



Full Length Article

Hydrothermal liquefaction of biomass: Influence of temperature and biomass composition on the bio-oil production



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HIGHLIGHTS

- HTL is a promising process for the production of high quality bio-oil.
- The optimum temperature of the process is highly dependent on biomass composition.
- A linear relationship between lignin biomass content and bio-oil yield exists.
- The maximum bio-oil yield is obtained for biomass with the highest lignin content.

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ABSTRACT

Hydrothermal liquefaction is a promising process for the production of high quality bio-oil from biomass. Aim of this study is to investigate the effect of temperature and biomass composition on the yield and quality of bio-oils produced from three different biomass such as natural hay, oak wood and walnut shell. The hydrothermal liquefaction of cellulose was also investigated. The experimental tests, conducted in water sub-critical conditions, were carried out in a microreactor in a temperature range of 240–320 °C with a reaction time of 30 min. All the products of the process were analyzed and characterized by elemental analysis and GC–MS. It was observed an increase of the bio-oil yields with the lignin content of biomass, being the maximum bio-oil yield obtained for walnut shell and the minimum one for cellulose. This trend is representative of the obtained bio-oils composition, where the phenolic compounds are the major constituents, while the other identified compounds were mainly alcohols, ketones and aldehydes.

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1. Introduction

Biomass is considered one of the most promising alternatives to fossil fuels for the production of bio-fuels, chemicals and energy. The increasing CO₂ emissions, in fact, have challenged the scientific community to find new techniques to exploit renewable energy in order to meet the world's growing needs for energy while reducing greenhouse gases. Biomass meets all the requirements of renewable and CO₂ neutral materials and furthermore it is one of the largest sources of energy in the world. Biomass includes different kinds of biological matter: wood, agricultural waste, energy crops, algae, animal waste, organic fraction of municipal waste and others. In addition to the direct energy production, there is a growing attention to the development of technologies to convert biomass into more valuable fuels, such as bio-oil and bio-syngas, and into chemicals [1]. Traditional thermochemical processes such

as pyrolysis and gasification present some weak points: the necessity of dry feedstocks (biomass water content can reach up to 70% of the fuel weight) to achieve a positive energy balance and of further processes to upgrade the raw product in order to obtain commercially valuable liquid and gaseous fuels [2–4]. In this context, hydrothermal liquefaction (HTL), consisting in the decomposition of biomass in presence of water and under high pressure, can be an interesting technology to produce a liquid biofuel from a wet feedstock without the need of the energy consuming drying process [4]. Nonetheless, one of the most obvious drawbacks is the use of high pressure which can potentially lead to high cost in the equipment necessary for industrial scale processes. Also, the bio-oil obtained from the HTL typically presents higher yield and higher quality, lower oxygen and water content, giving much higher HHV (25–35 MJ kg⁻¹) compared to those of the traditional pyrolysis bio-oil (14–20 MJ kg⁻¹) [6,7]. In fact, during hydrothermal liquefaction the small polar organic compounds produced are recovered in the aqueous phase and not in the oily one as in the fast pyrolysis process occurs [8]. However the oxygen content

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remains still high compared to that of the fossil fuel oil (oxygen less than 1%) and so up-grading treatment are required to convert the obtained bio-oil into biofuels to be used as transportation and engine fuels.

HTL is a low temperature and high pressure process during which biomass is broken down into fragments of small molecules in a solvent, usually water. Four phases are formed during the process, the bio-oil, light gases, principally CO₂ and small amount of CH₄, CO and H₂, a solid residue, char, and a water phase having a high organic carbon content. In a HTL process, wet biomass and a supplementary amount of water, if needed (biomass: water weight ratio is in general kept in the range 1:10–1:5), are heated in the range of 280–370 °C under a pressure comprised between 10 and 25 MPa [5,9]. At these pressures and temperatures, water is still in liquid phase and near its critical point that occurs at 374 °C and 22.1 MPa. HTL processes taking place below the critical point are considered sub-critical, while the others super-critical. Water plays a fundamental role, acting not only as solvent but also as catalyst/reactant due to its particular properties in these conditions: dielectric constant decreases increasing the solubility of hydrophobic organic compounds, the viscosity decreases providing a higher diffusion coefficient that leads to higher global reaction rates [10,11]; furthermore, the ionic product increases so that water can act as an effective medium for acid-base catalyzed organic reactions such as hydrolysis reactions [12,13].

The production of bio-oil from HTL processes was extensively investigated in literature under different operative conditions. The parameters that influence more the process were found to be temperature, residence time and biomass to water ratio. Temperature is the most important parameter: an increase of temperature leads to an increase of the bio-oil yields until a limit value for which the opposite behavior takes place due to the occurring of bio-oil cracking reactions to form light gas species and repolymerization reactions to form char [14–16]. Typical residence times range between 5 and 30 min, the increase of residence time leads to higher bio-oil yields, however beyond a certain threshold further increase in the time of reaction produce the opposite results due to repolymerization reactions of bio-oil molecules. Biomass to water ratio is usually investigated in the range 1:2–1:15 and plays a key role in the biomass decomposition reactions. However there is not a common evidence on the effect of the increase of this parameter on the bio-oil yields. Singh et al. observed that the bio-oil yield is major when the water amount increases [17] while other researchers demonstrated that the decrease of biomass to water ratio has no positive effect on the bio-oil yields [18,19].

The biomass composition in terms of amount of cellulose, hemicellulose and lignin, also have a great influence on the bio-oil yield and quality. Many studies focused the attention on this factor reporting that the oil yield increases when the content of hemicellulose increases and decreases with the increase of lignin content [20–23]. However, the obtained results are very different from each others and it is difficult to find a unique trend that correlates the biomass composition to the bio-oil yield and quality.

In this work the hydrothermal liquefaction in a micro-batch reactor of three biomass having different chemical component composition was investigated at different temperatures and constant biomass to water ratio and reaction time. The biomass used in the experimental tests were natural hay, oak wood and walnut shell. Furthermore, tests were performed using pure cellulose in order to have yield values referred to one of the biomass components. The HTL products were all analyzed in terms of elemental composition (char and bio-oil), chemical composition (gas, bio-oil and water phase), and heating value. The yields of all HTL products

were measured and compared for the different temperatures and for the different biomass compositions.

2. Materials and methods

2.1. Materials

The different biomass were kindly provided by farms located in the Lazio region in Italy. Cellulose (medium fibers) was purchased from Sigma-Aldrich. The biomass were characterized by elemental analysis, performed with CHNS Elemental Analyzer (Eurovector EA3000). The samples were dried in a oven at 105 °C for 12 h to measure the amount of moisture and the ash content was determined using a muffle furnace at 600 °C for 4 h in static air atmosphere. In Table 1 the properties of the biomass are reported. The biochemical composition of the samples (Table 2) was in part measured experimentally, for what concern extractives and lignin content and as a consequence the holocellulose, and in part extracted from Phyllis Database [24], for cellulose and hemicellulose. The extractives content was measured following the method reported in de Caprariis et al. [25], while the lignin content was obtained following the procedure reported in the TAPPI test method [26]. The cellulose and hemicellulose were extracted from the Phyllis Database by selecting samples matching the measured content of extractives and lignin. The biomass were chosen in order to have remarkable differences in the biochemical composition, in fact lignin content ranges from 12% in natural hay and 53.5% in walnut shell. Before the tests the biomass samples were grinded with a Fritch Pulvisette Cutting Mill and sieved to particle size ranging between 200 and 500 µm.

2.2. Experimental procedure

The experiments were carried out in a stainless steel tubular microreactor with inner dimensions of 90 mm in length and 12 mm in diameter (internal volume ~10 mL). An amount of 1 g of biomass was weighed and loaded into the reactor, followed by the addition of 5 mL of distilled water in order to reach a feed-stock/water mass ratios 1:5. The dead volume of the reactor was maintained between 2 and 3 mL. The reactor was then sealed and the air inside the reactor was displaced by purging nitrogen several times. A K-type thermocouple was fit in one of the two threaded caps. The reactor is heated in a tubular oven; suspended inside it by means of a shaft connected to a mechanical stirrer needed to shake the reactor during the tests. The reactor is inserted in the oven and heated with a rate of 5 °C min⁻¹ till the temperature of the test was reached, this temperature was kept constant for 30 min. The experimental tests were performed in a temperature interval ranging between 240 and 320 °C in sub-critical condition.

After reaction, the reactor was quenched with water to room temperature and weighted. The reactor was successively weighted after venting the gaseous products to measure their amount. To remove the water phase, one of the threaded cap of the reactor was substituted with a porous metal threaded filter. In Fig. 1 each steps of the product separation process are reported. To assure the complete extraction of bio-oil, acetone was recirculated into the reactor for 30 min with a peristaltic pump. Bio-oil and residual water were obtained from the extract solution evaporating acetone at 60 °C by using a rotary evaporator. The acetone insoluble fraction remaining inside the reactor was dried at 105 °C for 12 h to yield the solid residue. All runs under identical conditions were carried out in triplicate to confirm the repeatability of results. The reported values are average ones.

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