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Biological pretreatment for production of lignocellulosic biofuel

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HIGHLIGHTS

- Lignocellulosic biomass (LCB) was submitted to a biological pretreatment under controlled conditions.
- Organic matter was characterised during the biodegradation process.
- Analysis of lipids and thermochemolysis were used to monitor bacterial activity.
- Humic/fulvic acids ratio, IR and TG analysis traduced OM complexification.
- Biodegradation improved the quality and the quantity of bio-oil.

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ABSTRACT

Lignocellulosic biomass was submitted to a biological pretreatment prior to a catalytic hydroliquefaction in order to produce biofuel. The biodegradation process was conducted over 3 months in a reactor under controlled conditions. During the biodegradation process the organic matter was characterised and its evolution was correlated with physico-chemical parameters. In parallel with the analysis of the lipidic fraction, analytical pyrolysis was used to monitor bacterial activity. The alterations of branched to linear fatty acids ratio and of mono- to diacids ratio were compared when determined by thermochemolysis and observed in the directly extractable lipids. The evolution of the phytol to the corresponding isoprenoic ketone ratio was observed to be dependent on the desorption technique since it decreases using headspace while it increases using pyrolysis. "Humic"/"fulvic acids" ratio, infrared spectroscopy and thermodifferential analysis were used to determine the degree of OM complexification.

1. Introduction

Regarding the evolution of oil price, the actual petroleum resources (Shafiee and Topal, 2009) and climate changes, it has become an emergency to find substitute to fossil fuel. Indeed the use of carbon fossil as a source of energy is probably one major cause of greenhouse effect (IPCC, 2007). Emissions of carbon dioxide can be limited with alternative sources of energy such as biofuels.

First generation biofuels are produced from agricultural cultures i.e. esters of lipids (vegetable oils) or ethanol resulting from glucids (beets, corn, etc.) fermentation. However, their use is controversial and several studies have shown that the impact on the climate (Fargione et al., 2008), biodiversity (Fitzherbert et al., 2008) and food price (Runge and Senauer, 2008) can be negative.

It is thus necessary to develop new processes to produce fuels from other sources of abundant and cheap raw materials. In this purpose organic waste and lignocellulosic materials including agricultural and forest residues are interesting regarding their disponibility. Indeed fuels produced from lignocellulosic biomass (LCB) are of particular interest since the amount of carbon dioxide resulting from biomass use is equal to those absorbed during its growing. Moreover, LCB valorisation is of environmental interest while it adds a solution to the problem of waste management. Furthermore, the production of biofuels, which can be used as additives with gas oil or gasoline, contributes to reduce energy dependence.

Production of liquid fuels by direct hydrogenation of biomass offers a promising alternative to the pyrolysis processes. Indeed, the oil obtained presents a low oxygen content and high heating value by using the direct technique (Li et al., 2008). The oxygen content and the higher heating value (HHV) are only about 6% and 40 MJ kg^{-1}. The oils mainly contain alkanes, aromatic hydrocarbons, phenol derivatives and alcohols with H/C ratio higher than 1.5.

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 has been studied. We demonstrated that the catalyst enhances the oil quality by increasing the hydrogen transfer

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between the solvent and the solvolysis oil. As a consequence the oxygen content decreased.

The present work aims at demonstrating that a biological pretreatment is relevant to optimise the production of biofuel from LCB in the same conditions of hydroliquefaction. Indeed a modification of the starting biomass by a biological treatment should enhance the yield and quality of the oil obtained through the liquefaction reaction. In order to evaluate the capacity of such a pretreatment to enhance biofuel production, hydroliquefaction of the original biomass was compared with the oil produced from the same biomass at different degree of biodegradation.

Before hydroliquefaction, wide parts of this work consisted to develop and optimise the pretreatment step. In this goal the initial biomass was characterised at the molecular level and compared with the LCB after different degree of pretreatment. Indeed the authors have previously demonstrated (Som et al., 2009) that structural characterisation of a LCB delivers informations which can be used to optimise its biodegradation. Moreover the correlation of molecular changes with hydroliquefaction results can be of a great interest to optimise the whole process.

Elemental analysis (organic C, total N and C/N ratio) and physico-chemical parameters (pH, OM content) were used. In the same time structural changes in the OM of the biomass were monitored using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Finally headspace and pyrolysis both coupled with gas chromatography and mass spectrometry (GC/MS) were used to characterise the OM at the molecular level.

2. Methods

The series of experiments was conducted using a LCB composed of 45% grass, 38% wood and 17% straw. The initial LCB contained a high level of OM (79% measured by TGA). The elemental composition expressed relatively to ash free organic matter was 54.5% C, 6.5% H, 2.3% N and 47.0% O (Table 2).

First LCB was crushed to obtain a particle size smaller than 0.4 mm, and then it was freeze-dried (Bioblock Scientific CHRIST ALPHA 1-4). The residual moisture determined by TGA (SDT Q600) was smaller than 5 wt.%. The elemental composition (C, H, N) was determined using an elemental analyser (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.

2.1. Biodegradation reactor

Several kinds of reactors are commonly used according to literature. They are characterised by a natural, passive or forced aeration mode. The forced aeration option was chosen in order to control the process. The biodegradation reactor (Fig. 1) is steel made, cylindrical shaped ($V = 85L$, $H = 80$ cm, $D = 40$ cm) with a double wall to minimise heat exchange with the external environment. A metal grid was placed 5 cm 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 in the centre 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% water holding capacity before being introduced into the reactor for biodegradation. The biodegradation process was conducted over 3 months (from June to August) using 5 kg of a dried LCB mixture. During biodegradation, 50 g of samples were removed from the system at appropriate intervals in order to characterise the OM at the molecular level.

2.2. Aeration

During the biodegradation process, the biomass was regularly (8, 22, 36 and 85 days after the beginning) taken out of the biodegradation reactor and mixed. Samplings for analysis were carried out at these moments. Most of the time this procedure was followed by an increase of the temperature measured in the bioreactor (Fig. 2), which traduces an enhancement of the biological activity (Kato and Miura, 2008). The airflow which is necessary to maintain biological activity throughout the process (He et al., 2000) was set at 250 L h^{-1}.

2.3. Moisture content

Moisture content was determined by measuring the amount of dry matter. Measurements were performed on 50 g of substrate at 105 °C for 48 h. The moisture content was measured every day and adjusted when necessary to 60% of dry biomass weight.

2.4. Temperature monitoring

The temperature inside the reactor was monitored using a platinum sensor and recorded every hour. The evolution of the temperature is presented Fig. 2. A light increase occurs at t 22 and 36 which corresponds to the sampling.

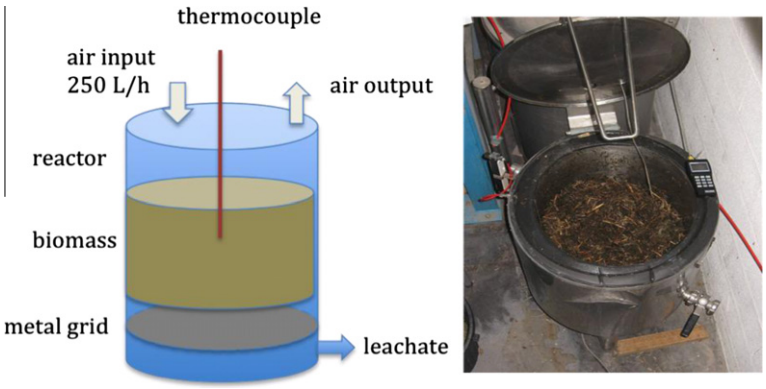

Fig. 1. Scheme and picture of the biodegradation reactor.