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Effect of *Chlorella vulgaris* growing conditions on bio-oil production via fast pyrolysis

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ABSTRACT

Microalgae have been recognized as one of the most promising biomass sources of energy, in particular for bio-fuels production. In this paper the production of bio-oil from a fast growing microalgae species with low lipids content is proposed. The influence of both the cultural medium and the reaction conditions on bio-oil yields and quality is investigated performing fixed and fast pyrolysis tests on *Chlorella vulgaris* grown in complete and nitrogen starved medium. Nitrogen starvation leads to a higher lipids amount in the biomass, increasing its calorific value. Fast pyrolysis of nitrogen starved microalgae is proposed to achieve high bio-oil yield and quality. In this case, experiments have pointed out a maximum bio-oil yield of about 72% mass on dry basis at 400 °C. Bio-oil products were characterized on the basis of GC–MS, elemental analysis and calorific content. In particular, the GC–MS analysis accounts for an oily fraction of the bio-oil formed by several hydrocarbons as well as oxygenated and nitrogenous species, including indoles, fatty acids and alcohols. The bio-oil produced from nitrogen starved biomass exhibits higher amount of fatty acids and lower amount of nitrogenous species, resulting in an improved quality. Furthermore, the higher lipids amount of the nitrogen starved biomass leads to a major carbon content in the bio-oil and thus to a slight increase of its calorific value.

For all the experimental tests the energy consumption ratio was calculated, and fast pyrolysis of nitrogen starved biomass has proved to be the most convenient process in the energetic valorization of microalgae.

1. Introduction

The environmental impact of fossil fuel exploitation is promoting the development of energetic conversion processes of renewable energy sources such as biomass. The use of biomass helps to reduce the dependence from fossil fuels as well as the carbon dioxide emissions responsible for the greenhouse effect, due to its CO_2 neutrality [1]. Nevertheless, biomass is not always suitable for direct use in combustion processes, due to a low heating value and a high water content, if compared to the same quantities referred to fossil fuels [2]. Thus, the interest in biochemical and thermochemical processes of biomass conversion to obtain gaseous and liquid biofuels with higher energy volume density than the former feedstock is increasing [3,4].

Microalgae have been identified as one of the most promising biomass source of energy [5]. In comparison with

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traditional terrestrial crops, microalgae do not require arable lands and can be produced all year round at high growth rate with a reduced use of fertilizers, pesticides and water [6]. In particular, microalgae have been appointed as ideal biodiesel feedstock in virtue of their high lipids content that can reach up to 80% of dry biomass mass [7]. Microalgae biomass can be thermochemically converted via pyrolysis into a liquid biofuel called bio-oil potentially suitable for energetic purposes [8,9]. Bio-oil is a multicomponent mixture composed of many chemical species derived from depolymerization and fragmentation reactions of the key biomass components [10]. When these reactions occur, the high oxygen content of the biomass involves the formation of water and oxygenated aliphatic and aromatic hydrocarbons, making the bio-oil high heating value lower than that of fossil fuels [9].

To avoid this drawback, slow pyrolysis of different microalgae species was investigated by many authors for several reaction conditions [11–13]. Furthermore fast pyrolysis was proposed as alternative process to improve bio-oil yields [14] and [15]. Miao and Wu [16] proposed the fast pyrolysis of two species of microalgae in a fluidized bed reactor obtaining a maximum bio-oil yields of 57.2%. On the other hand, catalytic pyrolysis in fixed bed reactor was suggested to obtain high quality bio-oil by several authors [17–19]. Fast catalytic pyrolysis of microalgae was investigated by Campanella and Harold [20] who, to combine the advantages of both the approaches in a single process, performed experimental tests on a falling solid reactor using ZSM-5 as catalyst, obtaining a better quality bio-oil with an enriched amounts of hydrocarbon compounds and a reduced fraction of oxygenated products.

Aim of this paper is to study the influence on bio-oil quality and yield of fast and slow pyrolysis of *Chlorella vulgaris* grown in complete and nitrogen limited medium. Nitrogen starvation triggers microalgae carbon fluxes toward lipid synthesis [21], preventing proteins and DNA synthesis and thus inhibiting cellular duplication. However, nitrogen starvation does not affect directly the energetic metabolism of microalgae, which can spend the energy saved from the absence of cellular duplication in the synthesis of new lipids [22]. In this way, the microalgae carbon content increases while the oxygen and nitrogen ones decrease affecting the pyrolysis process and products [23]. This approach, although represents an improvement for the suitability of *C. vulgaris* as biodiesel feedstock, still limits lipid productivity at a level incompatible with economical industrial applications. For these reasons thermochemical exploitation of this microalgae strain is proposed, allowing the whole microalgae cell conversion and increasing the bio-oil yield.

2. Material and methods

2.1. Algal cultures

C. vulgaris cultures were grown in BG-11 medium ($NaNO_3$: 1.50 g L^{-1}, K_2HPO_4: 0.04 g L^{-1}, $MgSO_4 \cdot 7H_2O$: 75.0 mg L^{-1}, $CaCl_2 \cdot 2H_2O$: 36.0 mg L^{-1}, citric acid ($C_6H_8O_7 \cdot 1H_2O$): 6.0 mg L^{-1}, ferric ammonium citrate ($C_{12}H_{22}FeN_3O_{14}$): 6.0 mg L^{-1}, Na_2CO_3: 20.0 mg L^{-1}, Na-EDTA: 1.0 mg L^{-1}, H_3BO_3: 2.86 mg L^{-1}, $MnCl_2 \cdot 4H_2O$: 1.81 mg L^{-1}, $ZnSO_4 \cdot 7H_2O$: 0.22 mg L^{-1}, $Na_2MoO_4 \cdot 2H_2O$: 0.39 mg L^{-1}, $CuSO_4 \cdot 5H_2O$: 79.0 μg L^{-1}, $Co(NO_3)_2 \cdot 6H_2O$: 49.4 μg L^{-1}) and in a BG-11 modified medium (N*) that differs from the standard recipe only for the complete lack of $NaNO_3$. All the cultures were conducted in 5.0 L flat-plate photobioreactors maintained at 25 ± 1 °C and exposed to a light intensity of 150 mmol photons m^{-2} s^{-1} provided by phytostimulant fluorescent tubes, with a light\dark photoperiod of 12:12 h.

Algal cell concentration was determined by measuring routinely the optical density (OD) at 686 nm (Sequoia-Turner 340 spectrophotometer) and by gravimetric analysis.

2.2. Biomass characterization

The microalgae strain of *C. vulgaris* used in this study was kindly provided by Prof. G. Torzillo (CNR, Institute of Ecosystem Study, Sesto Fiorentino, Italy). Algal biomass was first harvested by centrifugation (2757 RCF, 15 min) and dried under vacuum. Dried biomass was mortar-pulverized to ensure an average dimensional distribution within the range of 100 and 150 μm.

Biomass was characterized by proximate analysis (according to ASTM D5142), elemental analysis (EuroVector EA3000) and high heating value measured in a Mahler bomb calorimeter. Water content in the bio-oil oily fraction was measured by Karl-Fischer titrimetric method with an 899 Coulometer (Metrohm).

Lipids were extracted according to the protocol described by Bligh and Dyer [24] and the lipids content was determined gravimetrically by evaporating the solvents under vacuum and drying the extract for 4 h at 80 °C. Protein content was approximated by multiplying elemental nitrogen concentrations by a factor of 6.25 [25].

Thermogravimetric analyses (TGA) were performed at 50 °Cmin^{-1} with a TGA SDT Q600 (TA Instruments).

2.3. Fixed bed pyrolysis

Fixed bed pyrolysis tests were performed in a quartz tubular reactor 40 mm i.d. and 300 mm length, equipped with a quartz frit on the bottom side and heated by an external electric resistance (Fig. 1A). An amount of 15 g of biomass was loaded before the beginning of the test in the reactor, forming a 3 cm layer. Pyrolysis tests were performed at 400, 500, 600 and 700 °C under a downward nitrogen flow rate of 400 cm^3 min^{-1} at normal temperature and pressure and repeated three times to ensure the reliability of the reported data. Pyrolysis vapors were quenched to 40 °C in a series of two water-cooled traps placed immediately at the reactor outlet to ensure the complete recovery of the condensable vapors. By means of a thermocouple placed inside the biomass bed, the heating rate was measured to verify the typical value of 50 K min^{-1} which characterizes the slow pyrolysis process [26].

2.4. Fast pyrolysis

Fast pyrolysis tests were performed in a quartz tubular reactor 0.8 cm i.d. and 70 cm long, heated by an external electric resistance, with a tilt angle of 70° respect to the ground as