

Microwave Pyrolysis of Biomass

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ABSTRACT

Biomass can be seen as the oil well of the future; a renewable and widely distributed resource that should be increasingly exploited for the production of energy products with environmental, economic and social benefits. [1]

One method by which the bio-energy carriers and chemicals can be obtained is through pyrolysis. Pyrolysis is a feedstock agnostic technique capable of deconstructing biopolymers into more useful chemical, gas, bio-oil and bio-char products. Microwave irradiation can interact with different types of biomass at low temperatures by comparison with conventional flash pyrolysis. Building on our original work in pyrolysis and biorefining, [2], [3], [4] studies have continued progressing into ligno-cellulosic components and whole biomasses, mechanistic and process conditions, process measurement, product analysis and scale-up. The aims of the work are to make a commercial scale and economically viable route to chemicals and bio-energy through microwave processing of biomass.

Keywords: Biomass conversion, Bio-char, Bio-oil, Microwave, Pyrolysis.

1 INTRODUCTION

The replacement of fossil fuels with sustainable (renewable) alternatives is key to achieving the low-carbon solution to global energy supply. Biomass is a fully renewable, widely distributed resource that should increasingly be exploited for the production of heat, power, liquid fuels as well as chemicals and materials with substantial environmental, economic and social benefits [1,5].

The direct combustion of biomass for energy generation faces several problems. Biomass by nature is diverse; with it generally having the detrimental combination of low physical and energy density. The calorific value (heat of combustion) of biomass is typically around half that of coal. Poorer physical characteristics such as higher water content and poorer grindability generally mean that transportation and use is not only challenging in terms of logistics and processing, but also questionable overall in terms of environmental benefits.

Alternatively to direct combustion thermochemical treatments are a way in which biomass can be converted into materials with more fuel-like characteristics and higher energy density.[6]

Microwave ovens have gained acceptance as a mild and controllable tool, allowing simple and rapid processing.

Microwave irradiation is rapid and volumetric, with the entire material heated simultaneously. In contrast, conventional heating is slow and the heat is introduced into the sample from the surface. This feature of microwaves is very important for processing poor thermal conducting materials such as wood [7].

Microwaves for pyrolysis of biomass is relatively new and dates back to the early 1980's [8]. Processes were conducted at high temperatures typically in excess of 350°C (similar to conventional pyrolysis) with primary focus on pyrolysis, gasification and liquefaction to fuels.

This article discusses low temperature microwave technology which can be used to process a variety of biomass types into valuable chemicals and energy products with *in-situ* fractionation from both an applied and fundamental view. Currently studies have included model compounds: cellulose, hemi-cellulose, lignin, xylan & alginic acid along side native biomasses including: wood, algae (macro & micro), oat straw, wheat straw, barley straw, barley dust, waste paper, rape straw, bracken, reed canary grass and *miscanthus*.

2 RESULTS AND DISCUSSION

2.1 Low Temperature Process

There are such large numbers of different types of biomass it would be unfeasible to investigate each and every one under microwave pyrolysis conditions. To develop understanding of the mechanism of interaction of microwave irradiation with biomass, model compounds (cellulose, hemi-cellulose and dextrin) were studied.

The liquid products of pyrolysis are a complex mixture of chemicals in both aqueous and oil phases. Preliminary investigations have demonstrated that the make up of these liquids can vary drastically dependant on the biomass source. Char conversely, has proven to be more reproducible between biomasses. Furthermore, commercially the most important attribute of char is its calorific value for energy generation. For these reasons, calorific value of char was selected as the metric of choice for comparing the conditions applied.

Figure 1 shows a lowering in decomposition temperatures (by around 100 °C) of cellulosic components under microwave conditions in the conventional torrefaction temperature range. The chars have similar calorific values and physical properties to coal, making it an improved feedstock for co-firing in power stations. In contrast to direct biomass burning or co-firing, the material

offers advantages in homogeneity and better combustion properties. Remarkably, the maximum calorific values of bio-chars obtained from dextrin, cellulose and hemicellulose were higher for the microwave treatment than convection heating.

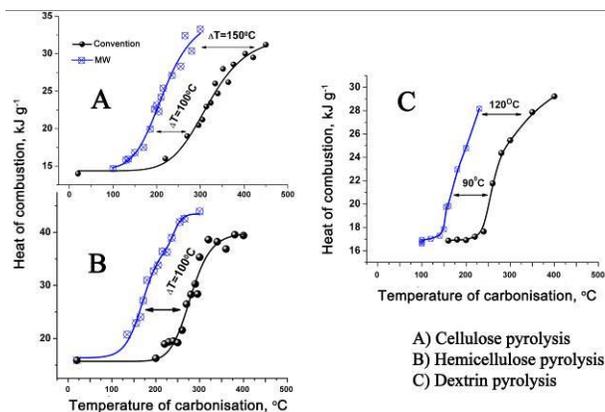


Figure 1. Influence of carbonization temperature on the heat of combustion of chars obtained from A) cellulose and B) hemi-cellulose, C) Dextrin

A process parameter investigation has led to the understanding of common factors which effect pyrolysis depends on biomass thermal properties. Results indicated a thermal event is linked to the temperature of pyrolysis at which maximum microwave heating is observed. To explain this phenomenon modulated differential scanning calorimetry (MDSC) was applied.

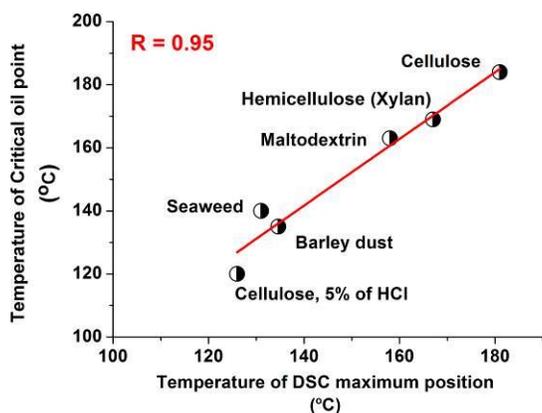


Figure 2. Correlation between temperature of maximum microwave pyrolysis and temperature of structural change.

These results provided us with a clearer understanding of the mechanism by which microwave irradiation can interact with biomass. Maximum rate of microwave heating (and pyrolysis) mirrors a thermal event observed by MDSC. This can be explained as a structural transition temperature at which there is a weakening in the hydrogen bonding network and softening of the macrostructure, parts of the polymer become free to rotate and vibrate which

allows the functional groups to absorb microwave energy more efficiently, a glass transition.

The correlation between the temperature of maximum microwave pyrolysis and temperature of polymer structural change can be seen in figure 2, with a linear relationship between these values been shown for both model and complex biomasses.

2.2 Temperature Measurement

During our work and in discussions with the microwave and pyrolysis community it has become clear that measurement of temperature is a key issue for both microwave chemistry and pyrolysis. Bulk temperature cannot be directly measured as inside the microwave cavity most temperature probes will be either directly heated at a different rate to the substrate under investigation and by the nature of temperature as a concept it cannot be measured in a non-equilibrium energy-transfer situation as occurs under microwave irradiation (*i.e.* direct excitation of rotational levels leads to non-Boltzmann distribution), but only after this energy has been dissipated (probably relatively quickly). External temperature measurement systems suffer from the traditional issues of lag time caused by the heating of the material followed by transfer to the vessel by conduction.

In essence, we can see from the discussion above, one should have limited confidence in temperature measured within a microwave cavity as a consequence of the physical chemistry occurring. Furthermore, it is well known that within microwave fields, due to differences in absorption of microwave energy it is possible to have hot-spots with temperatures far in excess of the bulk temperature.[9]

Thorough work by Delft TU of the Netherlands investigated the issue of temperature measurement within microwaves, the associated accuracy or inaccuracy, probe application and spatial variation.[10] In their work, it was observed that there was a considerable but predictable difference between in sample fibre-optic probe and exterior infra-red detection. In correlation with this work, we have observed a difference in temperature measurement between sources. In our work, below 100°C the reproducibility between the two methods is good; this is due to water vapour being evenly distributed within the biomass bulk. The critical difference between our work and the Dutch work is we see a change in which method reads the higher value, whereas, the literature data always shows the fibre optic (internal) measurement to be higher than the infra-red probe (external). In our data, a difference exists between the measurement methods, due to hot spots, however as volatiles are evolved the hot spot is cooled by evaporation of pyrolysis product and these gaseous products distribute the heat more evenly through the sample. The fibre optic measurements are alternating above and below the IR trend due to the response lag of the method. The fibre-optic probe is held within a glass guide tube which leads to a

delay in heat transfer to the probe. As described earlier in this work a structural change as observed by conventional heating in MDSC equipment, is closely correlated with the temperature at which pyrolysis is observed to begin. This phenomenon has been reproduced in different items of equipment and with different biomasses and therefore adds evidence to the correct measurement of temperature within the microwave cavity.

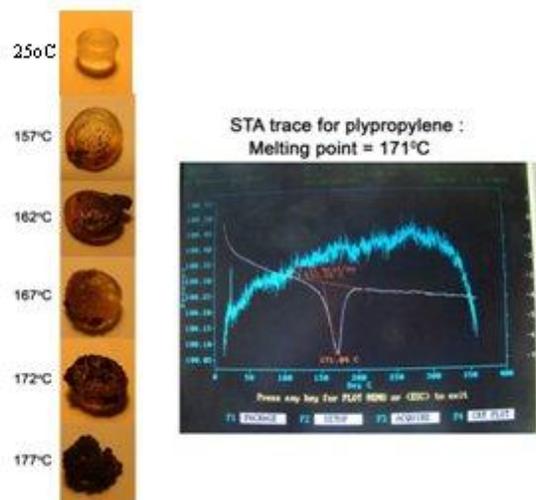


Figure 3: Polypropylene for temperature measurement *in situ*. Left, polypropylene bead in various stages of melting. Right, an STA trace showing the melting point of polypropylene.

To further add confidence to the hypothesis that temperature measurement by external temperature probes were correct, experiments were carried out using a novel technique of adding non-microwave adsorbing polymer beads of known melting point to the reaction mixture. Reactions are carried out at a range of temperatures – as observed by the external infra-red probe. The results are shown in Figure 3. As can be seen in the photographs of the melted polypropylene bead the probe-measured temperature follows the melting trend of the polymer bead (as shown in the STA trace), which gives us confidence in our infra-red temperature measurement technique as providing a fair and reliable representation of the temperature of the bulk material. As further verification we plan to prove using the direct observation by conventional heating the effect.

2.3 Products of Pyrolysis

Microwave-mediated pyrolysis yields a range of products, the relative yield of which is dependant on the conditions employed and the biomass under investigation. Tunability between products is possible. Firstly a gas is generated from the process. This gas is a mixture of hydrogen, methane, carbon monoxide and carbon dioxide along with volatile organic acids and aldehydes. These gases arise from the depolymerisation of the biomass and

account for ~14% of the energy content of the product mixture.

The liquid components are of two major fractions, aqueous and bio-oil. Bio-oil has advantages over conventional biomass pyrolysis bio-oils and has applications as a liquid fuel (following upgrading) or as a source of chemicals as it has lower water content, higher energy content and lower alkaline metal content. Investigations into process conditions have developed a knowledge of critical process conditions and methods to tune the system outputs. Figure 4 shows bio-oil as generated under differing processing conditions from the same source feedstock (macro-algae). Chromatogram A shows predominantly sugars being produced whereas chromatogram B shows a range of furans, aromatics, phenols, sugars and fatty acids being generated from the same material. This tunable nature means that the technology can be used to generate high value chemicals or energy products at the wish of the operator.

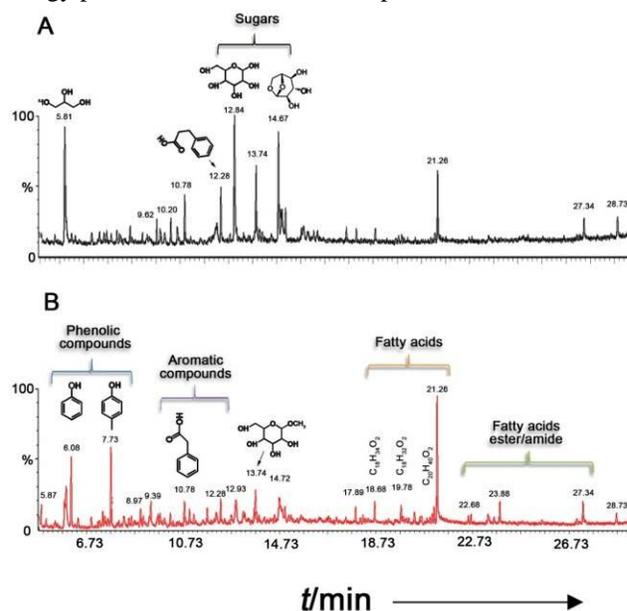


Figure 4. GC-MS spectrum of bio oil obtained from macroalgae using differing processing conditions.

Different biomass feedstocks offer differing pyrolysis behaviour, both physically and in their product composition. For example, seaweed (macro-algae) decomposes at extremely low temperatures (below 130 °C) at a high decomposition rate generating vast quantities of gas. Bracken yields an oil with a very high energy density. Barley dust, a food waste, generates an oil with high quantities of aromatic compounds. Paper waste yields an oil highly enriched in the platform molecule levoglucosan. The aqueous phase is described in the next section.

The solid product, bio-char, has good characteristics for co-firing with coal for stationary power generation. The calorific value is high (up to 30 kJ/g) and in line with mid-range fossil coals. Additionally, microwave-derived bio-

chars show good water stability and good grindability, key parameters for co-firing application.

2.4 *In-Situ* Separation of Products

The aim of this work is to separate the various fractions and sub-fractionate *in-situ*. The benefits of this are multi-fold as post-process separation is extremely energy and time consuming in comparison with the process itself and the resultant water-oil mixture is prone to decomposition caused by the acids present. Conventional pyrolysis generates a mixed liquid fraction which normally leads to short shelf-lives of bio-oil. Microwave pyrolysis lends itself to condensation fractionation of the products which are generated as volatile liquids. Figure 5 shows a photograph components obtained from *in situ* of a wood bio-oil. Fraction N1, the physisorbed water, intrinsic to the native biomass. Following this, at the pyrolysis temperature (as defined by the generation of oil and colour change), a continuous vapour stream is observed. Using the various condensers as described earlier the *in-situ* separation of process water (fraction N2) and oil fractions (N3-N5) can be achieved.

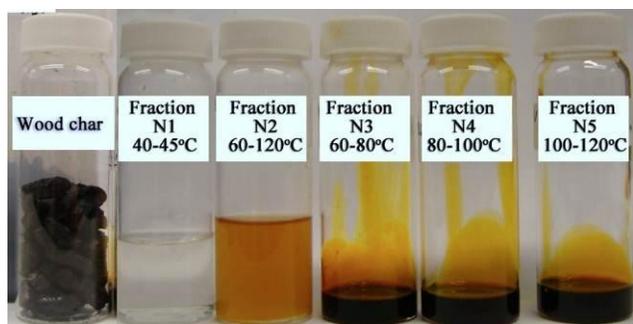


Figure 5 Photograph of five different liquid fractions and solid residue derived from microwave pyrolysis of wood.

3 CONCLUSIONS AND FUTURE WORK

A wide variety of biomasses have been studied under microwave conditions, each proving to have differing pyrolysis features both physically and in the products generated.

In comparison to conventional systems temperatures of pyrolysis onset have been observed to be feedstock dependant and considerably lower, which allows for improved safety and simpler plant design. Crucially, an understanding of at what temperature the pyrolysis occurs has been made and a method to predict that has been developed. Proof of temperature measurement within microwave cavity has been investigated. Furthermore, an added benefit and process simplification over conventional pyrolysis has been observed from *in-situ* separation of bio-oil and water.

This technology may increase the application of renewables in power generation and supply a range of transport fuels and chemicals in the growing market for sustainable products. The process itself is conducted at

unusually low temperatures, which allows ease of process scale-up using existing microwave equipment. The scalability of our process has been proven through pilot scale trials using commercial equipment.

Microwave technology is often difficult to scale up due to wave penetration issues, however, this makes microwave irradiation in a continuous manner possible. Holding lower volumes of material at elevated temperatures and pressures is preferable as part of an inherently safer design. At the Green Chemistry Centre of Excellence we are currently in the process of building a continuous demonstration scale microwave pyrolysis system as part of a larger biorefinery. This technology has been proven as a green and flexible method of upgrading biomass for energy applications and chemicals, allowing progress to a society which is no longer reliant on fossil fuels.

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