

LOW TEMPERATURE MICROWAVE IRRADIATION AS AN ACTIVATOR OF BIOMASS PYROLYSIS

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Abstract— Biomass can be seen as the oil well of the future. It is a renewable and widely distributed resource from which a wealth of economically valuable products can be derived [1]. One method by which the bio-energy carriers and chemicals can be obtained is pyrolysis. This technique is capable of deconstructing biopolymers into more useful products. Microwave irradiation offers the potential to perform this process at markedly lower temperatures than is commonly observed for conventional flash pyrolysis. Building on our original work in microwave pyrolysis and biorefining ([2], [3], [4]), studies are now underway dealing with ligno-cellulosic compounds and whole biomasses. Substantial attention is given to the mechanistic understanding of the process, product analysis and scale-up. The prime aims of the work are to make economically viable routes to chemicals and bio-energy through microwave processing of biomass.

Keywords: Biomass conversion; Bio-char; Bio-oil; Microwave; Pyrolysis

I. INTRODUCTION

Since the 1990s, a range of factors such as decreasing petrochemical reserves, sustainability issues, rising oil prices, supply security concerns and negative environmental impacts have paved the way for the use of biomass as a renewable carbon neutral feedstock. The biorefinery concept that has emerged runs remarkably parallel with today's petroleum refineries; integrated facilities for the conversion of biomass into multiple value-added products including energy carriers, chemicals and materials.ⁱ However, many of these rely on single technologies and use feedstocks that compete with the food chain.ⁱⁱ Chemical and technological improvements as well as diversification towards low value (local) feedstocks are required in order to create flexible, zero waste networks. This will then allow challenging the current status quo and developing novel interconnecting product lines that can meet the needs and demands of existing and new industries.

The main technologies applicable to the biorefinery are extraction and a range of bio/thermochemical processes. Currently, these methodologies are mainly studied independently of one another, with each competing for primacy as the biorefinery technology of the future. However, it is essential that the strengths and weaknesses of all these technologies are recognized in order to maximise the number of applications and the diversity of the products.

The replacement of fossil fuels with sustainable (renewable) alternatives is essential to secure tomorrow's

global energy and chemicals supply. Biomass is a fully renewable and widely distributed resource from which these could be derived [1-5].

The direct combustion of biomass for energy generation faces several problems. Due to its diversity and heterogeneous nature it is often characterized by a low energy density. The calorific value of biomass is typically around half the one of coal. Also, poorer physical characteristics such as a high water content and inferior grindability make that its transportation and subsequent use is not straightforward in terms of logistics and processing [6].

Microwave ovens are establishing themselves as a mild and controllable tool, allowing for simple and rapid processing of biomaterials. Moreover, and much in contrast to conventional heating, microwave irradiation is known to heat the entire material at the same time. This feature of microwaves is very important for processing poorly thermally conducting materials such as wood [7].

The use of microwaves for the pyrolysis of biomass dates back to the early 1980's [8]. Back then, processes were conducted at high temperatures typically exceeding 350°C making them very similar to conventional pyrolysis. The prime focus was on gasification and liquefaction to fuels.

This article discusses the use of low temperature microwave pyrolysis for the creation of valuable chemicals and energy products. Moreover, the process allows for an *in-situ* fractionation. Currently, studies have included both model compounds - such as (hemi)-cellulose, lignin, xylan & alginic acid - and native biomasses e.g. wood, algae (macro & micro), oat-, wheat- and barley straw, barley dust, waste paper, rape straw, bracken, reed canary grass and miscanthus.

II. RESULTS AND DISCUSSION

A. Low Temperature Process

An example of a microwave biorefinery based on the processing of rapeseed is shown in figure 1. Crushing and microwave facilitated steam distillation allow for the removal of primary oil. This accounts for up to 50% of the total mass of which 80% primary oil. During the effective pyrolysis stage (130-300°C) 28% of the secondary bio-oil is generated and the remaining material (char) acquires as such a markedly higher calorific value, going from 18 to 28 kJg⁻¹.

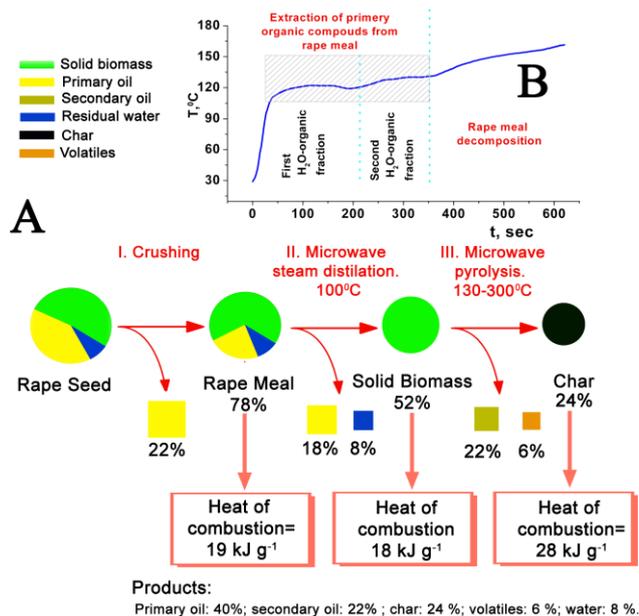


Figure 1: Illustration of a biorefinery concept based on rape seed processing

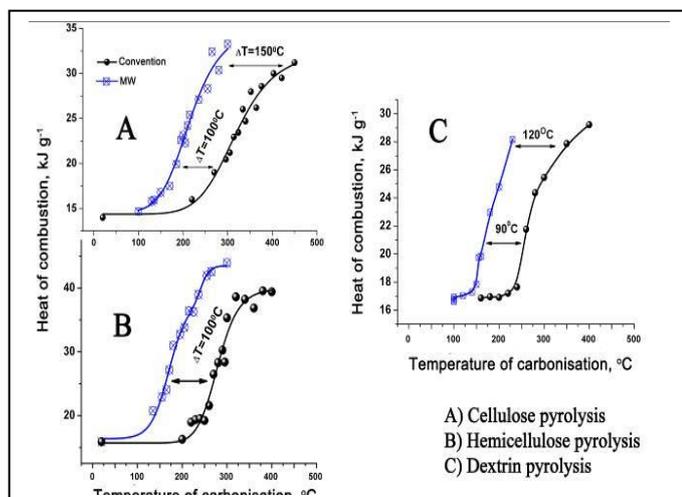


Figure 2: Influence of the carbonization temperature on the heat of combustion of chars obtained from A) cellulose B) hemi-cellulose and C) Dextrin

A most interesting observation is that microwave irradiation allows for a decrease of the decomposition temperature of cellulosic material with around 100°C (Figure 2). The as-observed temperatures are similar to those seen for conventional torrefaction processes. The remaining chars have similar calorific values and physical properties as coal, making them an improved feedstock for co-firing in power stations. In addition, *and much in contrast to direct biomass burning or co-firing*, these chars are substantially more homogeneous adding further to their improved combustion properties. Remarkably, the maximum calorific values of bio-chars, *and this irrespective their origin*, were found higher when microwaves were applied than when conventional heating was used.

The factors governing the microwave pyrolysis of biomass have been investigated. The maximal rate of microwave pyrolysis occurred at distinct temperatures which relate to particular thermal events occurring in the biomass. These were easily identified using modulated differential scanning calorimetry (MDSC). As such we gained appreciable understanding of the mechanism by which microwave irradiation interacts with biomass. It is proposed that the facilitation of microwave pyrolysis *around these specific temperatures* relates to the weakening of the hydrogen bonding network and hence softening of the macrostructure. This makes that parts of the polymer become free to rotate and vibrate therewith allowing the different functional groups present to absorb microwave energy more efficiently.

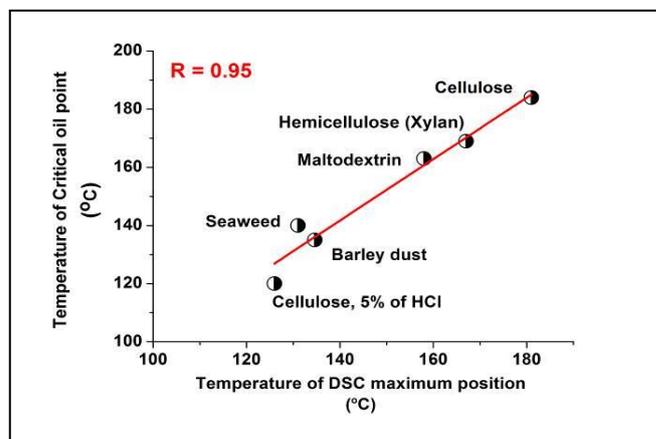


Figure 3: Correlation between the temperature of maximum microwave pyrolysis and the temperature of structural change.

Figure 3 illustrates nicely the correlation between the temperature at which the maximum microwave pyrolysis rate occurs and the temperature of polymer structural change. A clear linear relationship between these values can be observed and this both for model and complex biomasses.

B. Temperature Measurement

Measurement of temperature is a key issue. Within the microwave cavity the bulk temperature cannot be directly measured as the temperature probe will be instantly heated and this at a different rate than the substrate under investigation. On the other side external temperature measurement systems suffer from lag due to thermal gradients within the sample. In the literature a considerable but predictable difference can be found between internal fibre-optic and external infrared probes for inorganic oxide samples. There the latter technique showed an overshoot of up to 50°C which is believed to be the result of hot spots [9]. However, when pyrolysing seaweed we have found that there is little difference between these two measurement techniques and this especially when the temperature remains below 100°C. At higher temperatures, up to 170°C, the variance ranged between 4 to 12°. This difference in behaviour between inorganic oxides and seaweed could be explained by the fact that at lower temperatures physisorbed water vapour aids the thermal conduction. This allows for a more even temperature distribution through the

sample. At still higher temperatures, such as where pyrolysis occurs, the rather low variance is explained by escaping volatiles. The latter cool the hot spot through their evaporation hence distributing the heat more evenly throughout the sample.

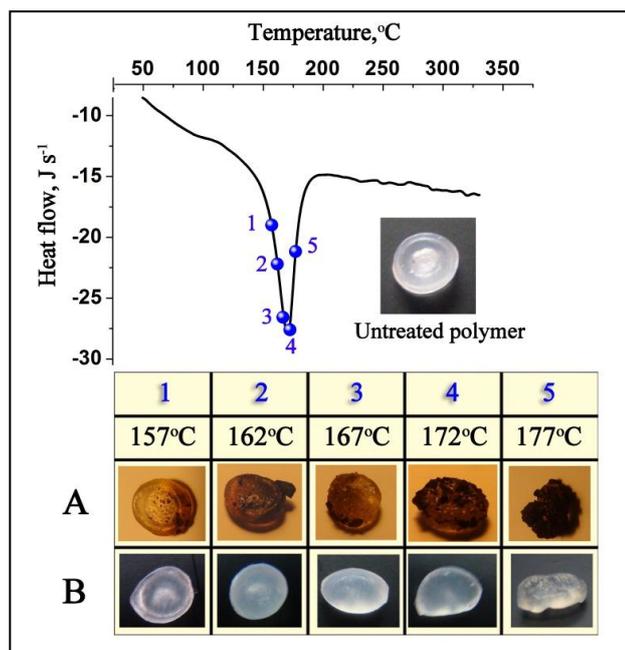


Figure 4: photographs and melting point of polypropylene (172°C) at a range of temperatures. A: inside the microwave cavity & B: under conventional heating.

In addition to these temperature measurement devices we also applied a more indicative technique in which polypropylene beads are added to the sample. These are transparent for microwaves and hence will only undergo physical changes such as melting. The recorded infrared probe data were then compared to the degree of melting of the polypropylene beads. Figure 4 shows beads heated by both microwave (A) and conventional heating (B). Similar deformation is observed for both heating methods approaching the melting point. This data suggests that the sample surface temperature, as measured by the IR probe, is within 5°C of the effective core temperature, thus confirming the low pyrolysis temperature.

C. Products of Pyrolysis

Microwave-mediated pyrolysis yields a wide range of products. Their nature and the obtained yields vary strongly with the type of biomass and the applied conditions. In the first stages of the reaction a gas typically consisting of hydrogen, methane and carbon monoxide/dioxide is generated. The latter accounts for approximately 14% of the energy content of the product mixture.

The liquid products can be divided into an aqueous and oily component. Most interesting, the generated microwave bio-oil has a lower water and alkaline content making it of a superior grade to conventional bio-oil. While it also has a higher energy content, potential exists for use as a liquid fuel. In

depth analysis of a range of different parameters has allowed us to fine tune the reaction product outcome. This is nicely illustrated in figure 5 for the microwave pyrolysis of macroalgae. More specifically we can direct the process to either the formation of sugars (chromatogram A) or shift the product composition substantially towards the formation of aromatics, furans and phenols (chromatogram B). This tunable nature of the process holds significant potential in that the eventual output may well be shifted between high value chemicals and energy rich products.

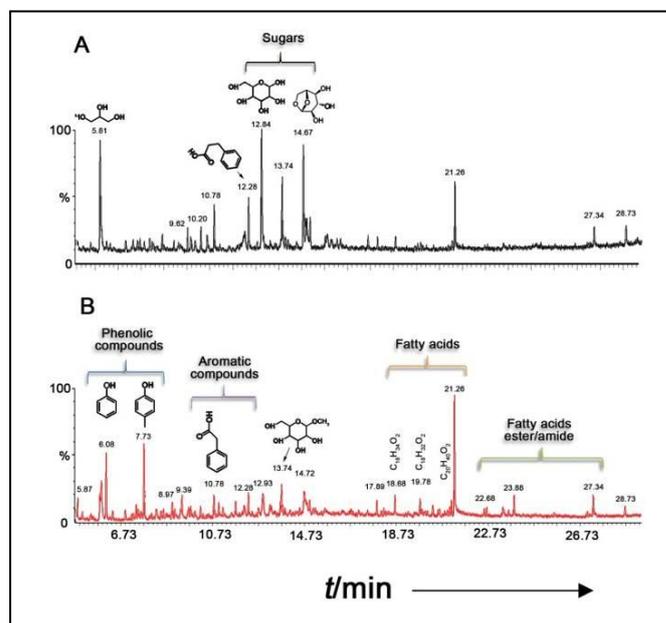


Figure 5: GC-MS spectrum of bio-oil obtained from macroalgae using different processing conditions.

Alternatively, the product outcomes can be influenced through the choice of the biomass. As such we have found that a high density oil can be derived from Bracken while Barley dust leads to an aromatic rich oil. As to paper waste, an oil highly enriched in the platform molecule levoglucosan is obtained. Seaweed forms a special case in that it decomposes rapidly giving predominantly gas.

The solid product, bio-char, often shows high calorific values (up to 30 kJg⁻¹). This offers potential for co-firing applications with coal. In this respect it's noteworthy that microwave-derived bio-chars show good water stability and good grindability which are of key-importance for co-firing applications.

D. In-situ Separation of Products

As an added advantage, we have designed our pyrolysis set-up allowing for an *in-situ* separation of the obtained products. This is of significant importance while post-process separation is highly energy intensive and time consuming. In addition, this also allows for the removal of a large part of the acid fraction. This improves markedly the shelf life of the oil. Note in this respect that it is exactly the presence of acid in the watery-oil mixtures from conventional pyrolysis facilities that

is truly problematic. Indeed these are at the basis of decomposition phenomena. In figure 6 the *in situ* obtained fractions from the pyrolysis of wood are shown. Fraction N1 represents physisorbed water, which is inherent to native biomass. Fractions N2-5 are the effective microwave pyrolysis generated fractions showing a decreasing water content.

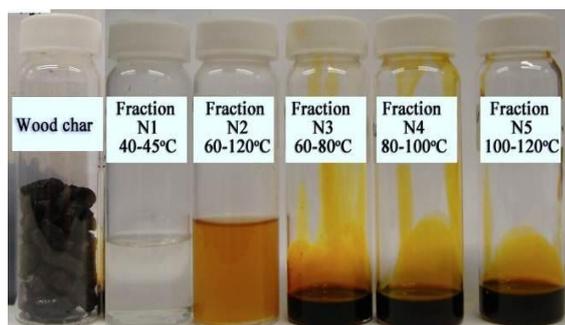


Figure 6: photograph of five different liquid fractions and the solid residue as derived from the microwave pyrolysis of wood.

E. Energetic considerations

Microwave driven pyrolysis holds a particularly important advantage over conventional pyrolysis in that the raw material can be used without a pre-drying step. The energetic input necessary for the pyrolysis of wheat straw indicated an energy requirement of 1.8 kJg^{-1} while conventional pyrolysis required 2.7 kJg^{-1} .

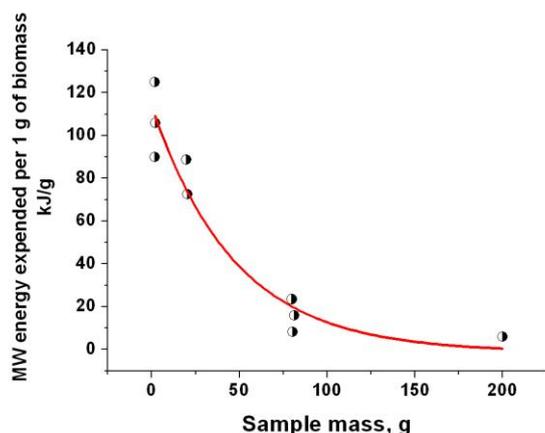


Figure 7: microwave energy required as a function of the sample size.

Moreover, we have experimentally verified that the microwave energy requirement decreased from 100 kJg^{-1} to 2.2 kJg^{-1} as the sample mass increased from 0.2g to 200g (figure 7) Pilot scale studies (30 kg/h) showed a further increase in energy efficiency, requiring as little as 1.9 kJ g^{-1} . As such it can be concluded that low temperature microwave

pyrolysis produces better quality oils and chars than conventional pyrolysis at 1.5 times the energy efficiency.

III. CONCLUSIONS AND FUTURE WORK

Microwave pyrolysis of a wide variety of biomasses has been studied. It was found that the pyrolysis temperature under microwave conditions is on average 100°C lower compared to conventional pyrolysis. This allows for a safer and simpler plant design. Importantly, a clear and correct measurement of the pyrolysis temperature *inside the microwave cavity* has been demonstrated. The *in situ* and continuous separation of bio-oil from water constitutes added benefit and largely simplifies the process over conventional pyrolysis. We have demonstrated the application of microwave chemistry/technology towards the biorefinery scene. In this respect it's noteworthy that the scalability of our process has already been proven through semi-pilot scale trials using commercial equipment. Moreover, linked to the Green Chemistry Centre of Excellence, the Biorenewables Development Centre (BDC) houses a custom built demonstration scale continuous microwave pyrolysis system. In conclusion, this technology holds vast potential as a green and flexible method of upgrading biomass, whether for energy applications and/or the production of chemicals, allowing progress to a society which is no longer reliant on fossil fuels.

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