the sugar products is less.

In this paper, hydrothermal gasification of mannose which is a model compound for hemicellulose and C-2 epimer of glucose was investigated in a batch reactor system. The temperature and pressure ranges were 500–700 °C and 20.0–42.5 MPa at a reaction time of 1 h. The reactions were performed in two cases: in the absence and presence of K_2CO_3. The main objective of this research is to highlight the effect of process parameters (temperature and pressure) on the yield and composition of the gaseous and aqueous products in both cases. The results are compared with the studies of other model substances (glucose, fructose, xylose, etc.) of cellulosic biomass. This work is promised to make a contribution with the studied range of experimental conditions. However, analysis of aqueous and gaseous product will provide fundamental insights on the reaction network underlying the conversion of mannose in near- and super-critical water at broad temperature and pressure ranges.

2. Experimental

2.1. Samples

D(+)-Mannose of 99% purity and other analytical reagents were obtained from Merck, Darmstadt, Germany.

2.2. Reactor system

The supercritical water gasification of mannose was carried out in a batch reactor which has an inner volume of 100 mL. Batch reactor is made of stainless steel (SS316) and constructed to endure 50 MPa at 650 °C. Detailed information on batch reactor system was given in a previous study [17].

2.3. Experimental procedure

Before starting this study, pre-experiments were performed to obtain desired pressure at operating temperature by adjusting the amount of feed. Firstly, the amounts of water and mannose that put into reactor were identified. The specified amount of mannose (between 0.55 and 1.60 g) was weighed out into the reactor, and a known volume of water (12.5 times of mannose amount) or solution of K_2CO_3 was added. Mannose concentration in the feedstock was 0.45 M (equals to 8 wt.%). The catalyst solution of K_2CO_3 in an amount corresponding to 10 wt.% of the mannose amount was prepared. Air inside the reactor was purged by using nitrogen gas. The reactor was heated with a heating rate of 6 K min^{-1} to the desired temperature. Operating pressure was reached at set temperature and the reaction time was 1 h. This time represents the specified time that the reactor was held at set temperature constantly. After completion of the reaction time, the reactor was cooled down to ambient temperature by using fans. The gaseous product passed through a gasometer to measure volume and they were sampled by using gas tight syringes. Deviation in the volume of gaseous product was calculated as ±10%. The inside of the reactor was washed with water and then filtered to separate aqueous product and solid residue. The pH of aqueous products was lowered to 2 by addition of 1–2 drops of concentrated sulphuric acid which was required to inhibit ionization of organic acids. Aqueous products were stored in a refrigerator at 4 °C. Detailed explanation on analysis of the gaseous, aqueous and solid products was given in the Section 2.4.

2.4. Product analysis

2.4.1. Gaseous product analysis

HP 7890A gas chromatography was used to analyze composition of the gaseous products (H_2, CO_2, CO and C_1–C_4 hydrocarbons). Gas chromatography was equipped with 3 detectors (FID–TCD–TCD) and serially connected 7 columns. Technical features and operating conditions of gas chromatography were given in Table 1. The standard deviation for the results of gas composition was calculated to be ±2%.

2.4.2. Aqueous product analysis

Total organic carbon (TOC) content of aqueous phase was analyzed by a TOC analyzer (Shimadzu TOC-V_{CPH}, Japan). Concentrations of the compounds (carboxylic acids, aldehydes, ketones, furfurals and phenols) in the aqueous products were analyzed by high performance liquid chromatography (HPLC, Japan). All HPLC analyses were carried out using a Shimadzu LC-20A series liquid chromatography device equipped with an Inertsil ODS-3 column. The HPLC system consisted of a DGU-20AS degassing module, LC-20AT gradient pump, CTO-10ASVP chromatography oven and SPD-20 multi-wavelength ultraviolet detector. Analysis of calibration standards repeated for 5 times and calibration