



Short Communication

Bio oil synthesis by coupling biological biomass pretreatment and catalytic hydroliquefaction process



S. Hamieh ^{a,b}, R. Beauchet ^a, L. Lemee ^a, J. Toufaily ^b, B. Koubaissy ^b, T. Hamieh ^b, Y. Pouilloux ^a, L. Pinard ^{a,*}

^a IC2MP, Institut de Chimie, des Milieux et Matériaux de Poitiers, University of Poitiers, 4 rue Michel Brunet, 86000 Poitiers, France

^b MCEMA, Laboratory of Materials, Catalysis, Environment and Analytical Methods, Faculty of Sciences I, Lebanese University, Campus Rafic Hariri, Hadath, Lebanon

HIGHLIGHTS

- Direct liquefaction reaction of waste organic matter using Raney Nickel and tetralin.
- Biological pretreatment enhances Humin content and the liquefaction process.
- Humin fraction as promoter and Humic acids as refractory to liquefaction reaction.
- Bio oil heating value close to biopetroleum.

GRAPHICAL ABSTRACT



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ABSTRACT

The bio-oil synthesis from a mixture of wastes (7 wt.% straw, 38 wt.% wood, and 45 wt.% grass) was carried out by direct liquefaction reaction using Raney Nickel as catalyst and tetralin as solvent. The green wastes were biologically degraded during 3 months. Longer the destructuration time; higher the yield into oil is. Biological pretreatment of green wastes promotes the liquefaction process. Among the components of degraded biomass, Humin, the major fraction (60–80 wt.%) that was favored by the biological treatment, yields to a bio oil extremely energetic with a HHV close to biopetroleum (40 MJ kg^{-1}), contrariwise, Fulvic acids (2–12 wt.%), the minor fraction is refractory to liquefaction reaction.

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1. Introduction

Waste organic matter, despite of their high oxygen content and low Higher Heating Value (HHV), have the potential to be a valuable substitute to fuel production through thermochemical conversion (Rezzoug and Capart, 2003). Contrariwise to gasification and pyrolysis processes, direct hydroliquefaction does not require drying of the feedstocks, which takes large quantities of energy and time (Minarick et al., 2011). Direct hydroliquefaction consist to add hydrogen to the hydrogen deficient organic structure of the biomass, breaking it down as far as is necessary to produce distillable liquids. This process is very versatile, and can be applied to a

wide range of biomasses such as municipal wastes, green wastes, primary sludge and microalgae (Lemoine et al., 2013), and many other high-moisture feedstocks (Elliott et al., 1988). It is a chemical reforming process in which the depolymerization, the deoxygenation of organic waste materials and the hydrogenation of reaction products occur at the same time (Chornet and Overend, 1985). To get a fuel (bio oil) of high quality, oxygen content must be lower than 6 wt.%, and the hydrogen to carbon ratio (H/C) higher than 1.5 (Wang et al., 2008). Therefore, both oxygen removal (through decarbonylation, decarboxylation and dehydration reactions) and hydrogen transfer are promoted in a heated, hydrogen pressurized enclosure. Hydrogen donor solvents as 1,2,3,4-tetrahydronaphtalene (tetralin) may be added to increase the hydrogen to carbon ratio and to reduce the oxygen to carbon ratio, thereby improving hydrocarbons yield (Johannes et al., 2012). Moreover, the addition

* Corresponding author. Tel.: +33 (0)5 49 45 39 05; fax: +33 (0)5 49 45 37 74.

E-mail address: ludovic.pinard@univ-poitiers.fr (L. Pinard).

of a catalyst favors the intensification of hydrogen transfer activity. In a previous study (Beauchet et al., 2011), the direct liquefaction of green wastes composed of straw, wood and grass was carried out using Raney Nickel (Ni) as catalyst and tetralin as solvent, it was demonstrated that this catalyst had practically no effect on the oil yield but amended the oil quality by decreasing the oxygen content and increasing the hydrogen one.

The deoxygenation rate could be enhanced by combining the hydrolification process with the biological pretreatment of raw materials (Lemée et al., 2012). The biological degradation of organic matter, that involves mild conditions, leads to physical and chemical modifications of the starting materials as the formation of Humic substances (Humic acids (HA), Fulvic acids (FA), and Humin (H)). FA are Humic acids of lower molecular weight and higher oxygen content than other Humic acids. H and FA represent a complex mixture consisting of several acids containing carboxyl and phenolate groups so that the mixture behaves functionally as a dibasic acid or, occasionally, as a tribasic acid.

As the thermal decomposition of OH and COOH terminal groups into water and CO₂ being easier than the cleavage of C–O–C bonds (major bonds on the raw materials), the biological pretreatment should favor the deoxygenation reaction during liquefaction process. Thus, the present work aims to evaluate if a biological pretreatment of green wastes improves the efficiency of the liquefaction process in terms of yield and quality of bio oil (oxygen content and energy value) or not. For that, green wastes (composed of a mixture of straw, wood and grass) biologically pretreated during 22, 36 and 85 days are tested in hydrolification under operating conditions similar to those used in Beauchet et al. (2011). It must be noted that samples characterizations have been already described by Lemée and his collaborators (Lemée et al., 2012, 2013; Lemoine et al., 2013).

The most effective sample in liquefaction process will be fractionated, following the IHSS protocol (International Humic Substance Society). The liquefaction results of these fractions will allow both identifying the resistant fractions in solvolysis and deoxygenation reactions, and optimizing the time of the biological pretreatment.

2. Methods

2.1. Carbonaceous materials and characterization techniques

The biological pretreatment of a model mixture (5 kg) of straw (17 wt.%), wood (38 wt.%) and grass (45 wt.%) was carried out in a steel reactor fed in the bottom with controlled air flow (Lemée et al., 2012). During biodegradation process, a sampling (50 g) was done at different time 22, 36 and 85 days.

The weight contents of raw materials in terms of moisture, organic matter (OM) and ash were quantified by total combustion using thermo gravimetric (TGA) and thermo differential (TDA) analyzes. In general, OM combustion, characterized by two exothermic peaks around 250–350 °C and 400–550 °C, respectively. The first one corresponds to the volatilization of light compounds such as aliphatic molecules, the second one to the degradation of more complex aromatic structures (Lemée et al., 2012).

The elemental composition (CHNS/O) of the feedstocks and of the bio oil were measured with an elemental analyzer (CE Instruments NA 2100 Protein) that allows calculating, from the Dulong's formula (Zhong and Wei, 2004), their Higher Heating Value (HHV, kJ kg⁻¹). The calculated values were close to those measured by calorimetric bomb (Lemoine et al., 2013). The IHSS (International Humic Substance Society) protocol was carried out on biological green waste in order to extract and quantify some various forms of organic matter such as lipids, Humin, Fulvic and Humic acids. The lipids content was determined using an automatic ASE 100

extractor working with a dichloromethane/methanol mixture (2/1, v/v). The recovered solvent was then evaporated and the mass of the residue was measured and considered as lipids (Calderoni and Schnitzer, 1984). The H and FA are extracted from organic materials into a strongly basic aqueous solution of sodium hydroxide (0.1 M). Humic acids are precipitated from this solution by adjusting the pH to 1 with hydrochloric acid, leaving the Fulvic acids in solution. This is the operational distinction between HA and FA. Humin is insoluble in dilute alkali. The experimental details were previously described in Som et al. (2009).

2.2. Hydrolification experiments

Hydrolification experiments were conducted in a batch reactor of 0.3 L, with 5 g green waste and a weight, tetralin (solvent) (Acros Organic, purity = 98%) to raw 1/14 ratio of materials. 1 g of Raney Ni slurry in water (Sigma Aldrich) was added to the feed and the hydrogen pressure was fixed to 16 bar. The autoclave was heated at 10 °C min⁻¹ without stirring up to the working temperature between 330 and 400 °C. Then, the reaction is carried out during 15 min with stirring (1000 tr min⁻¹), the total pressure that depends on reaction temperature ranged between 40 and 70 bar. After cooling down to room temperature and stopping the stirring, the reaction products (gas, liquid and solid materials) were separated and analyzed as described in previous publications (Beauchet et al., 2011; Lemoine et al., 2013).

Hydrolification experiments were duplicated; all the results obtained in terms of conversion and yield into oil are the same ±5%.

Before opening the reactor, the gas products were collected in Tedlar bags (1 L) to be analyzed and quantified by a GC equipped with a TCD. The solid residue, composed of spent catalyst, unconverted material and insoluble organic matter, was separated from the solvent by filtration. It was then washed with CH₂Cl₂ which was combined with the solvent. The solid residues were dried at 90 °C under vacuum during 3 h, and the solvent were separated by distillation. Products having a boiling point lower than tetralin, called light fraction oil, were analyzed but not quantified. This fraction contained water, guaiacol, phenolic, furanic and nitrogen-containing compounds. The total feedstock conversion *X* was deduced from the mass of insoluble materials, following Eq. (1):

$$X (\%) = \left(1 - \frac{(\text{mass of insoluble materials without ash and catalyst})}{(\text{mass of organic matter of material})} \right) \times 100 \quad (1)$$

The oil yield was calculated as the mass of oil divided by the mass of bone-dry organic matter in the sample:

$$\text{Yield into oil} = \frac{(\text{mass of oil})}{(\text{mass of dry organic matter of material})} \times 100 \quad (2)$$

The difference between the conversion and the oil and gas yields corresponded to the yield into "light oil".

The mass of hydrogen transferred from tetralin to the material (THT) was determined by analyzing the solvent by gas chromatography (Varian 3400, equipped with a 30 m DB5 type capillary column and a FID detector). THT was deduced from the concentration in naphthalene, which was directly linked to the conversion of tetralin. Under our experimental conditions, tetralin was only converted into naphthalene which showed that it acted as a reducing agent, and not as an oxidizing agent since only traces of decalin were observed. The mass of hydrogen (in milligrams) transferred from tetralin to the material was calculated as follows (on a 1000 mg basis): THT = 4000/132((*T.x*)/*M*) where *T* is the amount of tetralin (mg) in the starting mixture, *M* the amount of

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