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Pyrolysis of spirulina and zeolite cracking over HZSM-5. An analytical investigation on the chemical route of bio-oil from cultivation to combustion

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ABSTRACT

Spirulina (*Arthrospira platensis)* was cultivated in a 70 L indoor vertical photobioreactor and harvested at concentrations of 1.0 g L^{-1} dry biomass. Lyophilised algal biomass was pyrolysed at 500 °C under nitrogen and vapours were passed over pelletised HZSM5- zeolite (SiO_2/Al_2O_3 38). An organic fraction (bio-oil) overlaying an aqueous phase was obtained by cold trapping, while non-condensed bio-oil components (XAD fraction) were adsorbed onto a poly(styrene—*co*-divinylbenzene) resin. About 20% of the original algal carbon was converted into inorganic carbon in the aqueous (HCO_3^-/CO_3^{2-}) and gas phase (composed of 70% CO_2, 20% CO). Most of spirulina carbon ended up in char (30%) and coke (30%). Bio-oil and XAD fraction represented approximately 10% mass, 20% carbon and 20% energy of algal biomass. Bio-oil composition was dominated by alkylated monoaromatic hydrocarbons, with benzene concentrations below 10 g kg^{-1}. Large part of original nitrogen was dissolved in the aqueous phase (40%) and incorporated into char/coke (37%). A minor fraction (6%) of nitrogen ended up in bio-oil in the form of indoles, pyrroles, carbazoles, anilines. While deoxygenation was effective, denitrogenation was incomplete and probably counteracted by zeolite ammonisation. Microcombustion experiments showed that the bio-oil burnt efficiently, but with a sooting flame, and a tendency to form small solid carbonaceous residues probably associated with the presence of heavy compounds.

1. Introduction

Algal biomass is being encouraged among the potential feedstock to obtain liquid renewable fuels capable to "provide high greenhouse gas emission savings with a low risk of causing indirect land-use change, and do not compete directly for agricultural land for the food and feed markets" [1]. Lipid-rich oleaginous microalgae have been widely investigated as a source of biodiesel, but their cultivation and productivity resulted problematic, therefore the conversion of low-lipid microalgae has attracted increasing interest [2]. Among microalgae with low-lipid content, spirulina (*A.platensis*) has been considered as a potential energetic feedstock for its adaptability and resistance to grow in open ponds [3]. Under normal growth conditions spirulina is not rich in lipids or degradable carbohydrates convertible into biodiesel or bioethanol. Nutrient limitation, especially phosphorus given that cyanobacteria can fix nitrogen, can promote an increase in the lipid content of spirulina, but at expenses of biomass production [3]. Therefore, thermochemical treatments capable to transform the entire biomass into an organic liquid product, here named as bio-oil, exploitable as energy vector have become of interest for low-lipid microalgae, such as spirulina [4].

Bio-oil from spirulina can be obtained by hydrothermal liquefaction (HTL) and pyrolysis. HTL is the thermochemical treatment best suited to treat wet biomass, given that algae prosper in aqueous media. Accordingly, several studies have been conducted on HTL of spirulina [5–9]. However, the abundance of water necessary in HTL has an energetic cost [8], while the organic rich aqueous streams need adequate treatments or recycling [5,10]. Pyrolysis is a thermochemical treatment that requires dried spirulina [11–13], but the bio-oil can have improved characteristics over HTL bio-oil such as lower content of high molecular weight species [8]. Pyrolysis can be considered feasible to treat the residual biomass left from the extraction of valuable components such as lipids [4,8].

In comparison to bio-oils derived from lignocellulosic biomass, bio-oil from spirulina is characterised by a lower content of oxygen and acidity [12,13]. This is due to the inherently lower content of oxygen in biomass, and the fact that nucleophilic reactions brought about by nitrogen promote the elimination of oxygen in the form of water during

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pyrolysis [13]. However, residual nitrogen in bio-oil and the presence of high molecular weight components make upgrading an obliged step for a drop-in fuel [14]. Catalytic cracking over HZSM-5 has been investigated as a potential route to deoxygenate and denitrogenate pyrolysis vapours from protein-rich algae [12–19]. By comparing the performance of different zeolite catalysts (ZSM5, H-β, H-Y) by analytical pyrolysis (Py-GC–MS), it was demonstrated that acidic ZSM-5 provided the highest production of aromatic hydrocarbons from spirulina [16,17]. The Si/Al ratio is generally taken as an indication of Brønsted acidity which is principally due to protons neutralising the negative charge of tetrahedral Al sites that should favour cracking and aromatisation. Analytical pyrolysis experiments conducted on spirulina confirmed that the relative amount of aromatic compounds increased as the Si/Al ratios of ZSM-5 decreased [16,17]. Besides, the pore diameter of ZSM-5 (5 Å) was considered optimal in favouring the production of alkylated benzenes [20].

However, the occurrence of nitrogen-containing compounds (NCCs) in the pyrolysis vapours is expected to be a major issue in zeolite cracking. Due to their basic character, NCCs can block the acidic sites of zeolite decreasing cracking efficiency of hydrocarbons and increase coke production [21]. It is not clear yet which zeolite properties (acidity, pore shape, surface area) are most prominent in the denitrogenation of organic NCCs [17]. Therefore, understanding the fate of nitrogen is fundamental to assess the boundaries of zeolite cracking in the development of liquid biofuels from proteinaceus biomass. Ammonia (NH_3), hydrogen cyanide (HCN) and isocyanic acid (HNCO) are the principal inorganic NCCs evolved from pyrolysis of nitrogenated components in biomass, prevalently proteins [22–24]. Part of the initial N is incorporated into the solid residue, but at temperatures higher than 500 °C gaseous NCCs can be released from the thermal degradation of char during pyrolysis [25].

Wang and Brown reported that NCCs detected by direct pyrolysis of *Chlorella vulgaris* in a micro-furnace were completely eliminated from the products when the microalgae was pyrolysed in the presence of excess of HZSM-5 (SiO_2/Al_2O_3 23) at 700 °C [19]. This study showed that the initial nitrogen in *C.vulgaris* distributed essentially in the solid residue (coke + char) and in gaseous species, principally NH_3 with smaller amounts of HCN [19]. Similarly, nitrogen distributed primarily in ammonia and solid residue upon HZSM-5 cracking of protein-rich feedstock, such as sewage sludge [26] and distiller grains with solubles, a co-product of corn bioethanol production [27]. The distribution of nitrogen into gas or coke/char is dependent on a variety of factors, such as process conditions and the chemical nature of the substrates. With regard to this latter factor, Liu et al. studying catalytic pyrolysis of aliphatic linear (leucine) and cyclic (proline) amino acids found that proline tended to retain N in the coke, while leucine released N principally as ammonia [28]. The corresponding polypeptides produced different proportions of N-containing compounds (NCCs): poly(proline) decomposed mainly into HCN and HNCO, while the pathway leading to NH_3 was more pronounced for poly(leucine) [29]. As far as process conditions are concerned, the results from HZSM-5 cracking showed that the initial nitrogen remained essentially in the solid residue at temperatures lower than 500 °C, and in the gas products at higher temperatures [19]. In the condensable fraction, nitrogen occurs in the form of organic NCCs; in the case of spirulina, pyrroles, indoles, aliphatic and aromatic nitriles and amides were identified in the pyrolysates produced upon ZSM-5 cracking [12,16,17].

Although important information have been gathered by analytical pyrolysis [16,17] and bench-scale reactors [12], a full mass and elemental balance and detailed molecular analysis of all the fractions derived from HZSM-5 cracking of spirulina have not been conducted. Moreover, the combustive properties of the bio-oil obtained from catalytic pyrolysis of microalgae have not been investigated yet. Key chemical factors, especially carbon and nitrogen fate, in the production of a gasoline-like fuel from catalytic pyrolysis of spirulina have been considered in this study starting from algae cultivation to the combustive behaviour of the isolated bio-oil. To this purpose, a closed reactor system was set up in order to perform a consistent mass balance based on direct (weight determination) or indirect (gas chromatographic) measurements on each collected fraction. Pyrolysis was conducted separately from zeolite cracking enabling the isolation of char (here named as biochar).

2. Experimental

2.1. Reagents

Zeolite HZSM-5 in pellet (SiO_2/Al_2O_3 molar ratio 38, pore size ca. 5 Å, specific surface area > 250 $m^2 g^{-1}$) was purchased from ACS MATERIAL. Zeolite was activated by calcination in a muffle furnace at 550 °C for 6 h prior to use. Temperature programmed desorption with ammonia (TPD-NH_3, procedure described in [30]) of calcined zeolite resulted in a total acidity of 0.13 ± 0.03 mmol kg^{-1}, a value lower than expected from the Si/Al ratio, probably due to the dilution effect after pelletisation [31]. Amberlite XAD-2 Resin (Supelco) made of microspheric poly(styrene-*co*-divinylbenzene) was washed with methanol, ethyl acetate and acetonitrile (Sigma-Aldrich), dried at 100 °C and kept in a desiccator before its utilisation in pyrolysis-cracking experiments. Tedlar bags (1L Tedlar® PLV Gas Sampling Bag w/Thermogreen® LB-2 SeptaPush/Pull Lock Valve) were from Sigma-Aldrich Co.

2.2. Spirulina cultivation

A.platensis (SAG 8579) was cultivated in a 70 L column photobioreactor with internal illumination (M2 M Engineering, Italy)[18]; the culture was made in a Zarrouk medium with low flow rate air insufflation (1–2 L min^{-1}) to avoid breakage of algal cells, at a temperature of 25–27 °C, light intensity of 250–300 μmol photons $m^{-2} s^{-1}$, and a 16 h light: 8 h dark cycle. Dry weight of the algal biomass was determined filtering aliquots of 30–40 mL of algal suspension through a pre-weighted, pre-combusted (105 °C, 24 h) glass fibre filter (Whatman GF/C, 47 mm, nominal pore size 1.2 μm). The filters were then dried at 105 °C for 1–2 h to obtain a constant weight. *A. platensis* was collected by filtration when biomass concentration was around 1 g L^{-1} dry weight.

The protein concentration of *A. platensis* was estimated with the Folin Phenol reagent [32] using bovine serum albumin as standard. The protein determination was carried out using the algal pellets obtained by centrifugation at 5000 rpm at 4 °C for 20 min and preserved at −80 °C.

Nitrate analyses were performed on filtered culture medium aliquots (Whatman GF/C filters, pore size 1.2 μm) and analyzed spectrophotometrically (UV/VIS, JASCO 7800, Tokyo, Japan) [33]. The total N utilised from microalgae during the growth from day 0 to the harvesting day (10th day) was calculated from the residual nutrient concentrations in the medium and the difference in cell densities (g) between day 0 (0.2 g L^{-1}) and the last day.

2.3. Pyrolysis and zeolite cracking

The pyrolysis-zeolite cracking experiments were conducted in a closed apparatus similar to that described in [12]. Details with photos of the reactor and obtained fractions are shown in Fig. S1. Pyrolysis-cracking experiments were performed by single runs in triplicate to the purpose of determining mass balance. To the end of collecting a bio-oil sample for quantitative GC–MS analysis, ^1H NMR and microcombustion tests, one batch experiment that cumulated the liquid fraction from six single sequential runs was performed.