



Production of gaseous and liquid bio-fuels from the upgrading of lignocellulosic bio-oil in sub- and supercritical water: Effect of operating conditions on the process



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ARTICLE INFO

Article history:

Received 14 January 2016

Received in revised form 1 April 2016

Accepted 2 April 2016

Available online 13 April 2016

Keywords:

Bio-oil upgrading

Subcritical water

Supercritical water

Bio-fuels production

ABSTRACT

This work analyses the influence of the temperature (310–450 °C), pressure (200–260 bar), catalyst/bio-oil mass ratio (0–0.25 g catalyst/g bio-oil), and reaction time (0–60 min) on the reforming in sub- and supercritical water of bio-oil obtained from the fast pyrolysis of pinewood. The upgrading experiments were carried out in a batch micro-bomb reactor employing a co-precipitated Ni-Co/Al-Mg catalyst. This reforming process turned out to be highly customisable for the valorisation of bio-oil for the production of either gaseous or liquid bio-fuels. Depending on the operating conditions and water regime (sub/supercritical), the yields to upgraded bio-oil (liquid), gas and solid varied as follows: 5–90%, 7–91% and 3–31%, respectively. The gas phase, having a LHV ranging from 2 to 17 MJ/m³ STP, was made up of a mixture of H₂ (9–31 vol.%), CO₂ (41–84 vol.%), CO (1–22 vol.%) and CH₄ (1–45 vol.%). The greatest H₂ production from bio-oil (76% gas yield with a relative amount of H₂ of 30 vol.%) was achieved under supercritical conditions at a temperature of 339 °C, 200 bar of pressure and using a catalyst/bio-oil ratio of 0.2 g/g for 60 min. The amount of C, H and O (wt.%) in the upgraded bio-oil varied from 48 to 74, 4 to 9 and 13 to 48, respectively. This represents an increase of up to 37% and 171% in the proportions of C and H, respectively, as well as a decrease of up to 69% in the proportion of O. The HHV of the treated bio-oil shifted from 20 to 35 MJ/kg, which corresponds to an increase of up to 89% with respect to the HHV of the original bio-oil. With a temperature of around 344 °C, a pressure of 233 bar, a catalyst/bio-oil ratio of 0.16 g/g and a reaction time of 9 min a compromise was reached between the yield and the quality of the upgraded liquid, enabling the transformation of 62% of the bio-oil into liquid with a HHV (29 MJ/kg) about twice as high as that of the original feedstock (17 MJ/kg).

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1. Introduction

Dwindling resources and the exponential growth in the demand for fossil fuels have motivated researchers to explore alternative energy supplies and technologies to produce both fuels and chemicals [1,2]. In this context, biomass waste processing technologies are receiving increasing attention mainly because biomass is the only renewable source of carbon that can be converted into solid, liquid and gaseous products through different conversion routes [3]. Furthermore, these technologies meet the difficult challenge of producing energy and fuels through so-called environmentally friendly processes.

The thermochemical conversion of biomass is a promising route for the production of chemicals and energy from renewable resources [4–6]. Among all the possible thermochemical processes, fast pyrolysis is one of the most mature technologies used industrially for biomass conversion. This process allows the transformation of biomass into bio-oil, a combustible liquid that is easy to store and transport. Yields of 50–75% of bio-oil with a much higher volume energy density than the original feedstock can typically be obtained [7]. Bio-oils obtained from lignocellulosic biomass are dark brown organic liquids containing the degradation products of cellulose, hemicellulose and lignin [8]. They normally consist of a complex mixture of many different organic compounds such as aldehydes, ketones, sugars, carboxylic acids and phenols [9] whose specific chemical composition depends on the biomass source as well as the processing conditions under which the pyrolysis takes place [10].

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The percentage of hydrogen in bio-oil (5.5–7 wt.%) makes it suitable for H₂ production [11]. Two different thermochemical processes have normally been used for this. The first is non-catalytic steam reforming, which operates at high temperatures (1000–1400 °C) [12]. The second is catalytic steam reforming, which allows carrying out the process at a lower temperature (500–800 °C) but has the major drawback of the deactivation of the catalyst by coking. This motivated the implementation of a separation step in which bio-oil is split into two phases by water fractionation. The non-soluble fraction can be used for the production of high value-added chemicals, whereas the aqueous fraction is processed by catalytic steam reforming to produce H₂ [13].

With respect to the production of transportation fuels, bio-oils obtained from the pyrolysis of biomass are a possible source of bio-fuels [14,15]. They offer several environmental advantages over fossil fuels. They are CO₂/GHG neutral; SO_x emission-free and release more than 50% lower NO_x than diesel during combustion [8,16,17]. However, the potential of these liquids for substituting petroleum fuels is limited due to their high viscosity, high water and oxygen contents, low heating value, instability and high acidity (corrosiveness) [18–21]. Consequently, the upgrading of bio-oil is essential for providing a liquid product that can be used as a fuel. There have been extensive studies on bio-oil upgrading, and various technologies have been developed: hydrotreating (HDT), hydrocracking (HDC) and the use of supercritical fluids (SCFs) [8,16,17].

In this context, sub- and supercritical water reforming (SWR) of bio-oil, also called supercritical water gasification (SCWG), is an interesting process for bio-oil upgrading [8,16,17,22]. Cracking, reforming and hydrogenation reactions occur thanks to the generation of H₂ in the same process. In addition, the H₂ solubility limitation can be reduced as H₂ and the bio-oil are brought into a single phase with the employment of supercritical water [23]. The properties of water (sub/supercritical) enable the process to be customised with slight changes in the process conditions towards the production of liquids or gases, depending of the needs of the market. Therefore, this technology represents a very challenging tailor-made alternative for bio-oil valorisation. Moreover, the H₂ generated allows the in-situ hydrogenation of bio-oil to take place, which also decreases the oxygen content in the bio-oil. This enables an upgraded bio-oil to be obtained with better physico-chemical properties than the original feedstock, which may be used as a liquid fuel either alone or mixed with other petroleum-derived oils.

Studies concerning the treatment of lignocellulosic biomass and/or bio-oils in sub/supercritical water can be divided into two groups. The first addresses the direct conversion of biomass into H₂ using sub/supercritical water [24–26], while the second examines the upgrading of bio-oils previously produced from biomass. Although the former has to face several problems for the correct development of the technology, such as the preparation of wet biomass in the form of a fluid that can be fed with high-pressure pumps to the reformer reactor, studies in the latter group are very scarce. In addition, they are more focused on H₂ and/or CH₄ production from bio-oil than on producing liquid fuels, for which the only reported works concern algal bio-oils. There is, therefore, little research in the field of the production of gaseous and liquid biofuels from lignocellulosic bio-oil by sub- and supercritical water treatment.

Penninger and Rep [27] analysed the reforming of a bio-oil obtained from the pyrolysis of biomass by its treatment in supercritical water at 650 °C for H₂ production. It was found that the pressure of the aqueous reaction medium exerted a significant influence on the process. High pressures retarded the formation of gas and inhibited coke formation. Onwudili and Williams [28] investigated the catalytic supercritical water gasification of a heavy

dewatered bio-oil in a batch reactor using a Ru/Al₂O₃ catalyst (5–20 wt.% of Ru) at a temperature between 400 and 500 °C and pressure ranging from 265 to 400 bar, varying the holding time between 0 and 60 min. They found that gas production increased with increasing the holding time and reaction temperature. Higher Ru loadings led to increased carbon gasification efficiency, high CH₄ production and a dramatic reduction in both char and oil yields.

As regards algal bio-oil upgrading, several works, most of them by Duan et al. [29–32], have been carried out with sub/supercritical water aiming to improve the properties of the original feedstock for use as a liquid fuel. These include the hydrotreatment of crude algal bio-oil in supercritical water, a parametric study examining the effect on the process of the temperature (430–530 °C), time (2–6 h), catalyst type (Pt/C, Mo₂C, HZSM-5) and catalyst loading (5–20 wt.%) as well as the use of formic acid (2–37 mmol) as a H₂ donor. This upgrading technology proved suitable for improving bio-oil properties. The temperature was always the most influential operating variable. The catalyst loading exerted the greatest effect on the higher heating value and O/C ratio in the treated oil, while the reaction time significantly affected the H/C and N/C ratios.

Given this background, the main objective of this work is to analyse the influence of the operating conditions (temperature, pressure, catalyst/bio-oil mass ratio and reaction time) during the reforming in sub- and supercritical water of a bio-oil obtained from the fast pyrolysis of pinewood to produce gaseous and liquid biofuels. A full factorial design (DOE) with a statistical analysis of the results has been used to analyse the effect of the operating conditions. The product distribution (gas, liquid and solid) and properties of the gas and upgraded liquid obtained in the process have been addressed and fully discussed. The fact that the combined effect of the operating variables and their interactions on the valorisation of lignocellulosic bio-oil in different water regimens, i.e. subcritical and supercritical water conditions, has never been reported before demonstrates, together with the results provided by the in-depth study, that this work represents a novel investigation in this field.

2. Materials and methods

2.1. Bio-oil properties

The bio-oil used in this work, supplied by BTG, was obtained during the pyrolysis of pine sawdust using a rotating cone reactor. The properties of the crude bio-oil were determined by means of elemental analysis, chemical composition, water content, density, viscosity, pH and higher heating value (HHV). These are summarised in Table 1. The elemental analysis was carried out in an elemental analyser (Leco TruSpec Micro), and the viscosity was measured in a Cannon-Fenske routine viscometer (Cannon Instrument Co., model 150 T845) at 40 °C following the standard method EN ISO 3104. The water content was determined by means of Karl Fischer titration (Mettler-Toledo V20 volumetric KF titrator), the pH was measured with a pH meter and the HHV in a Ika-Werke C2000-basic calorimeter. The empirical correlation developed by Channiwala and Parikh [33] was used for estimating the HHV of the treated liquids due to the small amount of sample obtained in each experiment. To validate this empirical correlation, the water content in the bio-oil was reduced by means of a liquid–liquid extraction with chloroform and the HHV of this dewatered bio-oil was both determined experimentally and estimated theoretically. No statistically significant differences were found between the HHV of the dry bio-oil determined experimentally and making use of the experimental correlation with 95% confidence (*p*-value = 0.46). Therefore, this validates

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