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Short communication

Potential biofuels from liquefied industrial wastes – Preliminary evaluation of heats of combustion and van Krevelen correlations

Rui Galhano dos Santos*, João Carlos Bordado, Maria Margarida Mateus

Instituto de Biotecnologia e Bioengenharia, Departamento de Engenharia Química e Biológica, Torre Sul, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

This study aimed at the evaluation of industrial residues/wastes such as pinewood sawdust, swine manure, and paper sludge to produce liquefied products that can be used as potential biofuels. The afforded products, liquefied pinewood sawdust, liquefied paper sludge and liquefied swine manure were obtained in good yield and subject to chemical analysis. The bio-oils have presented higher carbon and hydrogen content when compared to their precursors while a significant decreased in moisture was observed. Plotting van Krevelen diagram demonstrated that the bio-oils are more closely related to hydrocarbon than to its primitive, raw material. This study also showed a strong potential of LPS to be used as a bio-oil, since it fulfilled two out of the three criteria needed to be considered as a bio-petroleum product.

1. Introduction

The expected depletion of fossil sources supplies along with the global warming are reasons more than enough to establish a bio-based economy by the development of the necessary technologies and procedures for exploiting other sustainable resources as feedstocks. This search for alternatives to petroleum products is gradually being foreseen as an approach to reduce the ecological footprint of humankind and greenhouse gas emissions (Fontoura et al., 2015; Malico et al., 2016) as well as to meet the new goals set by the government concerning the use bio-fuels(Bringezu et al., 2009). Being easily manageable and storable, liquefied products are believed to be an alternative source of chemicals or fuels(Behrendt et al., 2008). Direct liquefaction has been widely investigated and consists in the solubilization and depolymerization of biomass at high temperatures (Soares et al., 2014). Wood (Kurimoto et al., 2001), wheat straw (Chen and Lu, 2009), lignin (Jin et al., 2011), cork (dos Santos et al., 2015; Mateus et al., 2015), amongst others have been successfully converted into polyols, added-value chemicals and even fuels. Throughout liquefaction, products enriched in hydroxyl groups are obtained. Being highly reactive they can be readily used as starting materials in the development of environmental friendly polymeric products such as adhesives (Bordado et al., 2015), polyurethane foams (Lee et al., 2000) or even polyurethane films (Kurimoto et al., 2001). Lately, the use of such bio-oils as biofuels has also been explored (Seljak et al., 2012) The reaction mechanisms involved in liquefaction processes are still quite undisclosed. Lower molecular weight species and hemicelluloses are believed to be directly dissolved while polymeric cellulose and lignin undergo catalyzed degradation reactions (Soares et al., 2014). Polysaccharides are firstly converted to its congener glycosides which are then hydrolyzed to levulinic glycosides (Kržan and Žagar, 2009). The reaction pathway of lignin depolymerization is also quite unknown, but it was shown that the presence of lignin plays a major role in the post-liquefaction recondensation reactions, leading to insoluble precipitates (Kobayashi et al., 2004).

Our group has been, over the last years, investigating the use of industry wastes as a source of biomass for the acid liquefaction in polyhydric alcohols. The liquefaction of paper sludge and swine manure is quite understudied requiring further investigation on the outcome of their depolymerization. Herein, we aimed at the

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* Corresponding author.
E-mail address: rui.galhano@ist.utl.pt (R. Galhano dos Santos).

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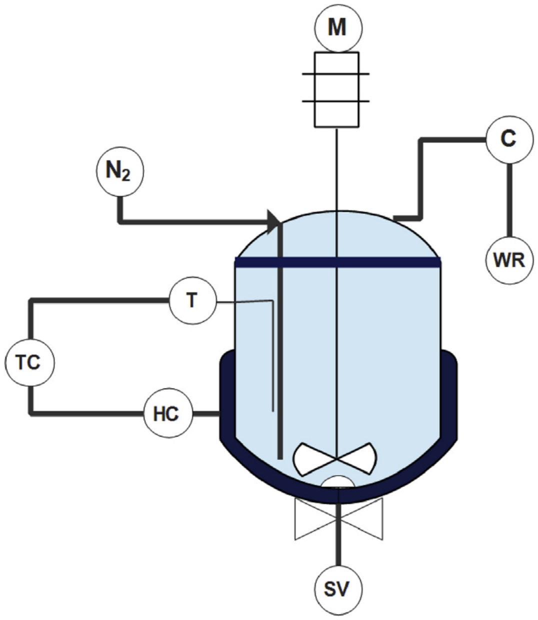

Fig. 1. General Scheme of experimental apparatus: M – Motor, C – Condenser, WR – Water Collector, N_2 – nitrogen input, SV – Sample Valve, HC – Heater Controller, T – Thermocouple, TC – Temperature Controller.

evaluation of the use of liquefaction of those raw materials for the production of biofuels mitigating, thus, the negative impact on the environment of those wastes by reducing the amount of residues to be deposited in landfills and by decreasing the use of fossil fuels. With this study, we also hope, modestly, to provide a contribution to building the three pillars of sustainability: profit, people, and the planet, by converting the excess biomass into useful by-products or energy (Ali et al., 2015).

This paper aims to present the liquefaction of industrial residues and to study its potential use as biofuels. The yields of the liquefaction processes were determined, the feeding raw materials, as well as the liquefied products, were chemically analyzed, and their higher heating values (HHV) were estimated for further comparing by van Krevelen's correlations.

2. Materials and methods

2.1. Materials and chemicals

Paper sludge and swine manure were supplied by SECIL and pinewood sawdust was acquired from a local pet store. All feedstocks were used without any further treatments whatsoever. The reagents used were chemical grade and purchased from Sigma-Aldrich.

2.2. Liquefaction procedure

The liquefaction apparatus was assembled as indicated in Fig. 1. The experimental procedure adopted was as described by Mateus et al. (2015): the reactor was loaded with a mixture of solvents with a 1/2 w/w of 2-ethylhexanol and diethylene glycol, containing a 3% of *p*-toluene sulfonic acid and 10% w/w of biomass based on its dry weight. The temperature was set at 160 °C, and the reactional mixture stirred for the desired time. Afterward, the reactors were allowed to cool to room temperature.

2.3. Measurement of liquefaction extent

The conversion yield was gravimetrically evaluated on the basis of the residue content (unreacted raw material). A sample of the reaction mixture was diluted with acetone. The diluted resultant was filtered and washed with acetone. The obtained residue was dried in an oven set to 120 °C until no change in weight was observed. The conversion rate percent was calculated by the equation (1). $M_2 \times M_m$

$$\text{Conversion yield }(\%) = \left(1 - (M_2 \times M_m)/_{(M_S \times M_1)}\right) \times 100 \tag{1}$$

where M_1 is the initial mass of cork, M_2 the mass of the residue obtained, M_s the mass of the sample withdrawn and the M_m is the initial mass of the reaction mixture.

2.4. Samples analysis

The chemical composition data concerning carbon, hydrogen, and nitrogen were obtained via elemental analysis using an LECO TruSpec CHN analyzer instrument. While for sulfur, the determination was carried out in an LECO CNS2000. The oxygen content was estimated by difference, using the equation (2),

$$\mathrm{O}(\%) = 100 - (\mathrm{C} + \mathrm{H} + \mathrm{N} + \mathrm{S})(\%) \tag{2}$$

The calorific values were determined with an LECO AC500.

2.5. Van Krevelen correlation

Van Krevelen diagrams are graphical plots developed and used to study the difference in chemical composition of kerogen. This diagram cross-plots the hydrogen: carbon as a function of the oxygen: carbon atomic ratios of carbon compounds. The Van Krevelen diagram thus appears well suited to amplify and expose compositional differences within and between organic products(Wu et al., 2004). A wide variety of compounds was used to plot a van Krevelen diagram to obtain very differentiated zones of the different feedstock types.

3. Results and discussion

The studies were conducted according to with flowchart presented in Fig. 2. Pinewood sawdust (PWS) was used as standard feedstock since its acid-catalyzed liquefaction is well established, being the liquefaction of swine manure (SM) and paper sludge (PS) conducted for further evaluation of their use as biofuels. The feedstock liquefaction proceeded smoothly without pre-treatments leading to the desired bio-oils in high yields (Table 1, Fig. 3). The water content as well as that resulting from the hydrolysis/cleavage reactions, which occurs throughout the processes, were removed by distillation leading to low moisture content products when compared to their initial values (Table 2).

The higher heating values were evaluated. A comparison between the HHV of the starting raw material with that of the resulting liquefied products, clearly indicated a substantial increase in their values indicating, thus that the products could, potentially, produce more energy than their initial precursors (Table 2, Fig. 3). When compared with the initial values, the products presented low moisture, high H:C ratio and a much lower amount of oxygen in their chemical composition, which explains the significant increase in their heating values.

Van Krevelen diagram (Fig. 4A) were plotted using the data