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Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials

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HIGHLIGHTS

- Catalytic pyrolysis of wood biomass was studied in an auger reactor.
- Several low cost materials were tested as catalysts.
- Catalyst to biomass ratio resulted critical to increase bio-oil yield.
- The studied materials reduced viscosity of bio-oil and improved its stability.
- Sepiolite and red mud produced a decrease in the acidity of bio-oil.

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ABSTRACT

Production of upgraded bio-oils by catalytic pyrolysis of wood biomass was studied in an auger reactor using low cost materials as catalysts. These materials included several clay minerals (sepiolite, bentonite and attapulgite) and an industrial waste from alumina production, known as red mud. The influence of temperature (400–500 °C) and the effect of catalyst to biomass ratio (3:1–1:6, in weight) were also analysed. A temperature of 450 °C and the lowest catalyst proportion (1:6, in weight) were selected as the most appropriate to aim the pyrolysis for bio-oil production. Catalyst to biomass ratio resulted critical since an excess on catalyst addition seemed to reduce liquid production while char yield increased. Under the selected conditions, the catalysts tested improved the characteristics of the obtained bio-oil as fuel (viscosity, acidity, oxygen content and calorific value). For every catalyst, the viscosity of the organic liquid fraction decreased (up to 34% in case of bentonite) while lower heating value increased (up to 20% in red mud tests). Concerning acidity, sepiolite and red mud produced a decrease in the total acid number (around 29% and 23%, respectively). The stability of the organic fraction after aging test (equivalent to long time storage) was also improved by each catalyst.

1. Introduction

Biomass has become an interesting source to obtain energy, allowing lower dependency from fossil fuels with the consequent benefits from an ecological and economical perspective. Several processes allow transforming biomass in products that could be used as fuels. Thermal degradation of lignocellulosic materials is one of the most promising routes to obtain energy sources and chemicals from biomass [1]. Pyrolysis is included within this group. In this process, the organic matter is converted by heating under an inert atmosphere into non-condensable gases, condensable gases (which are then recovered as the liquid product) and a solid product (char).

Pyrolysis liquids obtained from biomass are commonly known as bio-oils and have been defined as dark brown, free-flowing organic liquids that have high polarity, containing approximately 35–40 wt.% oxygen (dry basis) [2,3]. Bio-oil is a promising product as fuel because it presents higher energy density than solid biomass, and can be easily stored and transported. Although properties from bio-oil are very different from petroleum derived fuels, bio-oil combustion in commercial engines is possible with some modifications to the current facilities. In this way, bio-oil has been successfully applied to replace heavy fuel oil in heating [3]. In addition, it is desired to replace also light fuel oil in stationary applications such as furnaces, boilers and even in energy generation by turbines [3]. Nevertheless, several improvements on liquid properties are needed for this aim regarding the high viscosity, density and acidity of the liquid, as well as its oxygen content [4,5].

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One way to improve the pyrolysis liquid characteristics is the introduction of catalysts to eliminate oxygen, increasing the hydrogen to carbon ratio of the final liquid products. Catalysts employed should be highly active, selective to particular products, resistant to deactivation, readily recycled and whenever possible, cheap and widely distributed. In case of low cost materials, it is not necessary to recover them after the process. Some cheap catalysts for example bulk metal oxides [6], alumina, and sulphide/oxide or metals supported mainly on alumina have been tested for biomass catalytic pyrolysis [7]. In a previous work developed in our group, oxygen content and acidity of liquid product were found to decrease in wood pyrolysis when cheap materials as CaO or CaO·MgO were used as catalysts [8]. Several studies have analysed the application of other inexpensive materials, such as clay minerals. For example, experiences in biomass pyrolysis using sepiolite (complex magnesium silicate) showed an improvement on liquid yield (≈46%) respect to non-catalytic tests [9]. Also bentonite (aluminium phyllosilicate, consisting mostly of montmorillonite) when used in pyrolysis of peat, showed an increase in bio-oil production (48%) [10]. Nevertheless, other results indicated an opposite effect for bentonite in pyrolysis of cellulose and polyethylene [11]. Attapulgite has been also cited as catalyst in tar cracking reactions that improve gas yields [12]. Within the low cost materials that could act as catalysts, wastes obtained from several processes could be a very interesting alternative. A promising material could be bauxite waste, also called red mud, which is obtained from Bayer process (to produce alumina). This material is Fe-based, and also contains aluminium and titanium oxides, and smaller amounts of Si, Ca and Na [13]. Red mud used without activation has been previously studied as *in situ* catalyst in biomass pyrolysis in fluidised bed by Yathavan and Agblevor [14]. These authors found an improvement in bio-oil quality, such as lower viscosity, less oxygen and less acidity. Likewise, pyrolysis of plastics was also assessed using red mud without pre-treatment, showing increases in gas yield and decreases in liquid and viscosity [15]. Therefore, there is a wide range of materials that could act as catalysts in pyrolysis, without elevated costs neither supply problems.

From the different technologies proposed in pyrolysis, the auger reactor constitutes an interesting option because allows the continuity in operation, and heating can be obtained with cycled heat carriers [16]. Besides, this configuration presents relatively simple design, low carrier gas flow and adaptability to be used with large biomass particles and heterogeneous materials with difficult handling [5]. Nevertheless, few publications analysed the use of heat carriers with catalytic properties in this type of reactors [8,17].

Therefore, the objective of this paper is to study the catalytic pyrolysis of biomass in a single screw auger reactor by using a mixture of sand and several low cost materials as catalysts (sepiolite, bentonite, attapulgite and red mud). To reach this aim, the effect of these materials on pyrolysis products was studied, being more widely analysed the liquid product characteristics. In addition, the storage stability of the pyrolysis liquids produced was assessed following an accelerated aging test [18].

2. Materials and methods

2.1. Biomass

The biomass used in the present study was forest pine woodchips (*Pinus halepensis*) obtained from the north east area of Spain. The samples of biomass were received as woodchips with bark and were ground and sieved to provide a maximum size of 15 mm. The value obtained for lower heating value (LHV) was 18.0 MJ/kg (determined by means of a calorimeter IKA C-2000, standard procedure: UNE 164001 EX). Proximate analysis of the received biomass showed a moisture percentage of 4.0 wt.% (ISO-589-1981), ash proportion of 1.1 wt.% (ISO-1171-1976), volatile matter of 78.6 wt.% (ISO-5623-1974), while fixed carbon was 16.3 wt.% (determined by balance). Ultimate analysis of the received biomass showed a composition of C: 49.6 wt.%, H: 6.4 wt.%, N: 0.2 wt.%, S: <0.1 wt.% (by Thermo flash 1112, UNE EN 5104) and O: 43.8 wt.% (by balance). Biomass was initially dried up to <2 wt.% moisture.

2.2. Minerals

Silica sand, sepiolite (MYTA-SAMCA S.A.), bentonite (MYTA-SAMCA S.A.), attapulgite (MYTA-SAMCA S.A.) and red mud (Alcoa Europe-Alúmina Española S.A.) were tested in this work. These materials were sieved and the smallest particle fraction (<300 μm) was discarded, while solids between 300 and 1000 μm were used in the experimental work. Previous to each test, minerals were heat-treated at the corresponding experimental temperature (400–500 °C) under static air in a muffle furnace during approximately 2 h, to assure its stability and remove the adsorbed water.

2.3. Auger reactor facility

Experiments were carried out in an auger reactor of 100 kWth of nominal capacity for woody biomass. The reactor operated at atmospheric pressure, feeding biomass and a mixture of sand and catalysts continuously, and with non-stop products removal systems. The experimental equipment is widely described in Supplementary data and in previous publications [8,19,20].

2.4. Experimental procedure

Experiments performed were grouped into three sections: first, the influence of pyrolysis temperature on products yield was studied in non-catalytic tests and also using sepiolite as catalyst. A ratio of sepiolite or sand to biomass of 3:1 (weight ratio) was analysed in the range of 400–500 °C. Second, the influence of proportion of sepiolite to biomass was assessed at 450 °C, by varying the weight ratio from 3:1 to 1:6 (always keeping the ratio of sand + catalyst to biomass equal to 3:1, in weight). Finally, several low cost materials (sepiolite, attapulgite, bentonite and red mud) were probed and compared at the catalyst to biomass ratio and temperature selected from the previous experiments. The storage stability of the organic liquids obtained for the different catalysts tested was assessed following an accelerated aging test (24 h at 80 °C) [18].

2.5. Product characterization

Gas, liquid and solid products were characterised and quantified after each experiment. A wide description of the procedures followed is included as Supplementary data.

The non-condensable fraction was sampled at ambient temperature during the experiment using Tedlar bags, once the steady state was reached. After the experiment was finished, the composition of the non-condensable fraction was determined by GC/TCD. Thus, gas yield was calculated from N_2 percentage in gas stream, which was used as an internal standard to quantify the outside gas production. The char and liquid yields were determined by weight. Catalysts and produced char samples were separated by sieving and ultimate, moisture, ash and LHV analysis were performed to the carbonaceous solid. Liquid product were stored in bottles and kept refrigerated before characterization. This product was obtained as a heterogeneous liquid in which two different phases were observed. The whole sample was treated in aliquots of 50 mL that were centrifuged at 1500 rpm during 1 h. Two liquid phases (known as aqueous and organic according to their water