Hydrothermal liquefaction of wheat straw in hot compressed water and subcritical water–alcohol mixtures

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ABSTRACT

Hydrothermal liquefaction of lignocellulosic biomass (wheat straw) into bio-oil has been investigated under subcritical conditions (temperature up to 350 °C, pressure up to 200 bar) in water and water–alcohol mixtures using ethanol and isopropanol in a continuously operated tubular reactor. The effect of different reaction parameters such as temperature, pressure and water–alcohol ratio on the biomass conversion, cracking products yield and the higher heating value (HHV) of the received bio-oil was studied. The water–ethanol mixture was found to be a very reactive medium showing a complete biomass conversion and >30 wt% yield of high caloric oil (HCO). A maximum HHV of 28 MJ/kg for HCO was achieved. In addition, Ru (5 wt%) on H-Beta support was used as catalyst in a run with hydrogen in the feed showing deeper deoxygenation of reaction intermediates and highest HHV of the product oil (30 MJ/kg). This work demonstrated the usability of water–ethanol mixtures for an effective depolymerization of lignocellulosic biomass to bio-oils under subcritical reaction conditions with more than doubled HHV compared to the feedstock, in particular using a catalyst and the presence of hydrogen for further deoxygenation.

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1. Introduction

The steadily increasing market price and foreseeable shortage of oil and gas are the movers for the use of biomass as a renewable feedstock in the energy sector besides solar and wind power uses. Therefore, the alternative production of energy, fuels and a wide variety of chemicals and polymers from biomass has attracted immense attention in recent years (e.g. [1–5]). It is absolutely true that "biomass is the only practical source of renewable liquid fuel" [6] but it is also very clear that biomass cannot cover the demand, neither today nor in the future. Therefore, our future energy, fuel and chemicals pool will be much more diverse than today.

Lignocellulosic biomass has a complex nature and it consists of 40–50% cellulose, 20–35% hemicellulose and 20–40% lignin depending on the origin. This composition and lignocellulosic stability make a selective conversion toward specific products or product classes quite difficult because different bond types have to be cleaved and it necessitates more drastic conditions such as high temperature and pressure in addition to specific separation technologies [7]. Combustion (for the production of heat), gasification (for the production of syngas, i.e. CO/H_2), pyrolysis and liquefaction (for the production of liquid bio-oil or bio-crude) are

the most commonly used methods applied for converting biomass into energy or fuels. The bio-oil production methods seem to be privileged due to its higher energy density output, and it is easier to transport and store than bulky solid biomass itself or gaseous products. The hydrothermal liquefaction using hot compressed water (HCW) in particular is a cost-effective method and has been focused for long time due to its relatively mild conditions and potential for producing bio-oil in high yields [8,9]. The main advantage of hydrothermal liquefaction of biomass is that the feedstock needs not to be dry or pre-treated in other ways, making it an economical process, probably. Under hydrothermal conditions, water and its mixtures with other fluids attain properties suitable for biomass liquefaction such as still high density to increase solvent power, good heat and mass transfer capabilities like in gases, fast decomposition of organics due to solvent reactivity, and utilization of variable solubility for extraction/separation effects. Due to the large number of reaction types and mechanisms involved, the process of biomass liquefaction is very complex: biomass materials are depolymerized into fragments, first by hydrolysis, and then degraded to smaller compounds by dehydration, deoxygenation, and hydrodeoxygenation (e.g. [9,10]). Moreover, HCW has been found to be very effective for promoting ionic, polar non-ionic, and free-radical reactions (depending on pressure and temperature), which make it a promising reaction medium for biomass conversion reactions [11]. Similarly, alcohols (e.g. EtOH) are interesting reaction media since their supercritical conditions can be attained

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at significant lower temperature and pressure than that of water [12].

Recently, Yu and co-workers have summarized the advances in hydrolysis of biomass in hot compressed water in comparison to acid or base hydrolysis as well as enzymatic hydrolysis [13]. Liquefaction of wood and other lignocellulosic materials in the presence of phenol under acidic (sulfuric, hydrochloric, phosphoric, and oxalic acids) or alkaline conditions (NaOH, Cu(OH)$_2$, NaHCO$_3$) and by using metal salts (AlCl$_3$, CuSO$_4$, FeSO$_4$, and NaH$_2$PO$_4$) is widely investigated (e.g. [14,15]). However, disadvantages of such processes using strong acids include partial carbonization of biomass during liquefaction and corrosion of the equipment. Various research is also known using sub- and supercritical media such as phenol [16], but the use of expensive phenol as the liquefaction solvent coupled with the difficulties in its recycling and environmental concerns make these processes unattractive. Alternatively, other organic solvents, such as alcohols and cyclic carbonates, were tested for low-temperature liquefaction of biomass (e.g. [10,17–19]). Yuan et al. [20] and Xu et al. [21] obtained a high bio-oil yield of 39.7% (from rice straw) and 65% (from pine sawdust), respectively, when alcohol was used as co-solvent along with water. These solvents could be recycled by evaporation after liquefaction and are much cheaper than phenol. A nice overview on basics of biomass conversion processes is given by Küçük and Demirbaş summarizing the literature up to the mid-1990s [22]. Möller et al. [23] reported in a very recent review on the state-of-art on hydrothermal biomass conversion. Further results were reported in a review from Toor et al. [24] on hydrothermal liquefaction under subcritical conditions. In addition, it looks that catalysts play an increasing role in biomass conversion into fuels [25]. Appell et al. already reported some decades ago that a woody biomass could be converted into liquid products in the presence of syngas or CO with aqueous sodium carbonate as a catalyst at elevated temperatures and pressures [26], other studies reported on the use of metallic catalysts [27].

Recently, we have reported on first trials of liquefaction of lignin under sub- and supercritical conditions of water and water–ethanol mixtures, respectively [28]. These tests were mainly carried out in batch mode. In continuation of this work, we were engaged in hydrothermal liquefaction of biomass into bio-oils in a semi-continuous apparatus. Wheat straw was used as model biomass and several experiments were carried out in HCW medium and further a detailed study was done using water–ethanol mixtures. The effect of the different reaction parameters such as temperature, pressure, alcohol proportion, addition of a heterogeneous catalyst, and reaction environment (phase behavior) on the straw conversion and yield of the bio-oil as well as on the higher heating value (HHV) of the product oils was monitored.

2. Experimental

2.1. Materials

Wheat straw chaff used in this study was received from a local agricultural supplier used as it is without any pretreatment. Ethanol (99.8%) and isopropanol (99.7%) were procured from Across Organics. Pressurized gases such as nitrogen or hydrogen used for the reactions were taken from commercially available cylinders (Air Liquide). For catalyzed runs, a 5 wt% Ru/H-Beta catalyst was prepared by impregnation method using ruthenium(III) chloride (Strem Chemicals) and H-Beta zeolite (Zeochem AG, BET = 669.9 m^2/g) as support. Ruthenium(III) chloride was dissolved in water and the calculated amount of H-Beta was added to this solution and stirred at room temperature for 2 h followed by evaporation of residual liquid under further stirring at moderate temperature (70 °C). Thus obtained catalyst was dried in an oven at 110 °C over night (15 h) and calcined using synthetic air (Air Liquide) and reduced under hydrogen (Air Liquide) at 400 °C for 5 h.

2.2. Instrumental setup

The setup used for the liquefaction runs consisted of a stainless steel tubular reactor that was placed in a heating box (up to 200 °C) to avoid undesired condensation of vapors (Fig. 1). The reactor (i.d. = 10 mm, l = 400 mm, V (reaction zone) = 10 ml) was heated by an electric heating coil. Reactor heater temperature was controlled by using a thermocouple installed in the heating coil; in addition, a movable thermocouple was placed in a guiding tube inside the straw package to measure the temperature inside the reactor. In general, the biomass was loaded between two stainless steel frits in the vertical mid of the reactor, placed on a tubular spacer. For some catalyzed runs, a catalyst bed was additionally positioned at the reactor outlet side between the lower end of the biomass and the lower frit. Liquids (water, ethanol, water–ethanol or water–isopropanol mixtures) were pumped by a HPLC pump (Shimadzu). Inert gas for dilution and use as internal standard or hydrogen to support deoxygenation was fed from commercial gas cylinders as already mentioned. Downstream of reactor outlet a countercurrent water cooler was installed. A two-stage back-pressure regulation released the reaction pressure to ambient; the gaseous phase was separated from the liquid one and both the phases were analyzed by means of gas chromatography and other methods.

2.3. Liquefaction experiments

The liquefaction experiments were carried out in the above described semi-continuously operating setup (see Fig. 1); the biomass (3–5 g) was placed in the reactor between the frits. The catalyst (5 wt% Ru/H-Beta, 0.5–1 g of solid, i.e. 0.5–1 ml) was placed in some runs just below the wheat straw assuming the gaseous biomass cracking products come in contact with the catalyst and facilitates the oxygen removal in presence of hydrogen. The feed solution composed of water, ethanol or water–ethanol (water–isopropanol) mixture was passed over the biomass using the high pressure pump with a liquid flow of 0.5–1 ml/min. In case of a catalyst present, the liquid hourly space velocity (LHSV) related to the used catalyst volume totalled to 60 h^{-1}. The reactor was operated at temperatures up to 350 °C and pressures up to 200 bar.

The workup techniques for the various product streams from the reactor are depicted schematically in Fig. 2. Gaseous products were analyzed online by GC (Hewlett Packard 5890, column 1 = Poraplot Q, l = 25 m, i.d. = 0.53 mm, f.t. = 0.20 μm; column 2 = HP PLOT molesieve, l = 25 m, i.d. = 0.53 mm) equipped with FID (CO, CH$_4$, CO$_2$ via methanizer) and TCD (N$_2$, H$_2$, CH$_4$, CO) detectors using Ar as carrier gas. The solid and liquid products were separated by filtration prior to analysis. The solid proportion was dried and weighed and included in calculation of wheat straw conversion. The liquid products were extracted using dichloromethane (2 ml × 25 ml) and two different types (phases) of oils, one with high heating value (high-caloric oil – HCO, dichloromethane soluble) and the other with low heating value (low-caloric oil – LCO, water soluble), were obtained after evaporation of the solvent. The HCO and LCO yields were calculated on a weight basis calculated on wheat straw placed in reactor. As an additional characteristic number, the "Higher Heating Value" (HHV) [29] of the bio-oils was calculated by using Dulong's formula (Eq. (1)) [30]. The formula considers the main biomass components such as carbon, hydrogen and oxygen with their percentage obtained from elemental analysis and the heating value of