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Evaluation of humic fractions potential to produce bio-oil through catalytic hydroliquefaction

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HIGHLIGHTS

- Humic substances were extracted from biodegraded lignocellulosic biomass.
- Their hydroliquefaction products were compared according to quantitative and qualitative aspects.
- Humin presented a high conversion rate and produced high amount in alkanes.
- The hexan soluble fraction from humin presented characteristics fully compatible with bio-oil.

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ABSTRACT

Humic substances were extracted from biodegraded lignocellulosic biomass (LCBb) and submitted to catalytic hydroliquefaction. The resulting bio-oils were compared with those of the initial biomass. Compared to fulvic and humic acids, humin presented a high conversion rate (74 wt.%) and the highest amount of liquid fraction (66 wt.%). Moreover it represented 78% of LCBb. Humin produced 43 wt.% of crude oil and 33 wt.% of hexane soluble fraction containing hydrocarbons which is a higher yield than those from other humic substances as well as from the initial biomass. Hydrocarbons were mainly aromatics, but humin produces the highest amount of aliphatics. Considering the quantity, the quality and the molecular composition of the humic fractions, a classification of the potential of the latter to produce fuel using hydroliquefaction process can be assess: Hu > AF > AH. The higher heating value (HHV) and oxygen content of HSF from humin were fully compatible with biofuel characteristics.

1. Introduction

As a part of the anthropology role on climate changes, oil production from lignocellulosic biomass (LCB) is of particular interest regarding the carbon balance. Indeed, in the long term, the amount of carbon dioxide produced using energy based on LCB is equal to those absorbed during its growth (Schlamadinger et al., 1995). LCB can be valorised via catalytic hydroliquefaction reaction (CHR) (Beauchet et al., 2011), which offers a promising alternative to the pyrolysis processes since the oil obtained from CHR process is stable and presents low oxygen content as well as a high heating value (Li et al., 2008). This process can be improved by using a hydrogen solvent and a catalyst. In a previous work (Beauchet et al., 2011), direct catalytic hydroliquefaction of a biomass composed of a green wastes mixture (straw, wood and grass) using Nickel Raney as catalyst and tetralin as a solvent was studied. We demonstrated that the catalyst improves the hydrogen transfer between the solvent and the solvolysis oil resulting in the oil quality enhancement especially by decreasing oxygen content.

Recently, Lemoine et al. (2013) shown that CHR process can be applied to a wide range of biomass such as municipal wastes, primary sludge and microalgae. This versatile process can be carried out either also carried with "green solvent" such as 2-methyl tetrahydrofuran (MeTHF) (Lemoine et al., 2013) or water (Torr et al., 2011). For economic and environmental reasons, solvents and catalyst must be recycled. Catalyst baskets can be provided for holding catalyst and recovering it. The CHR process can be performed without any auxiliary fuel, it produces a surplus energy (Itoh et al., 1994); hydroliquefaction process is suitable.

Biological treatment coupled with hydroliquefaction reaction enhances the bio oil yield and its quality (Lemée et al., 2012). Structural changes in the organic matter (OM) of the LCB during the biodegradation process increase yields in oil, HSF and aliphatic hydrocarbons thus optimizing the production of bio-oil in the same conditions of hydroliquefaction as a non-biodegraded biomass. Biological degradation of biomass leads to humification of the OM, by a decrease in soluble fractions (lipids, fulvic acids) and a relative increase in more stable fractions of OM (humic acids and

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humin). As a consequence, humin, which is an insoluble fraction, can reach up to 80% after biodegradation of LCB.

Usually, LCB is first characterized by the amount of cellulose, hemicellulose, lignin and extractives. Industrial processes use also fractionation of LCB into these fractions in order to facilitate the entire valorisation of the biomass by applying specific transformation to each fraction, such as hydrolysis and fermentation of cellulose to produce ethanol, or hydrolysis and dehydration of hemicelluloses to furfural. ... In this study, the strategic issue was to carried out an economical biological pre-treatment used to change the complete nature of the LCB, thus leading to other stable fractions of organic matter (OM) called humic substances that could be easily valorised with adapted treatment.

Conventionally, humic substances are quantified using the International Humic Substances (IHSS) Protocol. Humic acids (HA) and fulvic acids (FA) are extracted using a strong base (NaOH or KOH). HA are insoluble at low pH and are thus precipitated by adding strong acid (adjust to pH 1 with HCl). Humin (Hu) cannot be extracted with either a strong base or a strong acid.

The aim of the present work was to evaluate the potential of the different humic substances to produce bio-oil from a biodegraded LCB using hydroliquefaction reaction. The knowledge of the reactivity of the different fractions of OM would be very helpful for biological pretreatment optimization to form bio-oil or others green products.

2. Methods

The experiment was carried out using an initial LCB composed of 45% grass from public green space, 38% oak and chestnut tree wood, 17% wheat straw. This proportion was determined in order to obtain an optimum carbon to nitrogen ratio of 23.9. Indeed, previous studies have shown that a high initial C/N ratio causes a slower beginning of the biodegradation process increasing the total degradation time (Tuomela et al., 2000) while low initial C/N ratio results in emission of ammonia (Tiquia and Tam, 2000).

2.1. Biological pretreatment

The biological pretreatment was carried out in a biodegradation reactor, under controlled conditions, using 5 kg of a dried LCB mixture. The biodegradation reactor (Lemée et al., 2012) is steel made and cylindrical shaped (V = 85 L, H = 80 cm, D = 40 cm) with a double wall to minimize heat exchange with the external environment. A metal grid was placed at 5 cm apart from the bottom of the reactor in order to eliminate the water leaching through the lignocellulosic material. The temperature was monitored using a thermocouple (probe PT-1000) placed at the center of the mixture. Airflow controlled by a compressor is applied to the base of the reactor thus ensuring aeration of LCB during biodegradation. LCB was ground to 200 μm, mixed and moistened to 50 wt.% water holding capacity before being introduced into the reactor for biodegradation. The airflow which is necessary to maintain biological activity throughout the process (He et al., 2000) was set at 250 L h^{-1}.

2.2. Chemical composition of LCB

The Van Soest soluble fraction was obtained using the standardized method derived from the classic Van Soest procedure (Van Soest and Wine, 1967). The 3 steps extraction procedure included an initial extraction in hot water at 100 °C (water extractable fraction) followed by an extraction in a neutral detergent solution at 100 °C for 60 min (NDF) and an extraction in acid solutions (ADF and ADL).

2.2.1. Neutral detergent fiber (NDF)

The water extractable fraction was extracted from 1-g of LCB covered with 100 mL of hot water for 30 min. The soluble fraction was separated from the solid residue by centrifugation at 6000*g* for 15 min and then filtered through glass crucibles (porosity 40–90 μm).

The residues of the hot water extraction were extracted using 100 mL of neutral detergent solution (for 1 L distilled water: 30 g sodium lauryl sulfate, 18.61 g sodium dihydrogen ethylene-diamine tetraacetic, 6.81 g sodium tetraborate decahydrate; 4.56 g sodium hydrogen phosphate; and 10 mL triethylene glycol; pH between 6.9 and 7.1) for 60 min, after adding 10 drops of octanol to prevent foaming.

After centrifugation as described above, the residues (Neutral Detergent Fiber residue: NDF residue) were rinsed 10 times with 100 mL of hot distilled water (10 min agitation then centrifugation as previously). The residue is directly filtered, washed with hot water and dried with acetone. A 550 °C calcination step allowed determining the ash content. NDF includes hemicelluloses, cellulose and lignin.

2.2.2. Acid detergent fiber (ADF)

ADF is the organic matter not solubilized after 1 h under reflux in an acid detergent solution consisting of acetyltrimethylammonium bromide in 0.5 M sulfuric acid. The residue was filtered and washed with hot water and dried with acetone. A new step of calcination allowed determining the ash content. ADF includes cellulose and lignin.

2.2.3. Acid detergent lignin (ADL)

ADL is the organic matter not solubilized after 3 h of extraction with a 72 wt.% sulfuric acid solution.

Therefore, the hemicelluloses content could be obtained by subtracting the value of ADF from the value of NDF. The amount of cellulose is obtained by the difference between the values of ADF and ADL. ADL corresponds to the lignin fraction.

2.3. OM separation

A large amount (1 kg) of biomass was sampled, mixed and sieved to 2 mm and 50 g aliquot was used for analysis. The OM was fractionated according to the IHSS protocol (Calderoni and Schnitzer, 1984). Lipids were extracted from the LCB with a dichloromethane/methanol mixture: 2/1 (v/v) using solvent accelerated extractor (ASE 100, Dionex). Humic and fulvic acids were extracted from the residue by 0.1 M NaOH (10 mL/g) under a nitrogen atmosphere in order to prevent OM oxidation. "Humic acids" were separated from "fulvic acids" by acidification to pH 1 (6 M HCl solution) and centrifugation (30 min, 7000*g*). The alkaline-insoluble residue corresponds to "humin".

2.4. Physico-chemical analysis

Parameters such as pH (1/5 w/v in water), organic carbon content (OC), total nitrogen (N_T), oxygen content (O) were determined.

The elemental composition (C, H, N) was determined using an elemental analyzer (Thermo Electron Corporation Flash EA 1112 series) after total combustion at 970 °C under oxygen. Oxygen content was determined by pyrolysis at 1000 °C under an inert (helium) atmosphere, using the same apparatus.

OM percentage was determined using thermogravimetry (TGA) under an oxidant atmosphere; carried out on a TA Instrument SDT Q600. Samples were analyzed without any pre-treatment. The analyses were performed using platinum crucibles under air atmosphere (combustion). The following conditions were employed: heating rate of 5 °C min^{-1} from 25 to 900 °C and an isotherm of