Effect of temperature on product performance of a high ash biomass during fast pyrolysis and its bio-oil storage evaluation

N. Gómez[a], S.W. Banks[b], D.J. Nowakowski[b], J.G. Rosas[a], J. Cara[a], M.E. Sánchez[a,*], A.V. Bridgwater[b]

[a] Natural Resources Institute, Chemical and Environmental Engineering Group, University of León. Avda. de Portugal 41, 24071 León, Spain
[b] European Bioenergy Research Institute, Aston University, Birmingham B4 7ET, United Kingdom

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ABSTRACT

Bio-oil from the fast pyrolysis of agro-residues still needs to contemplate different production scenarios to look for its feasibility. For this reason, in this work the effect of a range of fast pyrolysis temperature (450, 480, 510 and 550 °C) processing rape straw biomass (with high K content) has been studied in a continuous bubbling fluidised bed reactor. It was found that the catalytic effect of the inorganic content was different at each fast pyrolysis temperature, with the lower temperatures resulting in the highest yield of bio-oil due to minor catalytic effect (up to 41.39 wt%). It was also found that at 480 °C the bio-oil presented the best combination of physico-chemical features such as non-separation phase and the lowest water content; yield (39.65 wt%) and HHV (19.23 MJ/kg), containing a high concentration of phenolic compounds. At the fast pyrolysis temperature of 510 °C and 550 °C, the conjunction effect of temperature and the catalytic effect provoked bio-oil separation into two phases and a higher gas yield than was expected. Then, the higher temperatures are not suitable for bio-oil production. Char is also an interesting co-product for all pyrolysis temperatures.

1. Introduction

Alternative energy demand through bioenergy processes is increasing in a current society that worries about the environmental impacts of the use of fuels. Fast pyrolysis is a thermal depolymerisation process in the absence of air yielding three products: a liquid fraction (bio-oil), a solid fraction (char) and a gaseous fraction (non-condensable gases), with the production of bio-oil being the focus. This technology produces biofuels from lignocellulosic biomass and can be used to manage biomass residues resulting in a dual benefit. It is a promising alternative for producing valuable products from renewable resources, as well as reducing the CO_2 carbon footprint and there is a large availability. Moreover, if they come from residues they can be properly removed.

The conditions that evolved fast pyrolysis are: high heating rates and very high heat transfer rates; careful control of the temperature typically 500 °C; short hot vapour residence times (< 2 s); rapid removal of char and rapid cooling of pyrolysis vapours [1]. Bio-oil yield is feedstock dependent as each biomass has a different proportion of its main components, cellulose, hemicellulose and lignin [2]. All three main components result in a variety of decomposition pathways during fast pyrolysis producing a complex combination of products in the

vapour phase [3]. The bio-oil constituents are typically oxygenated compounds that can be potentially used as fuels or sources of value-added compounds [4], whilst the char and non-condensable gases can also be used as fuels.

Previous studies have shown that woody biomass has better properties for bio-oil production at the same pyrolysis temperature [5]. Nonetheless, agricultural crop residues would be an interesting source of biomass feedstock for thermal processes because it generates high amount of residues that should be correctly managed through the "energy from waste" concept. This type of biomass is commonly linked with high ash content [6], which has been linked to lower bio-oil production as it provokes phase separation in bio-oils occurring due to the catalytic effect of the inorganic matter during the fast pyrolysis reactions [1]. There are some studies about minimising inorganic matter within biomass by pretreatment [7,8,9], [10], etc. However these practices result in higher processing costs and do not solve other issues of bio-oil characteristics. Experimental evaluation of pyrolysis temperatures has been done before in slow pyrolysis to explain biomass behavior and how they affect yields such as [11,12]. Focusing on fast pyrolysis, this work aims to study the effect of temperature (450 °C, 480 °C 510 °C and 550 °C) within a fluid bed fast pyrolysis reactor has on processing high ash content feedstock, in this case rape straw

(> 6 wt% ash content). The objective is to conclude if controlling the temperature can minimise the effect of inorganic matter has on bio-oil yields and their characteristics, for their subsequently upgrading through hydrodeoxygenation, catalytic cracking, emulsification, steam reforming [13] and get clean fuels or chemicals. Thus, the novelty of this work is to evaluate the real behavior of high ash biomass in a semi-pilot reactor finding their most suitable bio-oil production condition previous to their upgrading. The chemical composition of the fast pyrolysis products, the physical properties of bio-oil and the energy product distribution are priorities of this work. In addition, bio-oil stability has been analysed to assess how its final composition would affect its behavior in long term storage, for their management either for upgrading or direct use as the principal product of fast pyrolysis.

2. Materials and methods

2.1. Materials

The rape straw was grown at Villaturiel village, province of Leon (Spain). The rape straw was dried in a greenhouse for a period of 24 h to reduce the moisture content to 11 wt%. The material was then submitted to three different cutting processes as pretreatment to achieve specific particle size fractions for fast pyrolysis processing (0.25–2 mm) and biomass characterisation (0.15–0.25 mm).

2.2. Thermogravimetric studies

Thermogravimetric analysis was carried out using a PerkinElmer Pyris 1 thermobalance, following the standard ASTM E1131-03 [14]. Different samples of 5.0 $\pm$ 0.1 mg were pyrolysed at five heating rates (β: 2, 5, 10, 25 and 75 °C min^{-1}) up to a maximum temperature of 600 °C with a hold time of 15 min. The inert atmosphere was set with a nitrogen flow rate of 30 ml min^{-1}. Samples were analysed in triplicate.

2.3. Fast pyrolysis experiments

The fast pyrolysis tests were performed in a 1 kg h^{-1} continuous bubbling fluidised bed reactor at the Bioenergy Research Group (BERG, Aston University). The system is composed of the feeding system, the main pyrolysis reactor chamber and products' collection chambers. The biomass feed rate was 650 kg h^{-1} and was dependent on biomass density. The feeding system was an air-tight hopper with a nitrogen purge that fed into the lower part of the fluid bed reactor. The reactor bed material was 1 kg of sieved quartz sand with a particle size between 600 and 710 μm. The reactor was fluidized using pre-heated nitrogen as carrier gas (17 dm^3 min^{-1}). It was pre-heated in a chamber below the main reactor chamber. The hot vapour residence time was below 1.5 s in the reactor and associated hot pipework and cyclones. When the gas left the reactor it passed through two heated cyclones and the char was deposited on a chamber for its collection. After the cyclones the pyrolysis vapours from the gas condensed in a cooled quench column in contact with ISOPAR™ (ISOPAR V. CAS number: 64742-46-7. Supplier: Multisol Limited). A temperature between 20 and 25 °C was kept with a water jacket that surrounded the quench column. The aerosols remained in a wet walled electrostatic precipitator (20 kV and 0.2 mA), flushed with ISOPAR™. Following the electrostatic precipitator the gas passed through a water cooled condenser (0–15 °C), two dry ice–acetone condensers (at − 70 °C), a cotton wool filter, and 250 g of silica gel (silica gel orange, CAS number: 112926-00-8, 2–5 mm). An on-line Varian CP 4900 Micro-GC microgas chromatograph with a thermal conductivity detector (TCD) and two columns (Varian CP-5AMolsieve and CP-PortaPLOT) were used for the analysis of non-condensable gases. The gas (nitrogen and product gas) was analysed every 150 s, and its final composition was the average of readings. Temperatures were measured with K-type thermocouples joined to a Microlink 751 ADC unit and recorded using Windmill data logging software. System

pressures were measured to identify any blockages or leaks. Mass balances (wt% on dry basis) were calculated based on mass of biomass processed and bio-oil, char and non-condensable gases. Further details of the reactor configuration are described elsewhere [8].

Acceptable mass balance closures were achieved for all temperatures (> 88%). Previous tests have ranged between 84.76 and 94.24 wt % in the same equipment [8]. Losses in the mass balance are thought to be caused by: the size of the reactor (semi-pilot plant); the complexity of the system; errors in water content analysis, weight measurement and gas analysis caused by heavily diluted pyrolysis gases (content of nitrogen carrier gas above 95% in the gas stream).

2.4. Analysis techniques

2.4.1. Feedstock and char characterisation

Ultimate composition analysis for the feedstock and char obtained after fast pyrolysis were performed using a Carlo-Erba 1108 elemental analyser to determine the chemical elements: C, H and N, according to the standard ASTM 5373 [15]. Prior to analysis the materials were dried at 105 $\pm$ 2 °C for 24 h in order to remove moisture. The analysis were done in duplicates and the average value was determined. Oxygen content was obtained by difference.

The feedstock was also analysed for proximate composition (total moisture, volatile matter and ashes) according to the standard ASTM D3302 [16], the norm UNE 3219 UNE-EN ISO [17] and the standard ASTM E1755–01(2015) [18]. Moisture content was measured by duplicate in a Sartorious MA 35 moisture analyser. Ash content was determined with a Carbolite AAF1100 furnace, being previously dried at 105 $\pm$ 2 °C for 24 h in order to remove moisture content. Inorganic content (Al, Ca, Fe, K, Mg, Na, P and Si) was determined by acid digestion and carried out in an induced coupled plasma emission spectrometer Varian Vista MPX ICP-OES done in an external lab.

Char ash content was determined by combustion with a thermobalance in a stable air atmosphere, with a heating rate of 5 °C min^{-1} with a maximum temperature of 575 °C, held for 15 min at this temperature.

The high heating value (HHV) was calculated according to Friend et al., (2005) [19].

2.4.2. Gas fraction characterisation

The gas fraction was analysed by an on-line Varian CP 4900 Micro-GC microgas chromatograph. A thermal conductivity detector (TCD) and two columns, Varian CP-5A Molsieve and a Varian CP-PoraPLOT, were used to analyse the non-condensable gases (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethene, propane, propene, and n-butane). Samples of non-condensable gases were taken at intervals of 150 s for the entire length of fast pyrolysis experiment. Thus, the global gas composition for each run was calculated from the mean value of the entire data detection of each gaseous specie. The lower heating value was obtained theoretically from the norm UNE-EN-ISO 6976 [20] based on the volumetric composition and the heating value of each gaseous specie at 0 °C.

2.4.3. Bio-oil characterisation
2.4.3.1. Ultimate composition analysis and heating value determination. Ultimate composition analysis was determined on a wet basis following the procedure described in Section 2.4.1 for solids. The high heating value was also determined according to Friend et al., (2005) [19].

2.4.3.2. Water content, pH, and dynamic viscosity determination. The water content of liquid products was determined by volumetric Karl-Fischer (KF) titration using a Mettler Toledo V20 KF titrator. Hydranal (R) K and Hydranal (R) Composite 5 K were used as a medium and a titrant respectively. Prior to analysis, the KF instrument was calibrated with HPLC grade water and the system flushed with working medium