



Conventional and microwave-assisted pyrolysis of biomass under different heating rates



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ABSTRACT

Biomass was subjected to conventional and microwave pyrolysis, to determine the influence of each process on the yield and composition of the derived gas, oil and char products. The influence of pyrolysis temperature and heating rate for the conventional pyrolysis and the microwave power was investigated. Two major stages of gas release were observed during biomass pyrolysis, the first being CO/CO₂ and the second one CH₄/H₂. This two-stage gas release was much more obvious for the conventional pyrolysis. While similar yield of liquid was obtained for both cases of conventional and microwave pyrolysis (~46 wt.%), higher gas yield was produced for the conventional pyrolysis; it is suggested that microwave pyrolysis is much faster. When the heating rate was increased, the peak release of CO and CO₂ was moved to higher reaction temperature for both conventional (500 °C) and microwave pyrolysis (200 °C). The production of CH₄ and H₂ were very low at a conventional pyrolysis temperature of 310 °C and microwave pyrolysis temperature of 200 °C (600 and 900 W). However, at higher heating rate of microwave pyrolysis, clear release of CH₄ was observed. This work tentatively demonstrates possible connections and difference for biomass pyrolysis using two different heating resources (conventional and microwave heating).

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1. Introduction

The European Union has introduced several sustainability initiatives to reduce the emission of greenhouse gases, to increase the use of renewable resources, support a more efficient Europe and to create a low carbon economy [1,2]. Key to this strategy is the need for an increased use of renewable sources such as biomass. Because biomass is carbon neutral, there is increasing interest in the use of biomass to replace fossil fuels and thereby reduce the impacts of climate change. Thermochemical routes to utilise the potential of biomass include pyrolysis which, can generate useful end-products of bio-oil, syngas and bio-char. The bio-oil has a higher energy content per unit mass, than the raw biomass and can be used directly in fuel applications or as refinery feedstock or with upgrading to produce refined fuels and chemicals. The solid

char can be used as a solid fuel, alternatively the char can be used as bio-char for soil improvement, upgraded to activated carbon, or gasified to produce syngas. The gases generated have medium to high calorific values and may contain sufficient energy to supply the energy requirements of a pyrolysis plant.

Heating the biomass via an external heating source has been by far the most studied technology. The advantage of pyrolysis is that the yield of end-products can be altered depending on the process conditions; the temperature of pyrolysis and the heating rate are known to have most influence [3–6]. High char yields are obtained from biomass via slow heating rates to moderate temperatures of ~400 °C. Moderate heating rates in the range of about 10 °C min⁻¹ and maximum temperatures of 600 °C gives an approximate equal distribution of oils, char and gases referred to as conventional pyrolysis [5]. Fast pyrolysis involves high heating rates (~100 °C/s) and pyrolysis temperatures below 650 °C and coupled with rapid quenching of the pyrolysis products produces a mainly liquid product [6]. High pyrolysis temperatures result in the thermal cracking of the oil to produce a high gas yield.

In comparison to conventional heating, microwave pyrolysis involves transfer of energy to the biomass through the interaction

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of the molecules within the biomass [10–12]. Heating of biomass occurs when the microwaves cause dipolar molecules to attempt to rotate in phase with the alternating field of the microwaves [7]. Microwave heating has the advantages that heat is generated within the material rather than from an external source, resulting in of rapid heating and high heating efficiency [3,7]. Microwave pyrolysis has been applied to a range of materials, including biomass [8] and waste tyres and plastics [9]. However, biomass does not readily absorb microwave radiation and initially tyre biomass may be added to a transparent material such as carbon or water. Once pyrolysis progresses, the product carbonaceous char facilitates the microwave pyrolysis.

There are few direct comparisons between conventional and microwave pyrolysis of biomass [13–15]. Obtaining information about connections/differences between these two technologies will facilitate the development of biomass pyrolysis, e.g. using a combination of conventional and microwave heating methods. In this work, the same biomass sample was used in two types of reaction systems (conventional and microwave pyrolysis). In each type of pyrolysis, different heating rates were used; the changing trend of experimental results (product distribution, gas release and char content) derived from different heating rates were explored for both conventional and microwave pyrolysis.

2. Experimental

2.1. Materials

Wood biomass (average size 1.5 mm) was used for both conventional and microwave pyrolysis. A Shimadzu TGA-50 thermogravimetric analyser was used to determine the proximate analysis of the biomass samples and elemental analysis was carried out using a Carlo Erba Flash EA 11112 elemental analyser. The biomass moisture, volatile, fixed carbon and ash contents were 6.4, 74.8, 18.3 and 1.2 wt.% respectively. The carbon content was 36.17 wt%, hydrogen 6.30 wt%, nitrogen 1.78 wt% and the oxygen calculated by difference was 36.17 wt%.

2.2. Conventional pyrolysis of biomass

Conventional pyrolysis was carried out using a fixed bed stainless steel reactor of 16 cm length and internal diameter of 2.2 cm, heated externally by an electrical furnace and continually purged with nitrogen. Approximately 3 g of biomass was mixed with water (0.3 g of H₂O was added on the top of the biomass sample) and placed in a sample boat in the reactor and heated to the desired pyrolysis temperatures using different heating rates (5, 20 and 40 °C min⁻¹). Water was added due to the microwave processing of biomass required addition of water to aid microwave absorption. The gaseous pyrolysis products were passed through an air cooled condenser and a dry ice cooled condenser to trap the product liquids. Non-condensed gases were passed into an on-line gas analyser allowing for the determination of CO, CO₂, H₂ and CH₄. N₂ was used as the carrier gas with a flow rate of 80 ml min⁻¹. The conventional reaction system has been reported previously [16].

2.3. Microwave pyrolysis

Microwave pyrolysis was conducted using samples of 140 g of biomass mixed with about 14 g water. The samples were heated to 200 °C with different fixed microwave powers (600, 900 and 1200 W). It is noted that the heating rate is around 8, 15 and 20 °C min⁻¹, for microwave power of 600, 900 and 1200 W, respectively. For this purpose a Milestone ROTO Synth Rotative Solid Phase Microwave Reactor (Milestone Srl.) was used with an operating MW frequency of 2.45 GHz. A schematic diagram of the

microwave pyrolysis reactor system can be found in previous work [14]. Samples of the biomass were placed in 2 L glass flask within the cavity of the microwave. The temperature of the solid biomass was measured using an infra-red detector within the reactor cavity. In addition the temperature of the evolved volatile fractions was measured using a thermocouple on the exit tube. Both temperature measurements were within 15 °C of each other [14]. The generated liquid products were condensed in a water cooled vacuum trap using several consecutive flasks.

The non-condensable gases from the microwave pyrolysis system were collected using a 5 L Tedlar™ gas bag, which was analysed by two separate gas chromatographs. H₂, CO, O₂, N₂ and CO₂ were analysed by a Varian 3380 GC with two packed columns and with two thermal conductivity detectors (GC/TCD). Hydrogen, oxygen and carbon monoxide, methane and nitrogen were analysed on a 2 m length by 2 mm diameter column, packed with 60–80 mesh molecular sieve. Argon was used as the carrier gas. Carbon dioxide was analysed on a separate 2 m length by 2 mm diameter column with Haysep 80–100 mesh packing material. C₁ to C₄ hydrocarbons were analysed using a second Varian 3380 gas chromatograph with a flame ionisation detector, with a 80–100 mesh Hysep column and nitrogen carrier gas.

2.4. Oil analysis

Prior to analysis the liquid pyrolysis products from both the conventional and microwave experiments were dried using anhydrous sodium sulphate and diluted with dichloromethane (DCM). They were analysed by coupled gas chromatography (GC)–mass spectrometry (GC–MS) using a Varian CP-3800 GC coupled to a Varian Saturn 2200 mass spectrometer (MS). Detailed conditions for the GC–MS analysis of the oil fraction can be obtained from a previous report [17].

2.5. TGA–FTIR analysis

In addition to the conventional and microwave pyrolysis experiments, a Stanton–Redcroft thermogravimetric analyser (TGA) coupled to an FTIR analyser (Thermo Scientific iS10), was used to examine the release of gas products. Around 25 mg of biomass sample was pyrolysed in the TGA under nitrogen conditions.

3. Results and discussion

3.1. Effect of the heating rate on the product distribution

Table 1 shows the mass balances of the pyrolysis of biomass carried out using the conventional and microwave pyrolysis units. Direct comparison of the product yield between the two systems is difficult because of the nature of the size and configuration of the reactors in addition to the different heating systems. However, general trends in regard to heating rate for the conventional pyrolysis or microwave power which corresponds to heating rate can be drawn. From Table 1, the liquid (bio-oil) yield shows a small increase with the applied heating rate or microwave power. It can be seen from the data that with conventional pyrolysis an increase of the amount of liquids from 53.94 to 58.18 wt.% is observed with increasing heating rate, while in the case of microwave pyrolysis liquid yield increases from 43.23 to 47.10 wt.% with increasing microwave power. This is in agreement with other reports by Isahak et al. [18] and Mohan et al. [19]; they proposed the high yield of liquid is due to cracking reactions which are promoted at a higher heating rate.

Table 1 also shows that markedly lower char production is obtained when conventional pyrolysis (~23 wt.%) is used to pyrolyse biomass compared to microwave pyrolysis (~45 wt.%). It should

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