



Synergistic effects during the co-pyrolysis and co-gasification of high volatile bituminous coal with microalgae

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ABSTRACT

In this work, the co-pyrolysis and co-gasification of *Nannochloropsis* sp. microalgae (NM) and Colombian bituminous coal (CC) were performed in order to evaluate potential synergistic effects and the kinetic parameters, which are essential for advancing the co-utilization. The effect of the share of feedstock, microalgae and coal, on the co-pyrolysis and co-gasification behavior was studied under different heating rates and temperatures. There were synergistic effects between the two fuels during their co-pyrolysis process, especially for that mixture containing 50 wt% of microalgae. At conversion levels < 25 wt%, the activation energy (E_a) was found to be lower than the individual microalgae, 143 and 170 kJ/mol, respectively. Despite the acid leaching pre-treatment (NM-ac) showed a positive effect on the microalgae pyrolysis kinetics for conversion values < 60 wt%, the trend was inverted at higher conversions, due to the removal of alkali species from microalgae ash, which also slowed the CC/NM gasification. However, ash removal can potentially reduce operational issues related to presence of Cl and Na. Both synergistic and inhibiting effects were observed in the co-gasification experiments. Synergistic effect at temperatures higher than 800 °C was due to the microalgae high Na content that promoted coal char gasification, resulting in an E_a decrease for the coal from 189.9 to 146.1 kJ/mol. This reduction was higher to that expected if both fuels would behave according to the mixtures additive law (159.1 kJ/mol), Inhibiting effect at 750–800 °C can be linked to lower presence of Na on char surface and lower transformation of NaCl in gasification active species.

1. Introduction

Due to the challenge of greenhouse gas emission, renewable energy has gained increasing attention. Among all the renewable energy resources, biomass is the only renewable energy that can replace fossil fuel in all energy utilisation areas [1]. In the same time, coal is still the major energy resource in many countries, and its co-utilisation with biomass could provide many advantages, such as the reduction of CO₂ and other gaseous pollutants emissions and improve the overall efficiency via synergistic effects [2–4]. The recent use microalgae for energy production has received great attention due to their high production yield per area, high efficiency in CO₂ capture and solar energy conversion and absence of competition for land with food crops [5,6]. Conversion of algal biomass to a wide spectrum of biofuels such as ethanol, hydrogen, diesel and biogas is possible via biochemical (e.g. anaerobic digestion), chemical (e.g. transesterification) and thermochemical routes (e.g. gasification). Despite the fact that most of the R&D effort so far has been dedicated to the conversion of algae to biodiesel through transesterification, thermochemical routes are considered

better than the former on account of short reaction times, high conversion efficiencies and comparatively low costs [7]. This can be ascribed to the transesterification of algae constraints such as (i) the use only of a fraction of the whole algae, (ii) the need for effective lipids extraction methods (currently not available) and (iii), the presence of abundant “non-storage lipids” (e.g. glyco- and phospho-lipids), which cannot be used in biodiesel and require costly and difficult extraction processes [8].

In recent years, a number of studies have arisen dealing with co-processing of coal and microalgae, in particular co-pyrolysis and co-gasification [3,5,6,9–12]. Pyrolysis is a thermochemical decomposition process that, depending on the reaction conditions, can be used to transform a solid fuel directly into liquid, solid or gaseous fuels [13]. Pyrolysis is also the first stage of gasification, in which a solid fuel is converted into a combustible syngas [14]. In this respect, a systematic understanding of pyrolysis kinetics is a key factor for the assessment of feasibility, design, and scale-up of such fuel conversion processes for energy applications [15]. However, it is the second stage (char gasification) that really controls the overall gasification process due to being

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much slower than the devolatilization step [16]. For this reason, knowledge about the reactivity of chars, and their variation as reaction progresses, is fundamental for the design of gasification reactors and the optimization of the plant operating procedures, as char gasification determines the final conversion achieved in the process [17]. Thermogravimetric analysis (TGA) is the most commonly used technique to study the solid-phase thermal decomposition reactions [18]. Even though it operates in a different form in comparison to a real reactor (pyrolyser or gasifier), it provides an understanding of thermal degradation processes occurring during the fuel conversion. The thermal decomposition of all biomass samples proceeds via a very complex set of competitive and concurrent reactions and thus, the exact mechanism for biomass pyrolysis remains unknown. Each step likely has its own single apparent activation energy, and thus the use of an average, global apparent activation energy to define the kinetics of such processes could be interpreted as an inadequate simplification at best [19]. The so-called “model-free” dynamic kinetic methods, such as: Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO), founded on an iso-conversional basis do not require previous knowledge of the reaction mechanism for biomass thermal degradation [9]. There is also a recent modification of these methods developed by Campbell et al. [20] that involves the minimisation of a function. Since solid-state processes, such as biomass pyrolysis, frequently proceed via a complex suite of concurrent and consecutive reactions, each step likely has its own unique apparent activation energy, and thus the use of an average, global apparent activation energy to describe the kinetics of such processes could be construed as an inadequate oversimplification [18]. Instead, isoconversional (model-free) kinetic models (such as KAS and FWO) can be used to compute kinetic parameters during conversion without model-based assumptions, such as an a priori first order reaction. In these methods the activation energies are calculated at fixed conversions, taking advantage of the fact that the reaction rate depends exclusively on the reaction temperature [21]. Regarding the char gasification kinetics, there are different gas–solid reaction kinetic models in the literature that have been used to predict the behavior of coal and biomass during the gasification and calculate the kinetic parameters of the gasification reaction. The random pore model (RPM) proposed by Bhatia and Perlmutter [22] has been widely applied to the experimental data obtained from the gasification of individual or mixed carbonaceous materials [16,23–26].

The high thermochemical reactivity of microalgae and its high volatile matter content suggest that some synergistic effects can be expected in the simultaneous thermochemical treatment (pyrolysis or gasification) of coal and microalgae. Whether such effects will occur is dependent upon certain pyrolysis/gasification conditions such as feedstock type, direct particle contact, pressure, temperature, and reactor type [27]. This synergy during the co-processing is likely to be caused by the higher hydrogen and carbon molar ratio (H/C) of biomass compared with coal, which could facilitate coal decomposition [9,28], but also due to the high Alkali and Alkaline Earth Metals (AAEM), and especially Sodium and Potassium contained in biomass ash [3,16,29,30]. However, there are also some studies in the literature in which inhibiting [31] effects, or just no synergistic effect [32] during co-pyrolysis were observed that point out the importance of the biomass type and its ash content and composition among other factors [33].

Despite several studies are available on the co-pyrolysis and co-gasification of terrestrial biomasses and coal, to our knowledge, only three studies have been published on microalgae/coal mixtures on the same topic [3,34,35]. In light of the unique properties of microalgae, especially its high ash content, this research targets to clarify for the first time the feasibility of co-processing of algae with coal, both through co-pyrolysis and co-gasification. Therefore, the main objectives of this research are to investigate the possible synergistic (inhibiting or catalytic) effects of the addition of *Nannochloropsis* sp. to a high reactive Colombian bituminous coal on the co-pyrolysis and co-gasification and

to understand the reaction kinetics of both processes.

Previous works have indicated that K and Na alkali species can promote dehydration reactions leading to coke/char during gasification and pyrolysis [36]. It is also known that the rigid cell wall of microalgae can be disrupted by acid or alkali pre-treatment leading to the removal of the alkali species [37]. Therefore, the effect of the partial removal of the catalytically active elements contained in ash of microalgae, by an acid leaching pre-treatment, was also investigated to establish its effect on microalgae pyrolysis and gasification kinetics.

2. Materials and methods

2.1. Fuel samples

In this study, Colombian bituminous coal (CC) and *Nannochloropsis* sp. microalgae (NM) have been selected as fuels to be mixed for their co-utilisation under pyrolysis and gasification conditions. The samples were ground and sieved to obtain a particle size lower than 100 μm .

The blended ratios of coal (CC) and microalgae (NM) used during the co-pyrolysis and co-gasification experiments were 80%CC – 20%NM, and 50%CC – 50%NM.

The *Nannochloropsis* sp. microalgae (NM) was also subjected to an acid leaching pre-treatment with a sulfuric acid (H_2SO_4) solution (1 vol %), by mixing the dried microalgae with the acid solution at a ratio of 100 g/L for 30 min at mixing speed of 350 rpm and temperature of 25 °C [37]. The acid concentration was selected based on a previous study, where 1–3% H_2SO_4 resulted the best in disrupting the microalgae cell walls [37]. After the treatment, the mixture was rinsed with deionized water to achieve a pH of 7 and centrifuged for 3 h to separate out the leached microalgae. The residual solid was then oven dried at 60 °C to obtain constant weight. The acid-leached microalgae was named as NM-ac. This pre-treatment was carried out to investigate the effect of the partial removal of catalytically active elements contained in the microalgae ash, like Alkali and Alkaline Earth Metals (AAEM), on the pyrolysis and gasification processes.

2.2. Analytical techniques

The moisture content and the proximate analyses in dry basis (volatile matter (VM) and ash content (A)) of fuel samples were conducted according to ASTM standards: D2016, E872-82, D1102-84, respectively. Then, the fixed carbon, FC, was determined by difference according to the equation: $\text{FC} = 100 - \text{VM} - \text{A}$. Therefore, the term (FC) refers to the organic solid matter (i.e., without ash) that remains after the total volatiles of a solid fuel are thermally released under inert atmosphere. A thermogravimetric analyser, TGA (TA Q500) equipped with automatic sample handling was employed to assess the moisture, volatile matter and the ash contents of the coal and microalgae samples.

Thermogravimetric analysis is a well-established thermo-analytical technique for thermal degradation and conversion studies of solid materials, such as pyrolysis and gasification [18].

As mentioned above, the results of the TGA analysis are essential for feeding the design and the optimization of pyrolysis and gasification process in pilot scale. First of all, a detailed knowledge on the fuel behavior at different temperatures allows to optimize the geometry and the thermal profiles, as well as the operation criteria of gasification reactors, to maximize fuel conversion and reduce tar formation. In addition, the analysis allows to identify, with just few quick and cheap tests, possible interactions between fuels during co-gasification, thus allowing a process optimization in terms of fuel blend. Thus, the pyrolysis experiments were carried out by placing 25 mg of fuel sample in a Platinum crucible under non-isothermal conditions at heating rates of 10, 20, 40 and 80 °C/min up to 900 °C. The homogeneity of the samples mixtures was ensured by weighing the required amount of each sample (depending on their percentage in the mixture up to a total of 25 mg), in a microbalance (± 0.1 mg) placing them directly in a small agate

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