UNRAVELLING THE MECHANISMS OF MICROWAVE PYROLYSIS OF BIOMASS

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ABSTRACT

This study uses empirical observations and mass transfer simulations to establish a new mechanism for microwave pyrolysis of biomass. Experiments were conducted on cellulose and hemicellulose, using microwave equipment that could vary the observed heating rate. No microwave-absorbing additives were used. At high heating rates it is shown categorically that microwave pyrolysis can significantly reduce the pyrolysis temperatures for hemicellulose and cellulose, but when microwave heating is used to deliver a low heating rate the pyrolysis behaviour is identical to that obtained with conventional heating. Dielectric properties are shown to vary by over an order of magnitude depending on the heating rate. The implications of heating rate on mass transfer and phase behaviour are developed and discussed within the paper, with liquid-phase water identified as a key driver for the observed differences in the microwave pyrolysis process. This is the first study in microwave pyrolysis that is able to reconcile microwave heating phenomena against simple and well-understood mass transfer and phase equilibria effects. As a result, a number of processing strategies have emerged with the potential to use microwave heating to enable more selective pyrolysis and bio-oils with more targeted quality than has been possible with conventional approaches.

KEYWORDS

Pyrolysis, Microwave, Biomass, Mass Transfer, Dielectric Properties

INTRODUCTION

Microwave pyrolysis has received considerable attention in recent years, with researchers motivated by a vision for energy efficient heating and the production of higher grade fuel and chemical products than can be achieved using conventional pyrolysis techniques. Despite the widespread interest the mechanisms of microwave pyrolysis are largely unknown, and this is due to a host of factors: The complexity of the pyrolysis chemistry; the challenges around bio-oil analysis and quantification; a lack of understanding of the fundamentals of microwave heating, and the low intensity and poorly-controlled electric fields that are characteristic of domestic-type microwave ovens that continue to see widespread use within scientific studies and publications. Further challenges arise when attempting to accurately measure the temperature distribution within biomass during microwave heating, with even the most sophisticated laboratory equipment restricted to single point measurements on the sample surface rather than a comprehensive temperature distribution.

Some significant advances in empirical understanding have been made to-date. Most early studies in this area recognised that biomass could not be pyrolysed in a domestic oven, and these studies used dopants (microwave-absorbing additives) to allow pyrolysis to be achieved [1,2,3,4]. Our earlier studies showed that the dielectric properties were a strong function of temperature, and that the loss factor (the ability to convert electromagnetic energy to heat) is very low once the initial water in the biomass is removed. Despite these dielectric property observations we also showed that microwave-absorbing additives do not need to be used to initiate pyrolysis when using microwaves provided that the power density is above a set threshold [5], one that is higher than can be achieved in domestic microwave ovens. With sufficient electric field intensity biomass can be readily pyrolysed using microwaves, and in this case there are numerous reports of product being produced at lower temperatures than those used in conventional pyrolysis [3,6]. Corroborating claims associated with temperature are fraught with difficulty due to the well-known challenges of measuring temperature within a microwave environment [7], but these reports nonetheless present interesting empirical observations of different behaviour during microwave heating. Independent of the measured temperatures, there is a growing body of empirical evidence that microwave pyrolysis produces more sugar-derivatives such as levoglucosan than conventional pyrolysis processes [8,9]. Early studies proposed interactions between the microwaves and specific chemical groups on the cellulose and hemicellulose polymers, however microwaves are not sufficiently energetic to directly break covalent bonds [10]. Other explanations for this have been attributed to the 'cold-surrounding' that occurs during microwave heating, with the products being evolved into a cold environment (relative to conventional pyrolysis) that limits degradation of the primary pyrolysis products [9]. Whilst a feasible explanation from a physical standpoint it has not been proven empirically, and some doubts remain about whether levoglucosan is thermally-sensitive enough to degrade to the extent required to fit with experimental observations.

A number of key questions remain:

1. Are the observations of lower temperature pyrolysis genuine, and if so what are the underpinning mechanisms?

2. Why does microwave pyrolysis produce more levoglucosan and other sugar-derivatives than conventional pyrolysis?

This study aims to address these remaining questions by uncovering the physio-chemical mechanisms that underpin microwave pyrolysis. Where previous advances have come about through the combination of expertise in biomass/pyrolysis chemistry and microwave processing, this work extends the study to include physical phase behaviour and mass transfer as key elements that have been overlooked in previous work.

METHODOLOGY

Materials

Xylan (from beechwood) and microcrystalline cellulose were used for microwave pyrolysis experiments, and obtained from Sigma-Aldrich Co. LLC. Sycamore was used for both sets of dielectric measurements, and was obtained from Nottinghamshire Eco Fuels Limited.

Microwave Pyrolysis

A CEM Discover SP microwave was used for microwave pyrolysis of xylan and microcrystalline cellulose. Different masses of xylan or microcrystalline cellulose were weighed out into a standard 10 ml or 35 ml microwave tube (borosilicate glass) and inerted with nitrogen. All the experiments were run under closed vessel conditions, with the maximum temperature and pressure set to 300°C and 300 psi, respectively. A fixed power of 300 W was used in these experiments, and the headspace pressure was recorded over time to monitor the reaction progress according to the generation of volatile products. An infrared thermometer focussed on the bottom of the sample vessel was used to measure the surface temperature of the sample during microwave heating. Reaction products were mixed with dimethyl sulfoxide before analysis using liquid phase ^{H}NMR spectroscopy to identify furfural and levoglucosan as key decomposition marker compounds for hemicellulose and cellulose respectively. Quantification of the produced liquid composition was not required in this study.

Dielectric Property Measurements

1. Conventional heating

A cavity perturbation method was used in which a sample was placed in a 6 mm ID quartz tube, which was mounted such that it could be moved between a temperature-controlled furnace and a cylindrical TE cavity with resonant frequencies at specific spanning from 400 – 3000 MHz. Samples were held in the furnace for 10 minutes to achieve thermal equilibrium before being moved into the cavity using a step-motor, where the frequency shift and quality factor were measured using a vector network analyser. The sample was then returned to the furnace, and the sequential heat-hold-measure process was repeated for the required temperature range. Further description of the apparatus and method is given by Zhang et al. [11].

2. Simultaneous heating/measurement

A system based on microwave heating and dielectric characterisation was used [12]. The system consists of a cylindrical microwave cavity where 2 different resonant modes co-exist at the same time. Mode TE_{111} is used for microwave heating with incident power up to 100 W, and electronically controlled to be applied depending on the heating slope required. This mode has a maximum electric field in the centre [13], which corresponds to the sample position. The TM_{010} resonant mode coexists in the same cavity, and this is used to measure the changes of the resonant frequency to measure the sample permittivity. Both modes coexist in the same cavity, but are de-coupled with an excitation strategy that guarantees that the heating mode does not interfere in the permittivity measuring mode. With this strategy, simultaneous heating and dielectric characterisation can be done, ensuring that the sample is only heated by microwave energy.

RESULTS AND DISCUSSION

Controlled Pyrolysis of Hemicellulose

Xylan was used as a model hemicellulose compound, different masses of which were placed within the sealed reactor tube. The surface temperature of the sample was recorded using an IR Pyrometer, and the headspace pressure monitored during the experiments. The rate of change of headspace pressure was used to indicate the rate of pyrolysis, as this directly relates to the evolution of volatiles within the sealed reaction system. Figure 1 shows the relationship between headspace pressure gradient and surface temperature for each experiment.

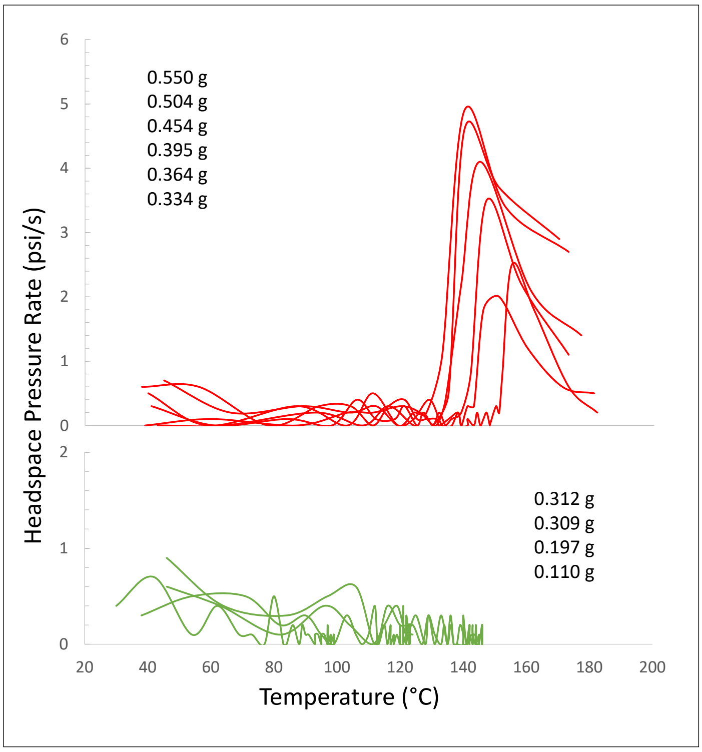


Figure 1 – Microwave pyrolysis of hemicellulose: Rate of change of headspace pressure plotted against temperature. Top segment shows samples >0.315g; Bottom segment <0.315g.

The rate of change of pressure is a function of temperature and sample mass. At low sample mass (<0.315 g) the rate of change of headspace pressure reduces throughout the duration of the experiment, achieving a value of zero at temperatures from 100-140°C. Above 0.315g the behaviour is significantly different, with peaks in pressure rate-of-change at temperatures of 130-150°C. This indicates rapid formation of pyrolysis products at these temperatures. The data shown in Figure 1 is typical of many microwave pyrolysis studies; it is carried out in standard laboratory equipment that allows for limited control of the microwave heating parameters and uses indirect methods of measurement to determine the extent of reaction. In this case the correlation with sample mass, although a genuine observation, is misleading from a mechanistic perspective. For relatively small samples in a microwave reactor, increasing sample mass will act to increase the amount of power that is absorbed, often proportionally more than the mass increase. As a result the rate of heating will increase the larger the sample mass. This can be seen as counter-intuitive, as in conventional heating systems increasing the sample mass would tend to decrease the heating rate as the same heat flow is distributed within a larger mass. This particular apparatus does not measure the reflected power so the absorbed power cannot be calculated, however the heating rate can be determined from the logged data, and is apparent in Figure 2.

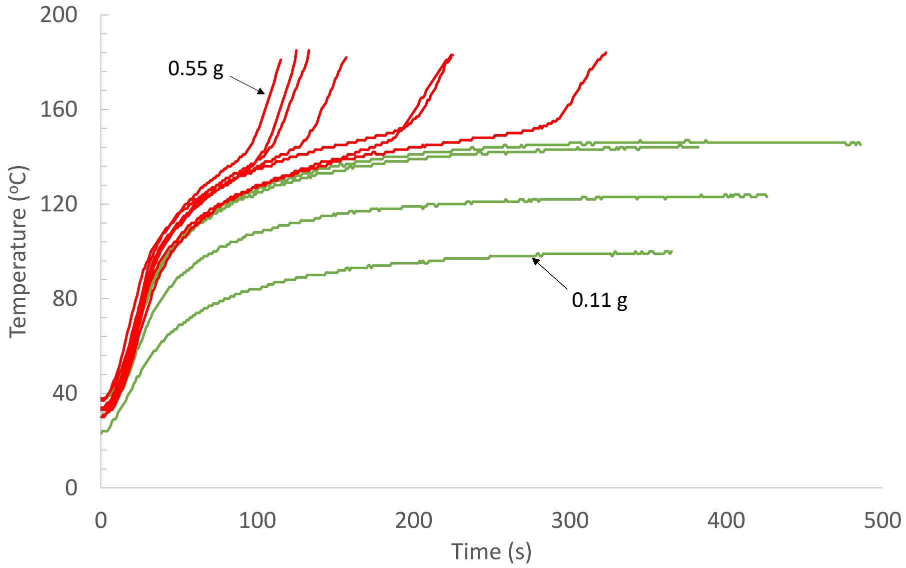


Figure 2 – Temperature vs time for Hemicellulose pyrolysis and variable sample mass. Curves are sequential from 0.11 g to 0.55 g. Red lines denote sample mass >0.315g, green lines denote <0.315g.

As expected, the amount of power absorbed and the corresponding heating rate increase with increasing sample mass. Up to 0.31 g there appears to be a temperature ceiling of 145°C. Extended microwave exposure under these conditions resulted in no further temperature or pressure increase, and in all cases below the sample mass threshold pyrolysis was <u>not</u> achieved. Larger samples, above 0.33 g meant that the temperature reached >145°C, at which point a rapid increase in temperature and pressure (Figure 1) was observed and pyrolytic products such as furfural were detected within the reaction vessel. The time taken to achieve pyrolysis decreased the higher the sample mass.

A key question arising from Figure 2 is whether the observed behaviour is attributable to the hemicellulose achieving a critical temperature (~145°C) or whether it is attributable to the rate of heating. The onset of the sharp increase in temperature does appear to occur at a lower temperature at high heating rates, however it is not possible to rule out thermal lag given the indirect nature of the temperature measurement and the short processing times.

Pyrolytic decomposition of hemicellulose is expected to occur at temperatures in excess of 200^{o}C [14]. Conventional pyrolysis was investigated using a pure hemicellulose feedstock and a kinetic model using the reaction schemes originally proposed by Ranzi [15]. Heating rates were varied, and the cumulative hemicellulose and pyrolytic product fractions were computed at temperatures up to 330°C. Figure 3 shows representative outputs from this analysis.

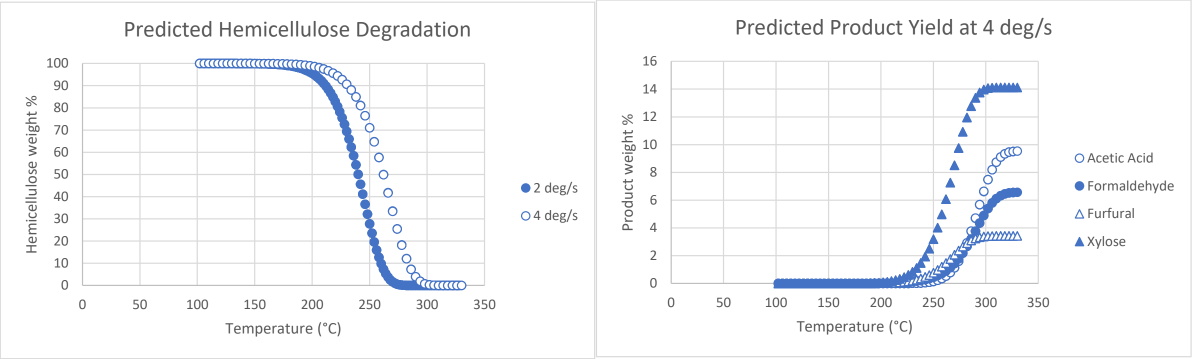


Figure 3 – Predicted Hemicellulose decomposition (left) and product formation (right) as a function of temperature.

As expected, temperatures in excess of 200°C are required before hemicellulose undergoes any conventional pyrolytic transformation. There does appear to be a heating-rate dependence, with 4°C/s resulting in a slightly later onset of degradation than the corresponding 2°C/s case. The difference is most apparent in the 200-300°C region, but there is no significant reduction in the temperature needed for pyrolysis to occur. Primary hemicellulose pyrolysis products such as acetic acid and furfural form at temperatures approaching 240°C.

The pyrolysis behaviour that occurs with conventional reaction schemes is in stark contrast to the microwave pyrolysis data. Hemicellulose pyrolysis simply should not occur below 200°C. With microwave heating, when the heating rate was above a key threshold then pyrolysis was observed at 140-146^{o}C, well below the conventional decomposition temperature for hemicellulose. It is well-known that accurate temperature measurement is challenging in microwave apparatus, with some discrepancies likely between the measured surface temperature and that in parts of the sample. Such a discrepancy will be minimised for small samples, and any thermal gradients within the sample will be minimised when heating times are the order of minutes rather than seconds. A study by Taqi et al. [16] suggests a temperature differential of <1°C between the sample centre and surface for biomass particles that are of the order of 1 mm in size. The observations in Figure 2 cannot therefore be attributed to discrepancies in temperature measurement. Clearly an alternative mechanism exists for microwave pyrolysis, but only above a critical heating rate. At lower heating rates the hemicellulose behaves in the same way as would be expected with conventional pyrolysis. This is explored further in a later section of the paper.

Controlled Pyrolysis of Cellulose

Microcrystalline cellulose was used as a model cellulose compound, different masses of which were placed within the sealed reactor tube. To extend the study beyond that attempted with hemicellulose two different moisture contents were studied, and two different sized reactor vessels were used. The surface temperature of the sample was recorded using an IR Pyrometer, and the headspace pressure monitored during the experiments. The rate of change of headspace pressure was used to indicate the rate of pyrolysis, as this directly relates to the evolution of volatiles within the sealed reaction system. Figure 4 shows collated headspace pressure data for different sample sizes, moisture content and reactor vessel volume.

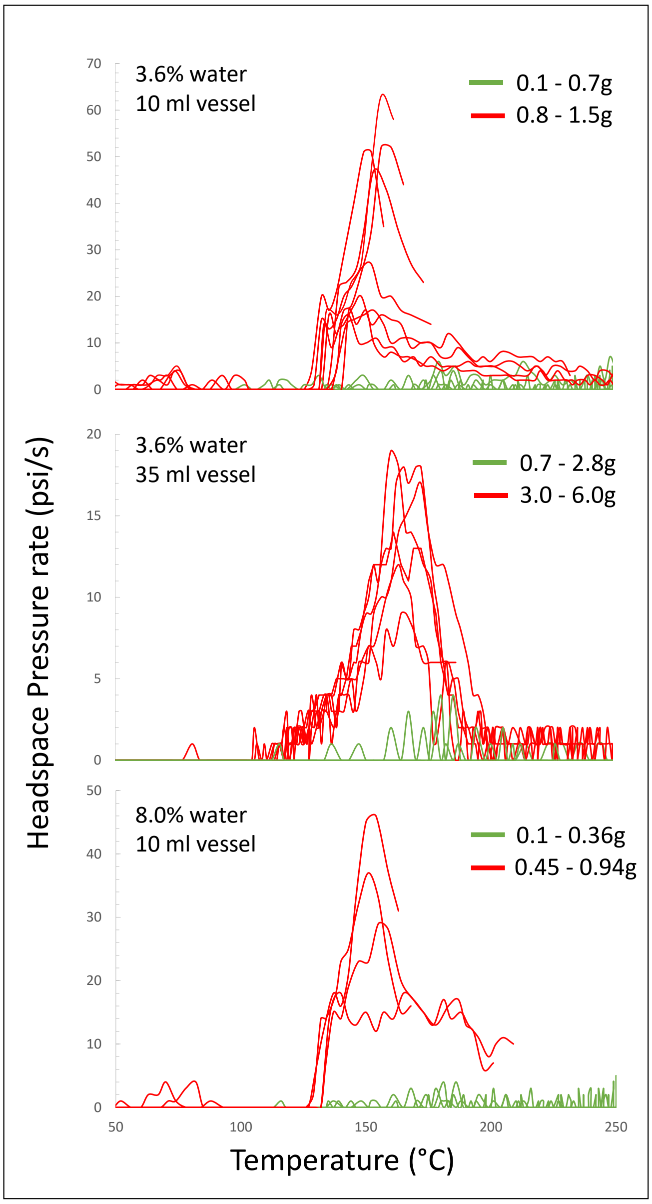


Figure 4 – Pressure differential during microwave pyrolysis of cellulose. Red lines denote pyrolysis to produce Levoglucosan, Green lines denote no Levoglucosan

Like the case with hemicellulose there appears to be a critical sample mass, above which rapid generation of volatiles takes place (corresponding to cellulose pyrolysis). Above the mass threshold the peak volatile generation occurs around 170-180°C. Also evident is that the same effect is observed with different vessel volumes and moisture content, but with a different value of the mass threshold in each case. Sample geometry will affect its position relative to the electric field and the water content will affect both the dielectric constant and loss factor, so it is to be expected that the amount of power absorbed will be different for different moisture content and vessel size.

In order to investigate the observed mass thresholds it is necessary to incorporate the heating rate, as this gives an indication of the amount of power absorbed in each case. Heating rate data is shown in Figure 5 for the 10 ml reaction vessel and moisture content of 3.6%.

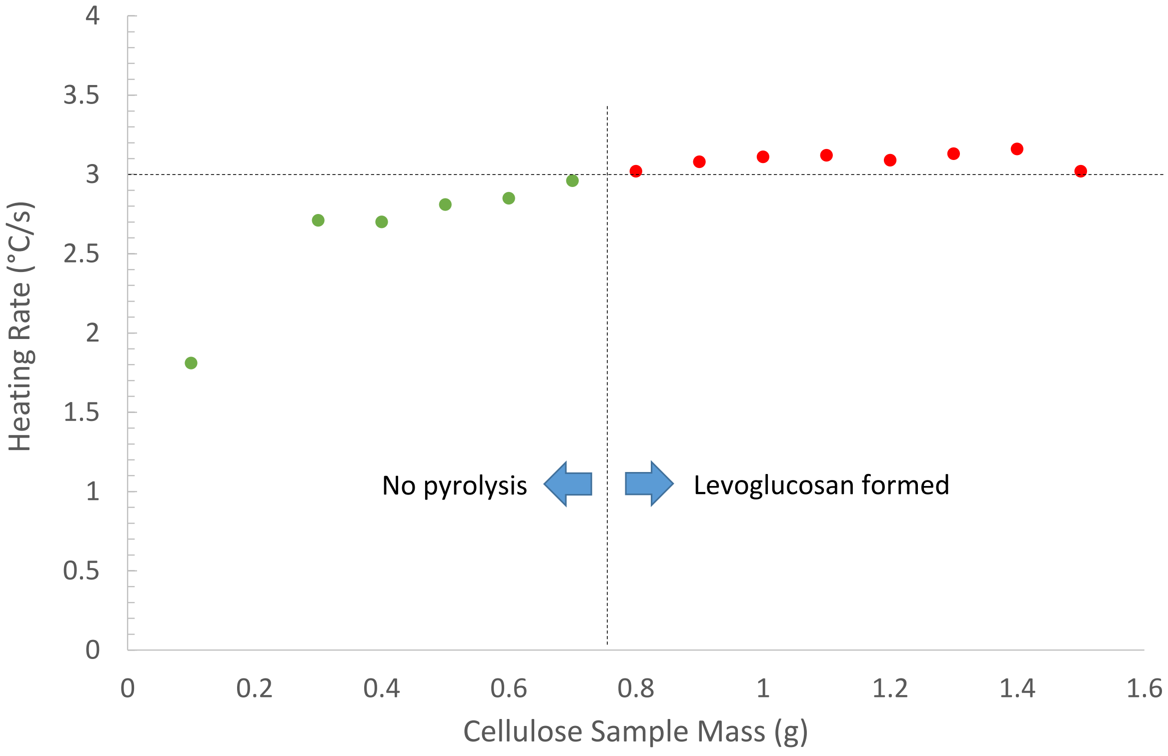


Figure 5 – Average heating rate against sample mass for experiments conducted in a 10ml vessel, with 3.6% moisture content.

As expected, the heating rate increases when increasing the sample mass from very small amounts. Above 0.7g there appears to be a critical heating rate above which no further increase in heating rate occurs, but at which the headspace pressure increases rapidly (Figure 4). In Figure 5 the critical heating rate is 3.0 °C/s. Heating rate is a function of the sample mass, water content, position within the reactor and applied microwave power, and as such it cannot be used as a primary control variable. Nonetheless, it appears to play a key role in the pyrolysis behaviour of both hemicellulose and cellulose. At high heating rates rapid pyrolysis of cellulose occurs at 170-180^{o}C, whereas at low heating rates pyrolysis is not achieved even though the same temperatures are attained. For hemicellulose pyrolysis (Figure 1) the temperatures achieved below the heating rate threshold did not exceed 145°C, however for cellulose it is possible to attain temperatures in excess of 250°C even if little or no volatile generation is achieved. Literature reports state that conventional pyrolysis of cellulose does not occur until temperatures approaching 300°C are achieved [14]. Using the kinetic schemes developed by Ranzi et al [15] it is possible to predict the cumulative degradation of cellulose and corresponding formation of levoglucosan at different heating rates. Figure 5 identified a heating rate threshold, above which different behaviour and product characteristics were observed. 2°C/s and 4°C/s were taken as representative heating rates below and above the threshold. Predicted levoglucosan yield and overall cellulose conversion under these conditions are shown in Figure 6.

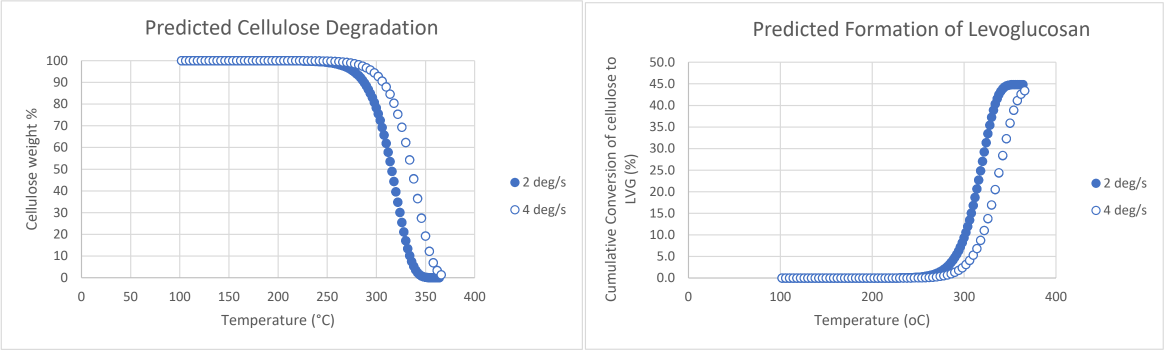


Figure 6 – Predicted cellulose degradation and levoglucosan yield with increasing temperature at 2°C/s and 4°C/s

The kinetic models show that cellulose does not undergo any pyrolytic decomposition until temperatures of 275°C are achieved. Between 275-325°C significant degradation occurs, with levoglucosan formed as the primary product. The heating rate does affect the decomposition profile, but only in the 275-325°C region. In conventional heating/pyrolysis of cellulose there is no change in the feedstock from 150-200°C, and a higher heating rate does not result in earlier onset of pyrolysis. The predictions obtained in Figure 6 from the kinetic reaction schemes are consistent with a wide range empirical observations from TGA analysis [17]. This conventional pyrolysis/decomposition behaviour is markedly different from the microwave pyrolysis experiments shown in Figure 4.

For both hemicellulose and cellulose it is apparent that the temperature needed to achieve pyrolysis can be reduced significantly when microwave heating is used, but only when the heating rate is above a critical threshold. At lower heating rates the process behaves in the same manner as conventional heating, with no furfural produced until 240°C and no levoglucosan produced until 275°C. One aspect that needs to be ruled out is the well-known limitation of temperature measurement within microwave reactors. The infra-red pyrometer produces a spot-measurement on the sample surface, and clearly the temperature within the depth of the biomass could have been higher than the measured value. This effect will be more pronounced for larger samples, but when <10 g of material is heated the temperature differential between depth and surface will be limited to a few degrees. The observations in Figure 4 that the thresholds exist across different sample sizes and water contents is very difficult to reconcile by considering temperature measurement alone.

From the observations in Figure 1 and Figure 4 it is clear that at high heating rates a different mechanistic pathway exists that allows hemicellulose pyrolysis to occur around 140°C and cellulose pyrolysis around 175°C – a mechanism that cannot be explained based solely on the temperature distribution throughout the biomass samples.

Understanding the Mechanism - Dielectric Properties

Dielectric properties of biomass are known to vary with moisture content, bulk density, frequency and temperature. The irregular geometry of biomass particles prevents the use of broadband coaxial-probe measurement techniques, where intimate contact between sample and probe is required. The cavity perturbation method overcomes this problem by containing the sample within a small diameter quartz tube, but the downside is that the heating and measurement need to be decoupled. The sample is heated externally in a furnace to the required temperature, before being moved into the resonant cavity for dielectric measurement. As a result the heating rate attainable with cavity perturbation is very low, and any specific effects of heating rate cannot be readily observed using this measurement technique. Cavity perturbation is widely accepted as a standard test method, but it is limited to very low heating rates.

A newly-developed dielectric measurement system was trialled at Universitat Politècnica de València, whereby the sample is heated within a microwave cavity using two different cylindrical modes to heat and measure simultaneously. This allows much higher heating rates to be achieved than is possible with cavity perturbation, and in effect allows the microwave pyrolysis process to be monitored in real-time. The technique requires a regular cylindrical sample geometry, which cannot be readily achieved for Xylan or cellulose but can be achieved for wood. The technique was also limited to 230^{o}C due to compatibility limitations with evolved vapours. Trials were carried out using sycamore, which contains both hemicellulose and cellulose, with samples from the same batch measured using cavity perturbation and the simultaneous heating methods. The dielectric loss factor obtained using each method is shown in Figure 7.

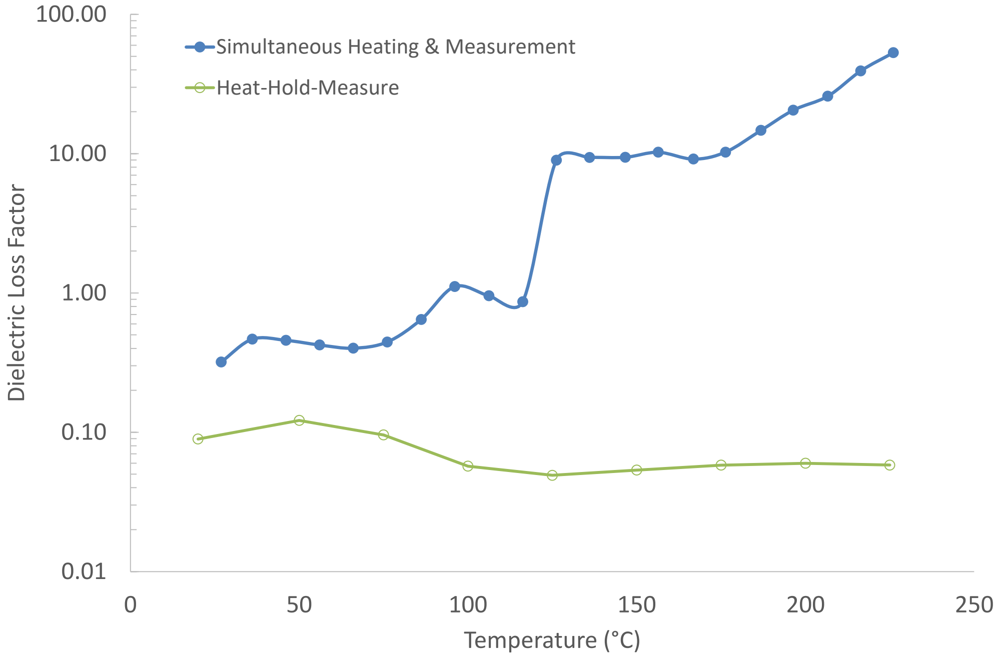


Figure 7 – Dielectric Loss Factor of sycamore measured using cavity perturbation (conventional heating) and in-situ (microwave heating) methods.

The two sets of dielectric data are markedly different. The conventional heating method shows the classical behaviour that has been observed many times previously, where the loss factor below 100°C indicates the presence of water, which when evaporated leaves a material with relatively low loss in the 100-300°C range. This data suggest that the material will readily absorb microwaves at temperatures up to 100°C, but it will be more challenging to heat beyond this temperature. The in-situ measurement method shows an increase in loss factor at 100°C, a sharp increase from 120-130°C and a further sustained increase above 175°C.

The different behaviour around 100°C is thought to be due to water. In the cavity perturbation system significant evaporation can occur in the time the sample is located within the furnace (typically 10 minutes between each measurement), so this method is likely to under-record the true loss factor. The in-situ method gives the instantaneous loss factor during the heating process, and it is thought that water is still present within the sample at temperatures above 100°C when high heating rates are applied. Cavity perturbation can be considered to be an equilibrium reading, rather than the actual transient value that occurs under high heating rates in the microwave.

The transitions in dielectric data at 120-130°C and ~175°C observed with the continuous heating method correlate with those detected for hemicellulose (Figure 1) and cellulose (Figure 4), both of which are present within sycamore. Furthermore, the large increases in loss factor indicate that the biomass is much more microwave absorbent under these conditions, and explains the early observations about the need for a high power density in order to achieve pyrolysis without using additives [5]. The transitions in dielectric data at 120-130°C and 175°C are thought to be due to either an intermediate or a pyrolysis product resulting from the microwave pyrolysis mechanism. At low heating rates these intermediates/products do not exist at these temperatures and hence they are not detected in the standard cavity perturbation measurement system. The most likely candidates for pyrolysis products are furfural from hemicellulose and levoglucosan from cellulose. These were obtained in pure form, and their dielectric properties measured using the cavity perturbation system as shown in Figure 8.

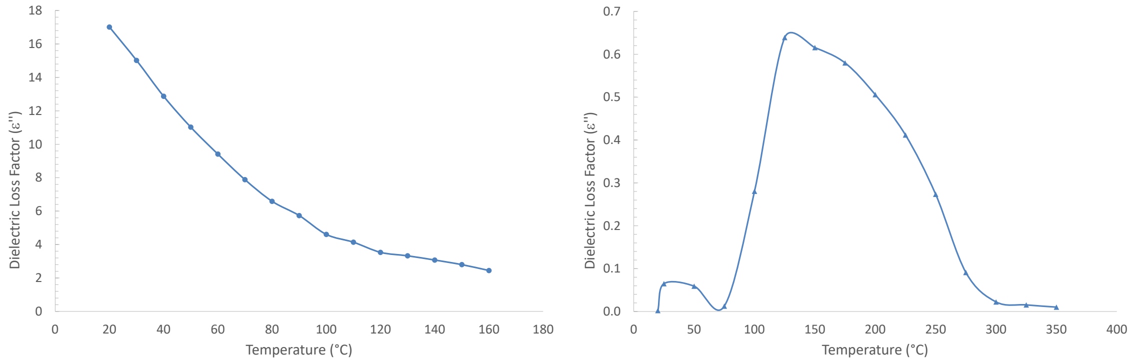


Figure 8 – Dielectric Loss Factor for Furfural (left) and Levoglucosan (right) at 2.45 GHz (note the scale on the x- and y-axes are not the same)

Furfural is in liquid form throughout the measured temperature range, and exhibits a very high loss factor. The loss decreases with temperature but maintains a value >2 approaching its normal boiling point, indicating that it will be a very strong microwave absorber even at this temperature. The data for levoglucosan is more complex. Levoglucosan is solid at room temperature and has very low loss, but once it starts to melt there is a higher degree of molecular mobility and the loss factor is relatively high. Further increases in temperature reduce the loss factor, which approaches zero towards the boiling point.

The data in Figure 8 fit well with the in-situ dielectric measurements on biomass in Figure 7. The step-change in loss factor from 120-130°C corresponds very well to the evolution of high-loss furfural from hemicellulose pyrolysis. The increase in loss factor above 175°C is consistent with the production of levoglucosan, however it should be noted that there are likely to be >100 compounds being formed during pyrolysis of sycamore, many of which could be microwave-absorbent and contribute to the measured loss in Figure 7.

It is clear from the results so far that both hemicellulose and cellulose pyrolysis can be achieved at lower temperatures when microwave heating is used, provided that the heating rate is above a key threshold value. Once pyrolysis of hemicellulose and cellulose is initiated, the primary products are themselves microwave-absorbent. Their presence allows the biomass to continue to absorb microwaves in the 120-300°C region, which allows continued heating and subsequent degradation of the lignin, through to full carbonisation/gasification of the biomass if required. At low heating rates the microwave-absorbent intermediates are not formed at 120°C or 175°C, and in this case the biomass remains relatively microwave-transparent, with pyrolysis not achievable without using microwave-absorbing additives.

The formation of compounds such as furfural and levoglucosan at lower temperatures explains the enhanced product quality that is observed with microwave pyrolysis. By reducing the decomposition temperature of hemicellulose and cellulose it is possible for the pyrolysis process to be much more selective, effectively targeting the sugar-derivatives and leaving behind the phenol-rich products from lignin degradation. This is a much more plausible explanation for empirical observations of pyrolysis oil quality from microwave heating than either the ‘cold surrounding’ hypothesis or claims of interactions with specific groups on the cellulose chain. However, it does not explain why the pyrolysis temperatures are lowered, nor why this is dependent upon the heating rate. The final part of our study addresses this.

Why do hemicellulose and cellulose pyrolysis reactions occur at lower temperatures, and why is this dependent upon the heating rate?

The key clue to understanding the low-temperature decomposition is the 100°C region of Figure 7. The in-situ dielectric property measurement shows a much larger dielectric response at 100°C compared to the conventional heating case, and at this temperature water is the only microwave-absorbing substance within biomass. Water vapour has zero loss, so the observation of a high loss factor in the 100°C region is down to the presence of liquid water. Liquid water is therefore suspected to remain within biomass at high heating rates, but vaporisation of this water occurs when the heating rate is low. Transport of water vapour through biomass is a physical process that is governed by Darcy’s Law. Water vapour has to travel a set distance through a porous structure with a defined permeability, and the driving force for vapour flow is the difference in pressure between the source of the vapour and the surrounding environment outside the biomass particle. The water vapour flux, J, can be expressed as:

$$J = -\frac{\kappa}{\mu}\frac{dP}{dx} \qquad \text{[Equation 1]}$$

Where κ is the permeability constant, μ the dynamic viscosity of the water vapour, P the pressure and x the distance travelled through the porous medium. Pressure is needed for the vapour to flow out of the biomass, and this pressure comes from the build-up of vapour within the biomass pore structure. If the resistance to vapour flow is greater than the resistance to heat transfer then the water will vaporise faster than it can be removed, which therefore generates higher internal pressures within the biomass. The pressure increase also acts to elevate the boiling point, meaning that liquid water can be present at temperatures in excess of 100°C. The mass transfer resistance is a function of the pore characteristics of the biomass, and the particle size. Mass transfer depends on the heating rate – when the heating rate is low the rate of vaporisation is low, meaning relatively low vapour build-up and a low internal pressure. At high heating rates the rate of vaporisation is increased, giving more vapour-build-up and higher internal pressure.

Having liquid water present within the biomass at elevated temperatures means that hydrolysis mechanisms could occur, rather than (or in combination with) pyrolysis. Both hemicellulose and cellulose are known to undergo hydrolysis reactions at elevated pressures and temperatures, and recent observations of Hydrothermal Carbonisation processes confirm that temperatures around 180-250°C are sufficient to degrade hemicellulose and cellulose [18] when liquid water is present. In this case the pH of water decreases markedly at temperatures above the normal boiling point, and therefore enables hydrolysis to take place.

The evidence gathered to date points towards a hydrolysis mechanism induced by a pressure build-up within the biomass from heating water present within the feedstock. This explains the low temperature decomposition of cellulose and hemi-cellulose, and explains the threshold heating rate below which the microwave process reverts to a standard conventional pyrolysis process. The final part of this work is to test whether the pressure build-up within the biomass is sufficient to maintain liquid water at ~140°C and/or ~175°C, given a plausible set of physical properties and microwave processing conditions.

Modelling the pressure build-up

Equation 1 can be used to establish a quantitative estimate of the pressure attained within biomass particles during microwave heating. A full dynamic model of the heating process is not required in this case, instead an equilibrium model can be used to equate the transport of water vapour through biomass with internal pressure. Sensible heat effects during the first few seconds of heating are ignored, so using fixed values of power density (*Pd*) in the water phase (within a known practical range) it is possible to infer the vaporisation rate as the absorbed power overcomes the latent heat and results in mass flow of vapour:

$$Pd = \rho\lambda\frac{dM}{dt} \qquad \text{[Equation 2]}$$

Where ρ is the water density, λ the latent heat of water, M the mass and t time. Volumetric flow is calculated from the mass flow, from which the flux can be obtained for a given cross-sectional area. In this case spherical particles were assumed, with water vapour generated uniformly throughout the volume of the sphere due to the presence of the electric field. The mass flow rate is calculated from Equation 2, however translating this quantity to a flux is complicated by fact that the cross-sectional area for flow within in a sphere is a function of the position from the centre. This is illustrated in

Figure 9.

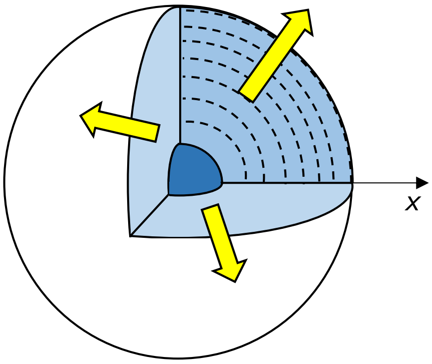


Figure 9 – Representation of spherical biomass particle used to model internal pressure. Arrows denote direction of flow of water vapour, dashed lines illustrate how the cross-sectional area varies with sphere radius.

A numerical method was used to calculate pressure and temperature. Particles were modelled as concentric spheres, comprising of ten layers and a constant radial increment from the outer edge to the particle centre. Vapour is generated volumetrically throughout the entire sphere, and passes through each radial increment with increasing cross-sectional area until it reaches the particle surface. Permeability and viscosity data were taken from literature as shown in Table 1. The pressure required to achieve the mass flux is subsequently computed within each of the ten layers, and used to calculate the equivalent boiling point temperature for water. An iterative procedure is then used to feedback temperature and pressure values to recalculate vapour density and hence the volumetric flow, and iteration carried out until the two sets of temperatures and pressures converge. The temperatures, which are based on microwave heating of water only, can then be compared with the empirical observations presented in Figure 1 and Figure 4. The output analysis for 5 mm diameter biomass particles is shown in Figure 10.

Parameter	**Value / Range**	**Notes / References**
Particle Diameter	1 – 10 mm	Covers the range typically used in literature studies
Permeability	10^{-17} – 10^{-15} m^2	Range stated in literature for wet biomass. 10^{-17} quoted for cellulose. [19,20,21].
Viscosity	3 x 10^{-5} kg/m.s	[22]
Power density	10^6 – 10^8 W/m^3	10^6 W/m^3 is typical of a domestic microwave oven; 10^8 W/m^3 can be achieved in a high power single mode cavity

Table 1 – Parameters used for internal pressure model

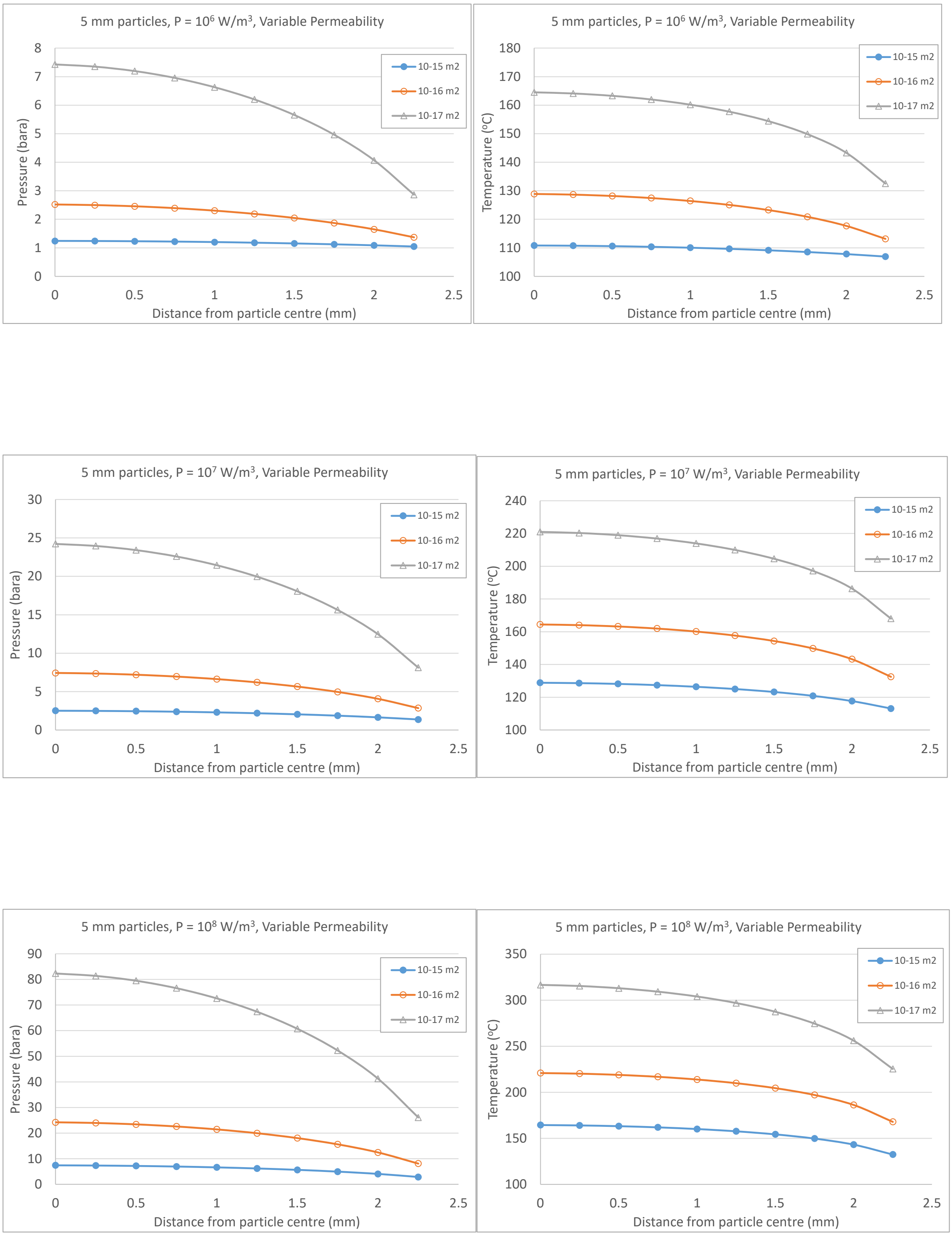
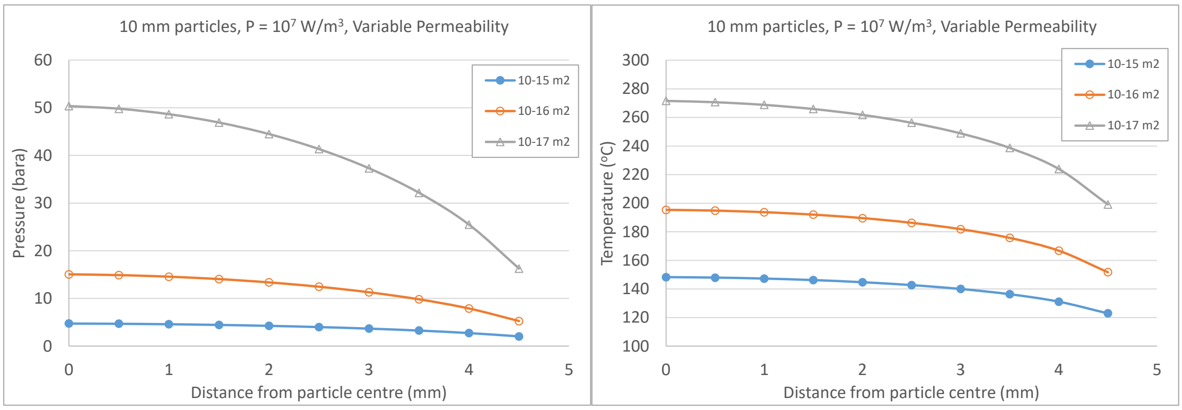


Figure 10 – Pressure (left) and corresponding boiling point temperature for water (right) within 5 mm biomass particles and variable power density and permeability. Legend denotes permeability.

Figure 10 shows that at low power density (10^6 W/m^3) and high permeability (10^{-15} m^2) the pressure barely exceeds 1 bar, and subsequently the maximum water temperature is limited to 110°C. 10^6 W/m^3 is typical of the power density in a domestic-type oven, and under these conditions the biomass has to be of the minimum feasible permeability in order to elevate the boiling point close to the temperatures identified in Figure 1. When the permeability is 10^{-17} m^2, which has been reported for cellulose, pressures in excess of 80 bar can be generated within the biomass when higher power densities are used, with a corresponding water boiling point >300°C. This temperature is clearly above that needed to achieve the onset of pyrolysis for both hemicellulose and cellulose. Indeed, at high power density it appears that all the physical conditions considered in the model will allow temperatures to be attained that are sufficient to pyrolyse hemicellulose at least (140°C). The outer edges of the particle support a lower pressure and hence a lower temperature than the centre, meaning that there is potential for the centre portion of the biomass particles to be subject to a different pyrolysis mechanism than the outer layer.

Further analysis for different particle sizes and a constant power density of 10^7 W/m^3 are shown in Figure 11 and Figure 12.


10 mm particles, P = 10^7 W/m^3, Variable Permeability

10 mm particles, P = 10^7 W/m^3, Variable Permeability

Figure 11 - Pressure (left) and corresponding boiling point temperature for water (right) within 10 mm biomass particles for constant power density and variable permeability

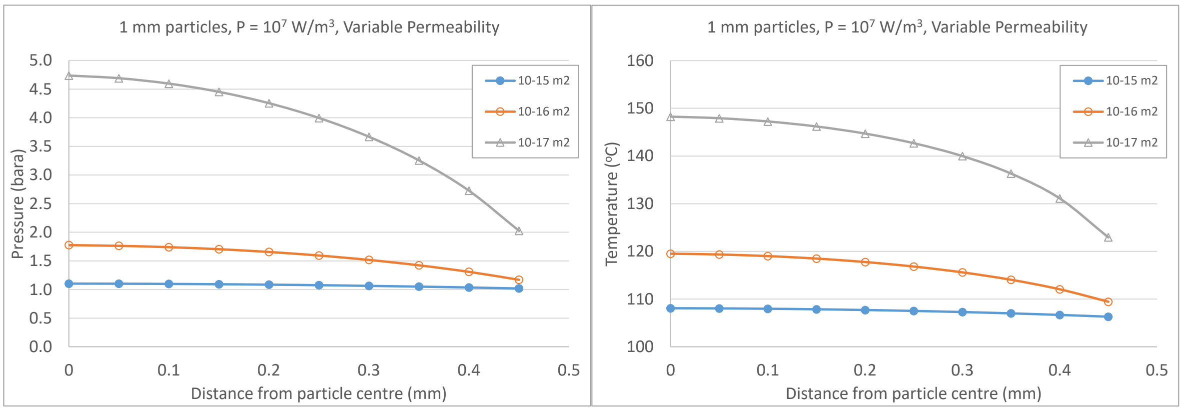


Figure 12 - Pressure (left) and corresponding boiling point temperature for water (right) within 1 mm biomass particles for constant power density and variable permeability

For 10 mm biomass particles the pressure build-up is more pronounced than the equivalent within 5 mm particles, as the extra radial depth provides a greater resistance to mass transfer. For 1 mm particles only the very low permeability case gives rise to significant internal pressure and temperature.

It is not possible to validate these models empirically, as doing so would require measurement of temperature and pressure throughout the depth of biomass samples with precisely-controlled permeability, and within a microwave environment. However, the investigation of power density, permeability and particle size over several orders of magnitude give confidence that the proposed mechanism is consistent with the basic physics of fluid flow through porous media.

The pressure and temperature models show that it is feasible to have liquid water present within biomass with a realistic set of physical properties and microwave heating conditions. The experimentally-observed threshold with heating rate has clear parallels in each of Figure 10 - Figure 12, but also apparent is that the biomass internal structure and bulk particle size are also expected to contribute to this effect. Also of note is that the high pressures required to elevate water boiling point are not just confined to the particle centre, but can be present throughout the majority of the particle volume. This means that the internal volume of the biomass can be subjected to the hydrolysis mechanisms, however the surface layer would be expected to behave conventionally due to the limited pressure that can be sustained within this region. Permeability will increase as volatilisation takes place, and further work is needed to extend this analysis to higher temperature regions where multiple pyrolysis/hydrolysis reactions may be taking place. However, given that the premise for this work was to prove how water alone can initiate the hydrolysis process for hemicellulose and cellulose, then literature-quoted permeability values for unprocessed biomass is a reasonable assumption.

Summary of Microwave vs Conventional Pyrolysis Mechanism and Processing Implications

The three different investigative techniques (microwave pyrolysis, dielectric measurement, fluid flow modelling) have been combined to establish the mechanism for microwave pyrolysis, and to understand the difference between conventional pyrolysis techniques. The key finding from this work is that the distinction is not microwave vs conventional, but rather it is low heating rate vs high heating rate. As microwave heating is not reliant on heat transfer it tends to lead to high heating rates, but with low microwave power or domestic microwave ovens the heating rate will be low, and comparable with conventional heating methods. When the heating rate is low the vaporisation rate of water within the biomass structure is also low. This means that pressures within the internal structure remain close to atmospheric. In this case the pyrolysis process proceeds as per conventional heating, with hemicellulose depolymerising at temperatures in excess of 200^{o}C, cellulose at 300^{o}C and lignin in the 220-400°C range. Products from pyrolysis of each bio-polymer are co-produced and result in bio-oils with a diverse chemical composition.

When the heating rate is high (microwave heating) the rate of vaporisation of water is also high. This results in a more significant pressure build-up within the biomass structure, which elevates the boiling point and results in liquid water remaining within the biomass at temperatures well over 100°C. This water induces hydrolysis of hemicellulose at ~130°C, with furfural the primary product. Hydrolysis of cellulose occurs at ~175°C, producing levoglucosan as the primary product. Further heating results in pyrolysis of lignin, which at this stage is believed to follow the same reaction schemes as conventional pyrolysis due to its general lack of hydrolysable linkages [23]. When the heating rate is sufficient to elevate the water boiling point it is possible to separate the products from the three biopolymers in a manner that is not possible with conventional pyrolysis, and this is illustrated in Figure 13.

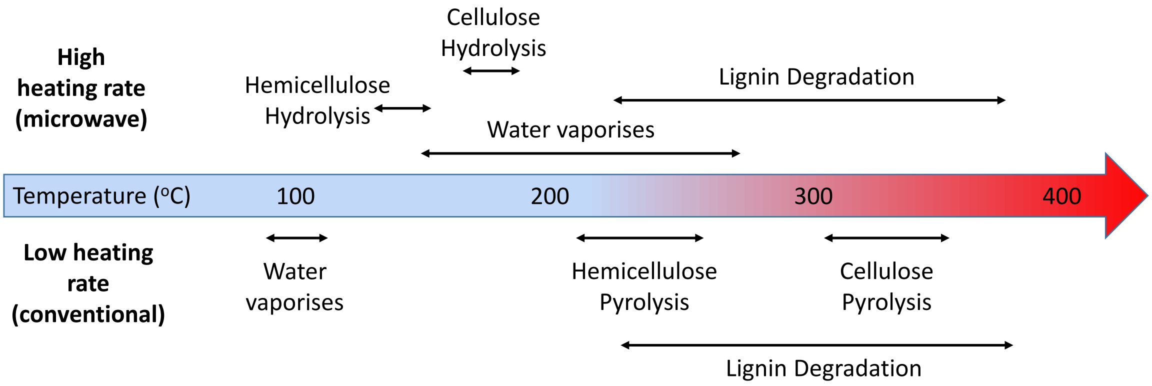


Figure 13 – Scheme for microwave and conventional pyrolysis

The mechanism for microwave pyrolysis, which is based on simple phase equilibria, explains why pyrolysis products are observed at lower temperatures, which in turn explains why microwave-derived bio-oils tend to contain more levoglucosan, more furfural and less water than conventionally produced oils. From Figure 13 it is theoretically possible to produce fractionated products from woody biomass, which will be of much higher quality and inherent value than conventional bio-oils. The heating rate and temperature need to be closely controlled in order to achieve this level of fractionation, and this is likely to need a continuous process with microwave heating in order to balance the electric field intensity and heating times to achieve the necessary control. Continuous systems are currently under development in order to test the extent to which the different biopolymer derivatives can be fractionated by the microwave heating process.

The distinction between the two mechanistic pathways is heating rate, as this is the driving force that results in pressure build-up within the biomass structure. Permeability is also important as a resistance term, as this also affects the internal pressure. A key hypothesis that arises from this study is that different pyrolysis behaviour with different biomasses occurs not because of their inherent chemistry, but their micro- and macro-structure as characterised by their permeability. High-permeability biomass would not be expected to support high pressures, and consequently we would not expect to observe significant differences between microwave and conventional pyrolysis. Low-permeability biomass does sustain high pressures during microwave heating, and in this case we would expect different mechanisms for low and high heating rates.

This study was focussed on answering a number of long-standing research questions on biomass pyrolysis. The proposed mechanism based on heating rate arises from fluid flow limitations in a porous material when volumetric heating is employed, and as such is likely to apply beyond just biomass. Applications in heterogeneous catalysis, solvent extraction and waste plastic pyrolysis will all feature fluid flow in porous materials, as will countless other applications. Where microwave heating is used then it is possible that the same physical mechanisms identified in this study could also prevail, leading to observed differences between microwave and conventional technologies.

CONCLUSIONS

Microwave pyrolysis of biomass can lead to lower pyrolysis temperatures and different product chemistry compared to conventional processes. The work presented in this paper used a combination of microwave pyrolysis experiments, dielectric properties measurement and fluid flow modelling to propose a rational explanation for this based on simple and well-understood mass transfer and phase equilibria effects. Pyrolysis experiments demonstrated that hemicellulose pyrolysis can be achieved at 145°C using microwaves but requires 210°C with conventional heating. Levoglucosan can be produced from cellulose at 180°C using microwave pyrolysis, compared to 300°C conventionally. A critical heating rate was identified, below which microwave pyrolysis behaves identically to conventional pyrolysis, with no reduction in the pyrolysis temperature. The heating rate was also shown to affect dielectric properties, with loss factors over an order of magnitude higher at high heating rates compared with low heating rates; this explains why microwave-absorbing dopants are not needed and why the behaviour of non-doped biomass subjected to high microwave power densities is not consistent with published dielectric property data (which is typically measured at low heating rates). The results have led to the proposal of a new mechanism for microwave pyrolysis with heating rate as the key determining factor, which in turn affects mass transfer and water phase equilibrium. Fluid flow modelling was used to demonstrate that liquid-phase water can still be present within biomass at 145°C, consistent with the lower pyrolysis temperature for hemicellulose. Consequently, it is proposed that a microwave-induced hydrolysis process occurs at high heating rates, compared to a standard pyrolysis process when the heating rate is lower and liquid water is no longer present. This gives rise to the opportunity to selectively pyrolyse hemicellulose and cellulose rather than lignin, yielding bio-oils with a narrower product distribution and a lack of phenolic compounds. This is the first study of microwave pyrolysis to categorically demonstrate that heating rate is the key driver in selective microwave-biomass pyrolysis. The approach used, which applies well-established mass transfer and phase equilibria principles, will be a powerful tool in the design of microwave processes in the future.

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