

Hydrothermal upgrading of biomass: Effect of K_2CO_3 concentration and biomass/water ratio on products distribution

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Abstract

Catalytic hydrothermal treatment of wood biomass was performed at 280 °C for 15 min in the presence of K_2CO_3 with different concentrations and biomass/water ratio (thermal). Oil products were extracted from both liquid and solid portion by different solvents and analyzed them individually. The biomass to water ratio has an important effect on product distribution and composition of oil products. Oil 1 (ether extract) with K_2CO_3 contained mainly phenolic compounds. Benzenediol derivatives were observed with 0.94 M K_2CO_3 concentration and they were not formed at lower concentrations (0.235 and 0.47 M). The decrease of solid residue was achieved to 4% with 0.94 M K_2CO_3 at 280 °C for 15 min. The volatility distribution of hydrocarbons (ether extract) were characterized by using C–NP gram. The distribution of oxygenated hydrocarbons changed depending upon the biomass to water ratio and concentration of K_2CO_3 solution.

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1. Introduction

The world reserves of economically exploitable fossil organic raw material (oil, gas, and coal) are limited and the expected growth of the world population (7 billion today to 10–14 billion in 2040 cf. UN estimates) is increasing rapidly. Under these circumstances, the sustainable growth scenario requires switching from fossil fuel to renewable forms of energy and organic raw material. Biomass is renewable and alternative energy source for obtaining fuel and valuable chemicals. There are various technologies and processes reported for the utilization of biomass as raw material for organic materials and for energy applications. Biomass can be converted into H_2 and medium heating value gas (Ferdous et al.,

2001), and for other applications such as catalyst support (Yamada et al., 2001). Biomass was also utilized for the preparation of nano-crystalline metal oxide catalysts (Muto et al., 2003). There have been various processes for utilization of biomass as an alternative energy resource. It was reported that the oil yield was about 18% at 650 °C with a 30 °C min⁻¹ heating rate. Biomass liquefaction for liquid fuel was carried by some solvents such as ethylene-glycol (Rezzoug and Capart, 2002), tetralin (Yan et al., 1999), and methanol. Hydrothermal process has a special importance, as water is unique and environmentally benign solvent. Direct liquefaction of wood by catalyst was carried out in the presence of K_2CO_3 (Ogi et al., 1985; Yokayama et al., 1986). It was reported that a marked catalytic effect of potassium carbonate was observed. Although separation and extraction procedure is the heart of biomass liquefaction, previous studies (Ogi et al., 1985; Yokayama et al., 1986; Minowa et al., 1997, 1998a,b;

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Saisu et al., 2003) did not concern an effective separation and extraction procedure to get the light and heavy products separately. Thus, the oil obtained in these studies can not be used either as a feedstock or fuel candidate. The decomposition of cellulose and glucose in hot-compressed water under catalyst-free conditions was studied (Minowa et al., 1998a,b). It was reported that in the range of 260–300 °C, the cellulose decomposes quickly, and the formation of oil, gas and char started. The effect of Na₂CO₃ on the decomposition of cellulose was also investigated (Minowa et al., 1997). However, we could not find an effective separation method with the detailed products distribution, effect of solvent (water) and catalyst concentrations on the compositions of liquid hydrocarbons (oil products) during the hydrothermal treatment of cellulose. In our earlier reports, affect of various reaction parameters (Karagoz et al., 2004a,b) and Rb and Cs carbonates for the production of phenols (Karagoz et al., 2004a,b) from wood biomass carried out. It has been reported in the literature that the use of K₂CO₃ was found to be effective catalyst for producing phenolic compounds during hydropyrolysis of glucose (Sinag et al., 2003). In the present investigation, the effect of biomass to water ratio, effect of K₂CO₃ solution concentration on the quantity and qualitative differences of products and their distribution with a systematic approach for the separation of products and identification compounds at different stages is reported.

2. Experimental

2.1. Materials

Wood biomass (sawdust from pine) used in this study was obtained from Yonebayashi Milling Co., Ishikawa prefecture, Japan and used as received. Ash content was measured by TGA analysis (TGA-51; Shimadzu). The solvents (acetone, ether, ethyl acetate) and base catalyst (K₂CO₃) were purchased from Wako Chemicals, Japan and used as received.

2.2. Experimental procedure

Hydrothermal liquefaction experiments were conducted in a 200 ml TaS-02-HC type autoclave at 280 °C for 15 min for all the runs used in the present investigation. Thermal run was also performed in the absence of catalyst (only water). Effect of biomass ratio to water was performed in the absence of catalyst. In a typical catalytic hydrothermal liquefaction experiment, the reactor was loaded with 5 g (dry basis) of wood biomass and 30 ml of alkaline solutions (different concentrations of K₂CO₃). The reactor was purged five times with nitrogen to remove the inside air. Reactants were

agitated vertically at 60 \cong cycles/min using stirrer as shown in Karagoz et al. (2004a,b). The temperature was then raised up to 280 °C at heating rate of 3 °C/min and kept for 15 min at 280 °C. After the reaction time, the reactor was cooled down to the room temperature by fan. The procedure for separation and extraction of reaction products are described in Scheme 1. The gaseous products were vented, as there were no significant changes in the composition of gaseous products observed in our earlier reports (Karagoz et al., 2004a,b). The solid and liquid products were rinsed from the autoclave with ion-exchanged water, then acidified to pH \sim 1–2 with HCl (1.7 M) covered and kept in the refrigerator overnight (12 h). Solid and liquid products were separated by filtration under vacuum for 15 min. During filtration, 100 ml of ion-exchanged water were used for washing solid products. The liquid portion was extracted with equal quantity of diethyl ether (600 ml). The ethereal solution thus obtained was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was weighed and designated as oil 1. The water phase was further extracted with equal quantity of ethyl acetate (200 ml). The ethyl acetate solution thus obtained was dried over anhydrous sodium sulfate. Upon removal of ethyl acetate under reduced pressure, this fraction was weighed and designated as oil 2. After extraction, the remaining water phase contains the water-soluble hydrocarbons (WSH).

Solid products were extracted with acetone (150 ml) in a Soxhlet extraction apparatus until the solvent in the thimble became colorless (about 20 h). After removal of the acetone under reduced pressure in a rotary evaporator, this fraction was weighed and designated as oil 3. Acetone insoluble fraction was dried at 105 °C then weighed and designated as solid residue (biochar). Standard deviations in all tables and figures are within \pm 0.5%.

2.3. Analysis of liquid products

Oils including oil 1, oil 2 and oil 3 obtained from low temperature hydrothermal liquefaction of wood biomass were analyzed by gas chromatograph equipped with a mass selective detector [GC–MS; HP 5973; column, HP-1; cross-linked methyl siloxane, 25 \times 0.32 mm \times 0.17 μ m; temperature program, 40 °C (hold 10 min) \rightarrow 300 °C (rate 5 °C/min) hold for 10 min (oil 1 and oil 2 for thermal and catalytic runs); temperature program for oil 3 of catalytic runs, 40 °C \rightarrow 150 °C (rate 5 °C/min) \rightarrow 240 °C (rate 3 °C/min) \rightarrow 300 °C (rate 10 °C/min) hold for 30 min]. Compounds were identified by means of the Wiley library-HP G1035A and NIST library of mass spectra and subsets-HP G1033A.

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