MICROFUEL

MOBILE PYROLYSIS PLANT TURNS BIOMASS INTO FUEL LOCALLY

DELIVERABLE 1.1

DIELECTRIC PROPERTIES OF VARIOUS FEEDSTOCKS AT VARIOUS TEMPERATURES AND TRANSFORMATION LEVELS AND RECOMMENDED GENERATOR FREQUENCY

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1 EXECUTIVE SUMMARY

The dielectric properties of two forestry waste samples have been characterised at two industrially-allocated frequencies and at temperatures from 20-800°C. Two measurement techniques have been used, based upon a cavity perturbation method to give accurate dielectric property readings at all temperatures. The dielectric constant and dielectric loss factor both vary significantly with temperature at both frequencies, and the behaviour is explained based on the water content and the degree of graphitisation due to combustion.

The forestry waste samples will absorb significant amounts of microwave energy at temperatures below 300°C and above 500°C. Between 300-500°C the samples are essentially transparent to microwaves, and this presents a significant challenge in the design of a microwave applicator for fast pyrolysis.

The measured values of ε' and ε'' obtained in this study can be used to inform the selection of appropriate scale-up concepts, simulation of the electric field strength and electric field distribution within a particular microwave applicator and the selection of the most appropriate cavity geometry during the design of the pilot scale system. However, further data which presents dielectric properties of the test materials in a more realistic form is required for the design of the process applicators in this project due to significant range of feed particles sizes expected in the material. This will be presented at the next review meeting.

2 DIELECTRIC PROPERTIES

2.1 BACKGROUND

Dielectric properties govern the behaviour of a material in the presence of an electric field at varying frequency. A good estimate of these properties is essential for effective design and scale-up of microwave heating processes to ensure a realistic prediction of power density i.e. the rate at which heat is absorbed into the material and electric field distribution within an applicator structure. Dielectric properties can vary greatly with composition, temperature, frequency of the electromagnetic wave and sample density (Salsman, 1991; Nelson, 1988; Altschuler *et al*., 1963). It is crucial to fully understand these variations in order to best fulfil the process requirements and determine the optimum conditions at which to apply the microwave energy.

The property that determines the behaviour of a dielectric under the influence of an electric field is known as the complex permittivity *(ε^*)*, which is expressed as a function of a real component, the real permittivity or dielectric constant *(ε')*; and an imaginary component, the dielectric loss factor *(ε'')*.

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

The ratio between the dielectric loss factor and the dielectric constant provides a measure as to how well a material absorbs the electromagnetic energy and dissipates it as heat throughout the material. This property, called loss tangent, *tanδ*, is often used to describe the ability of a material to heat in an externally applied electromagnetic field (Meredith, 1998).

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Specific measurements are necessary to obtain the essential parameters required to calculate the dielectric properties of a material. The dielectric constant and the dielectric loss factor quantify the capacitive and conductive components of the dielectric response

respectively. The dielectric constant is essentially therefore a measure of the ability of a material to store electromagnetic energy. It also defines the velocity of propagation of an electromagnetic wave through a dielectric (Meredith, 1998; Fletcher, 1995). The dielectric loss factor is a measure of the ability of a dielectric to dissipate internal energy stored in the material as heat. In general, materials with loss factors greater than 0.2 are deemed to be likely dielectric heaters (Metaxas and Meredith, 1983).

Dielectric properties can be used to calculate the power density, which is the power absorbed per unit volume of the material (W/m^3). The power density for a given material can be calculated by the following equation:

$$P_d = 2\pi f E^2 \varepsilon_0 \varepsilon''$$

Where: P_d = power density (W/m^3)

f = applied frequency (Hz)

E = electric field strength inside the material (V/m)

ε_0 = permittivity of free space (8.85×10^{-12} F/m)

It can be seen that power density is proportional to the square of the electric field within the material, and that power density varies linearly with frequency and loss factor. The electric field strength is a function of the applied power and the geometry of the microwave cavity.

2.2 PENETRATION DEPTH

Accurate knowledge of penetration depth of an incident wave into a dielectric material is essential for effective application of microwaves to industrial processes. As an electromagnetic wave propagates into a material, its amplitude diminishes as the power is absorbed. If any internally reflected waves are neglected, the power density falls exponentially with depth. Power absorbed is directly proportional to power density so also falls exponentially. Penetration depth D_p is defined as the depth into the material at which the power flux has fallen to 1/e (= 0.368) of its value at the surface (Metaxas and Meredith, 1983).

$$D_p = \frac{\lambda_0}{2\pi\sqrt{2\varepsilon'}} \times \frac{1}{\sqrt{\{1+(\varepsilon''/\varepsilon')^2\}^{0.5}-1}}$$

Where: λ_0 = wavelength of incident radiation in free space (12.2 cm at 2.45 GHz)

In many cases when $\varepsilon'' \leq \varepsilon'$, the penetration depth can be simplified, up to approximately 10% accuracy, as follows (Meredith, 1998):

$$D_p = \frac{\lambda_0}{2\pi\sqrt{(2\varepsilon')}}$$

Penetration depth is an important parameter as it provides a good indication of the heating uniformity throughout a sample. High frequencies and large values for the dielectric properties will lead to surface heating and while lower frequencies and smaller values of dielectric properties will lead to more volumetric heating (Clark *et al*., 2000; Thostenson and Chou, 1999).

2.3 DIELECTRIC PROPERTIES MEASUREMENT

Dielectric properties vary with frequency, temperature, composition and density (Metaxas and Meredith, 1993), hence many different methods are available for dielectric property measurement. Coaxial probes or resonant cylindrical cavity techniques are considered to be the most suitable for higher or low loss materials respectively at industrially applicable microwave frequencies. The dielectric properties of the forestry wastes were determined at 2.45 GHz and 915MHz by using a resonant cylindrical cavity technique as this was the most compatible with the heterogeneous physical and structural properties of the samples. Although simpler, coaxial probe techniques require flat, polished surfaces for measurement which cannot be easily achieved with the wood chippings supplied.

2.3.1 Resonant cylindrical cavity technique

This method is based perturbation of an electromagnetic field in a resonant cavity by the insertion of a small sample. This technique has been used extensively for measuring the dielectric properties of low loss materials (Metaxas and Meredith, 1993). The relative simplicity of its design and its inherent accuracy has encouraged many workers to use this technique for similar materials to those used in this project (Arai, 1995).

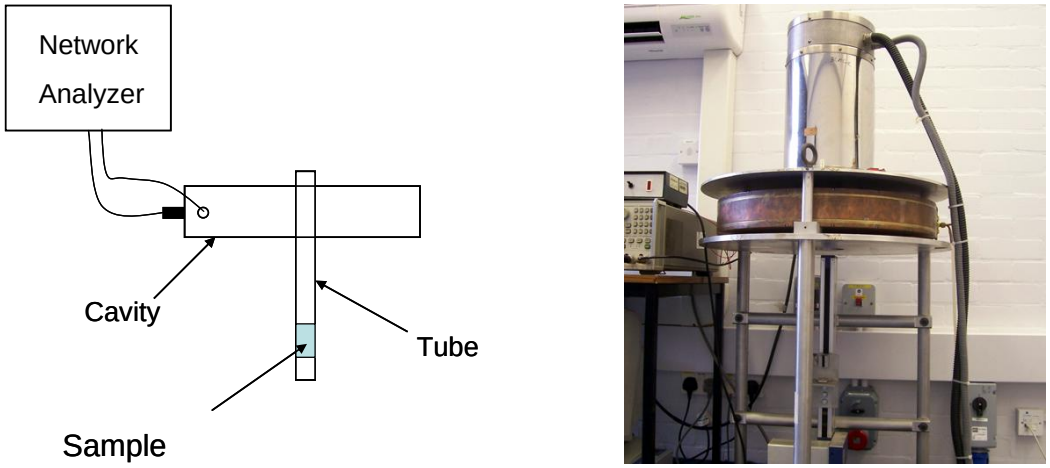


Figure 1. The cavity perturbation measurement system

A cavity is defined as a dielectric region of any shape completely surrounded by conducting walls. It is said to resonate if the stored electrical energy is equal to the stored magnetic energy. The frequencies at which this effect occurs are called the resonant frequency modes. During resonance, energy is dissipated in the walls of the empty cavity. This loss gives rise to the quality factor (Q) of the cavity (the ratio of total energy stored to the energy dissipated per cycle), which is a direct measurement of the energy loss. The insertion of a sample into the cavity alters the energy dissipation characteristics of the cavity as well as the resonant frequency, and knowledge of these alterations allows the dielectric properties of the sample to be estimated. The resonant cylindrical cavity technique is based on this perturbation theory, which assumes that the change in the stored energy in the cavity between the loaded and unloaded conditions is very small. This means that the electromagnetic fields in the cavity with and without the sample are approximately equal (Klein *et al*., 1993). The dielectric properties of any given material can then be calculated from the measured frequency shift and change of cavity Q factor before and after sample insertion, using Maxwell's Equations developed from the perturbation theory:

$$\varepsilon' = 1 + 2 \times J_1^2(X_{l,m}) \times \frac{V_c}{V_s} \times \frac{f_0 - f_s}{f_0} \qquad \varepsilon'' = J_1^2(X_{l,m}) \times \frac{V_c}{V_s} \times \left(\frac{1}{Q_s} - \frac{1}{Q_o}\right)$$

Where V_c is the volume of the cavity, V_s is the volume of the sample, f_o is the resonant frequency of the empty cavity, f_s is the resonant frequency of the cavity and sample (Hz), Q_s is the quality factor of the cavity and sample, Q_o is the quality factor of the empty cavity.

The resonant cavity is also equipped with a furnace in order to observe how the dielectric properties change with temperature. A procedure is followed so that the sample tube is heated in the furnace to the desired temperature, and then moved into the cavity (by an electric stepper motor) for the measurement. After the measurement is completed, the sample is moved back up into the furnace to be heated to the next set temperature in the procedure. The whole movement procedure takes less than 1 second so that the sample does not cool.

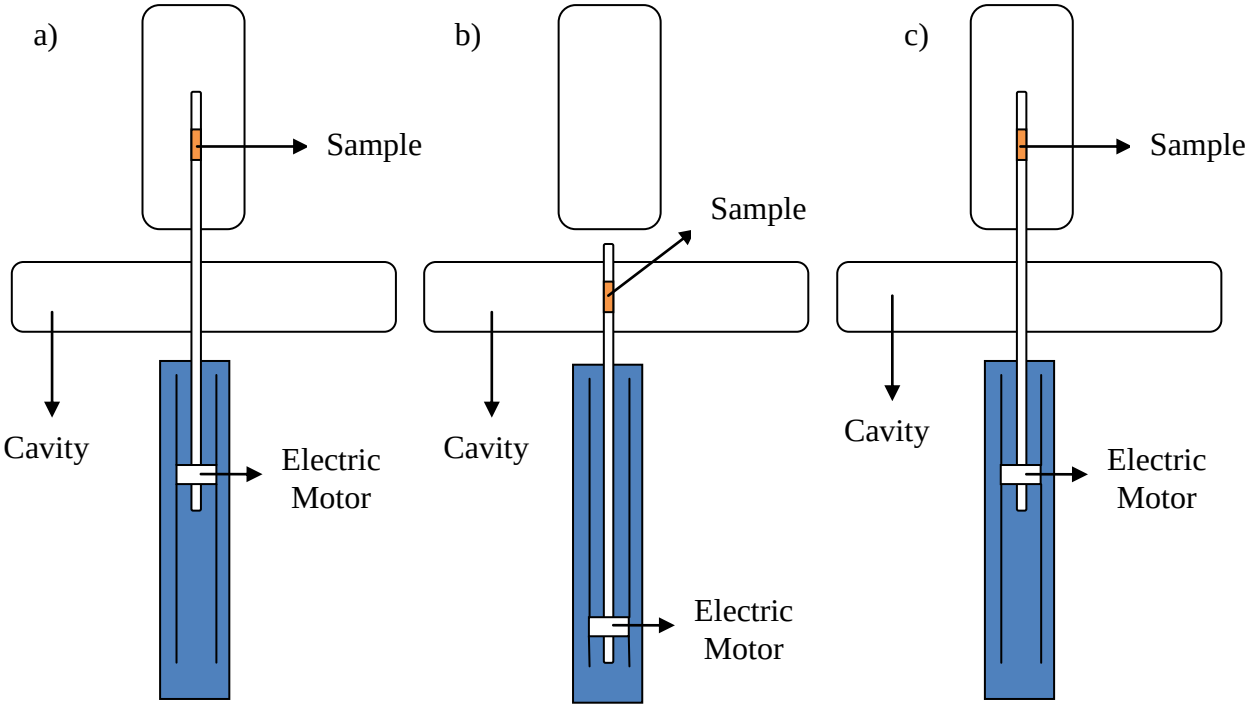


Figure 2. a) Sample is place in the furnace and heated to a set temperature (e.g. 300ºC). b) After the furnace reaches the set temperature (and maintained at that temperature for ten minutes), the sample is sent to the cavity for measurements. c) After measurements are completed, the sample is sent back to the furnace to be heated to the next set temperature (e.g. 400 ºC)

3 DIELECTRIC PROPERTIES OF FORESTRY WASTE

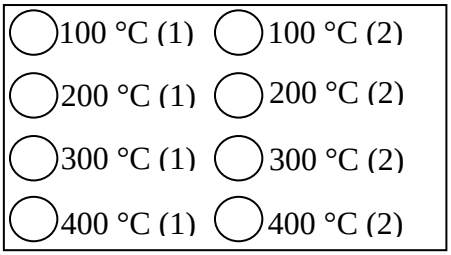
3.1 PROCEDURE

Samples of forestry waste were labelled and milled to less than 3mm particle size in a cutting mill. A sample was taken and packed in a quartz tube for dielectric measurements using the resonant cylindrical cavity technique described in section 1.3.1. Sample height and tube diameter were noted to 4 decimal places to allow calculation of volume and measurements were taken every 50ºC up to 800°C. After the run was completed it was observed that the sample had lost a substantial amount of volume, probably caused by pyrolysis and combustion at high temperatures. For accurate measurements the precise volume is required for the calculation of the dielectric constant and dielectric loss factor, as shown in the perturbation equations on the previous page. This means that in this form the measurement technique is unsuitable and is there required to be modified.

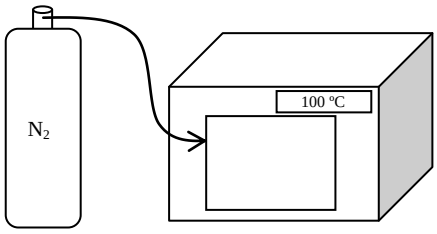
3.2 AMENDED PROCEDURE

A new procedure is proposed to measure the dielectric properties of forestry waste whilst overcoming the error caused by the change in volume. To do this, samples were prepared beforehand in a furnace flushed with nitrogen. A schematic of the procedure is summarised in Figure 3.

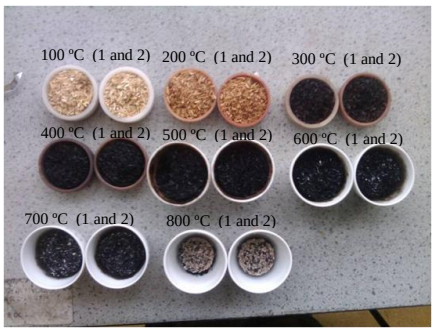
1) 16 samples are obtained from milled buckets. All samples are weighed, labelled and placed on a heat proof mat (2 samples for every temperature up to 800 °C)



2) Samples are placed in a furnace flushed with nitrogen (to simulate pyrolysis) and temperature set to 100ºC.



3) After Furnace stabilizes at 100ºC for 30 minutes, samples 100°C (1) and 100 °C (2) are taken out and weighed. Samples taken out are placed in a desacator and furnace temperature is increase to 200 °C. Procedure is repeated until 800 °C



4) Room temperature dielectric measurements may now be carried out on the different samples, thus, eliminated the unknown volume issue.

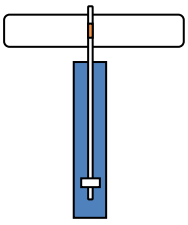


Figure 3 – Procedure for measuring dielectric properties at high temperatures to avoid volume changes.

4 MATERIALS

4.1 FORESTRY WASTE SAMPLES

The following samples were submitted for analysis, supplied by project partners.

Sample ID	Description	Received From	Remarks
A	Blend	Estonia	No Data Given
B	Pine	Estonia	>50 mm Wet
C	Pine	Estonia	>50 mm Dry
D	Juniperus Communis	Estonia	>50 mm Wet
E	Silver Birch	Estonia	No Data Given
F	Pine	Estonia	<35 mm Dry
G	Scotland	Scotland	No Data Given
H	Pine	Estonia	<35 mm Wet
I	Black Alder	Estonia	No Data Given
J	Mix (Pine, Larch, Birch, Spruce) Chips	Retford	No Data Given
K	SRC Mixed (Willow and Pine) Pellets	Retford	No Data Given
L	Pine Chips	Retford	No Data Given
M	SRC Willow Chips	Retford	No Data Given
N	SRC Willow Chips	Retford	No Data Given
O	Pine Pellets	Retford	No Data Given

Table 1 : - Sample Submitted by Project Partners for Testing

The samples obtained are shown in Table 1. The dielectric property measurements for Deliverable 1.1 focussed on samples C, D and J as these were identified as being of primary interest to the future pyrolysis work and scale-up of a microwave assisted fast-pyrolysis system, other results will follow in due course.

5 RESULTS

5.1 MASS LOSS WITH TEMPERATURE

The change in mass of samples C and J with temperature is shown in Figures 4 and 5, with tests carried out in an inert atmosphere. These measurements indicate the water content and pyrolysis behaviour of the different samples, and provide a useful reference to which the dielectric property data can be compared.

The free water content can be deduced from the mass change at 100°C. Figure 4 shows a mass loss of 20%, indicating that Sample C contains 20% free water. Figure 5 indicates that sample J contains 50% water, considerably more than Sample C. The mass loss from 100 – 400°C corresponds to the release of bound water, free oils and other volatiles within the cell structure of the wood. Pyrolysis starts to occur at temperatures above 400°C, where liquid and gaseous products are formed from the decomposition of the cellular material within the wood. Above 800°C only a small fraction of the original sample mass remains as a solid.

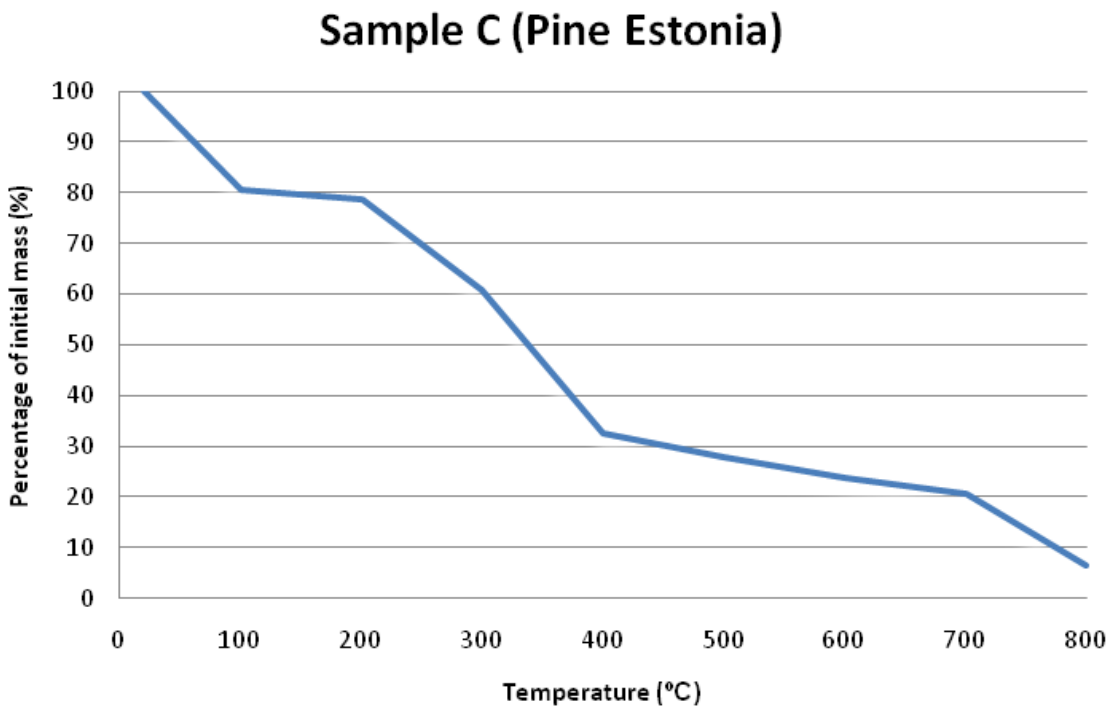


Figure 4 : - Sample C (Pine Estonia) in Nitrogen Furnace.

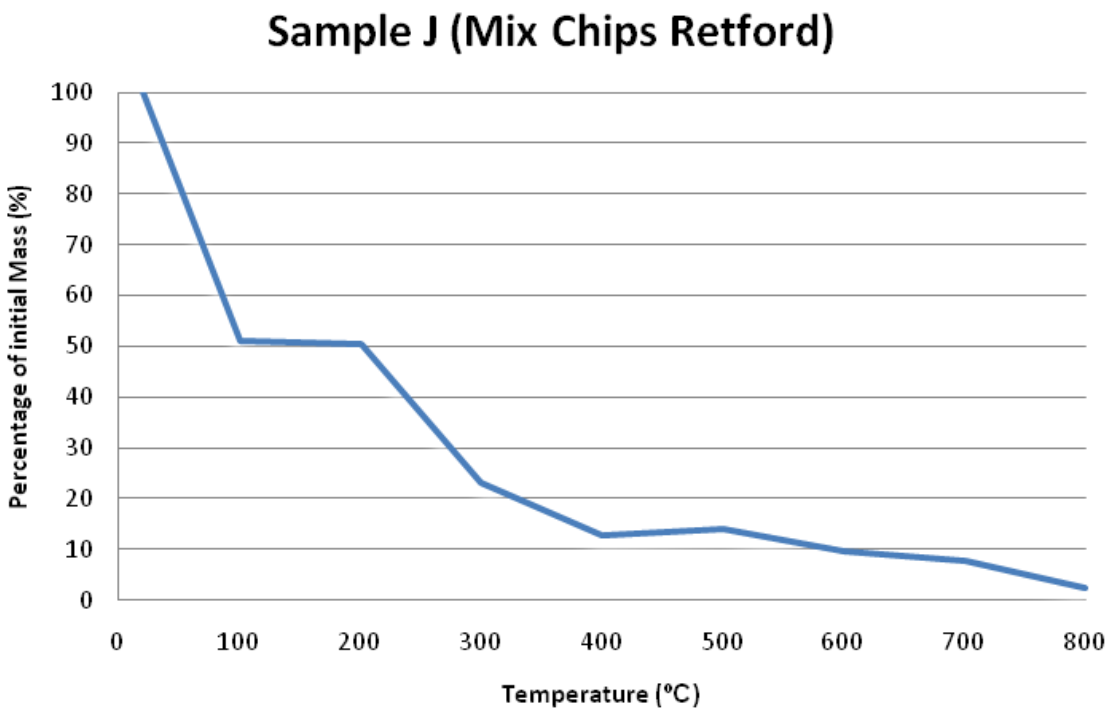


Figure 5 : - Sample J (Mix Chips Retford) in Nitrogen.

5.2 DIELECTRIC PROPERTY MEASURMENTS

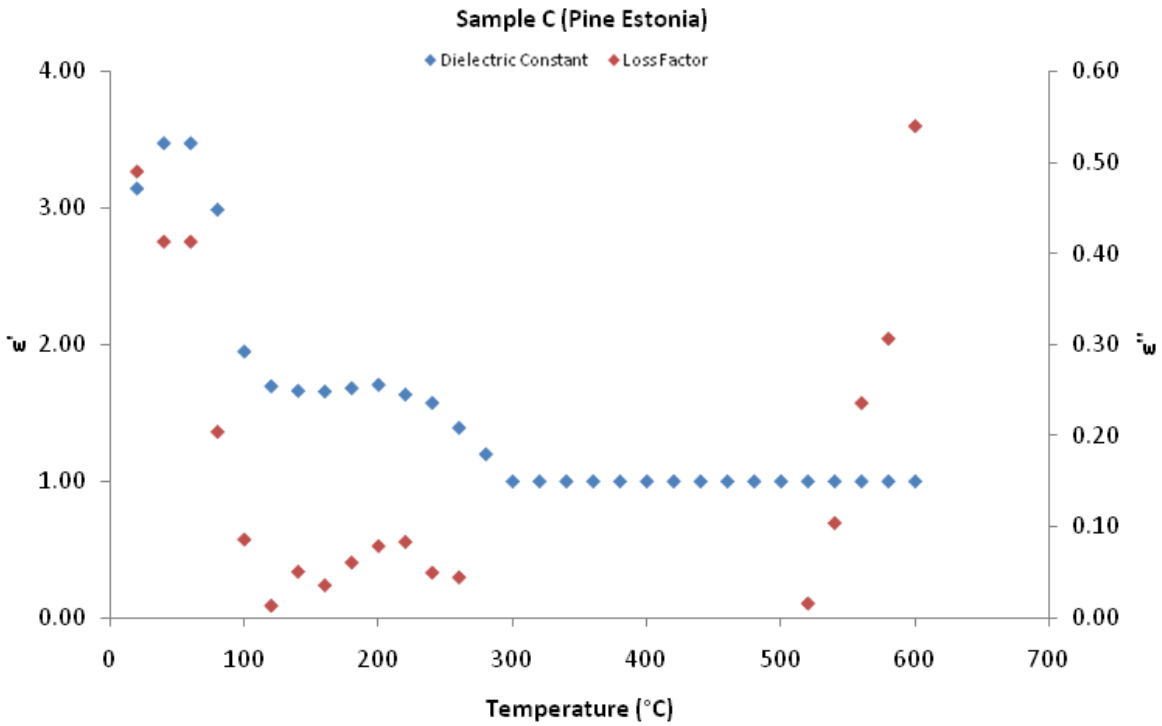
5.2.1 Cavity perturbation results Method 1

The cavity perturbation method requires that the sample volume does not change during the experiment as shown by the equations on page 6. As previously explained, the wood samples changed their volume as a result of combustion. Therefore, the data shown in figures 6 and 7 should be considered accurate only up to about 250 degrees and after this should be considered to show comparative trends rather than absolute values. Experiments to address this issue are presented in the next section of the report.

The dielectric constant (ε′) and dielectric loss factor (ε″) for Sample C are shown at two ISM frequencies. Figure 6 shows the dielectric properties at 912 MHz, which corresponds to the frequency range of 890-920MHz allocated for microwave heating. Figure 7 shows the dielectric properties at 2.47 GHz, which corresponds closely to the allocated frequency of 2.45 GHz that is utilised by most laboratory scale microwave equipment. In both cases the effect of temperature on the dielectric properties is similar; however the different

frequencies yield different values for ε′ and ε″. Several temperature regions can be defined in Figures 6 and 7:

- At room temperature and 2.47GHz (Figure 7) Sample C exhibits a dielectric constant of around 3, and a loss factor of 0.6. These values indicate that the forestry waste sample will absorb microwave energy at this temperature.
- As the temperature is increased to 100°C the dielectric constant increases initially, before decreasing to around 2. On the other hand the loss factor decreases to 0.1. The behaviour of both ε′ and ε″from 25-100°C is characteristic of water liberation and evaporation within the wood sample. The dielectric constant of pure water increases with temperature, and the loss factor decreases. The trends shown in Figure 6 and Figure 7 reflect this, and are also influenced by the vaporisation of free water during heating. At 100°C little free water remains and the loss factor is relatively low.
- From 100-200°C the dielectric properties appear to be relatively consistent, before decreasing from 200-300°C. This further reduction is likely to correspond to the removal of capillary or bound water within the structure of the wood.
- From 300-500°C the dielectric constant is low, and the loss factor is too low to be measured with confidence and is not presented.
- At higher temperatures, pyrolysis of the sample occurs, producing gases and residual char. The electronic structure of char means that it is a good microwave absorber, with a relatively large value of ε″.



- *Figure 6:- Dielectric Properties sample C in air at 912 MHz*

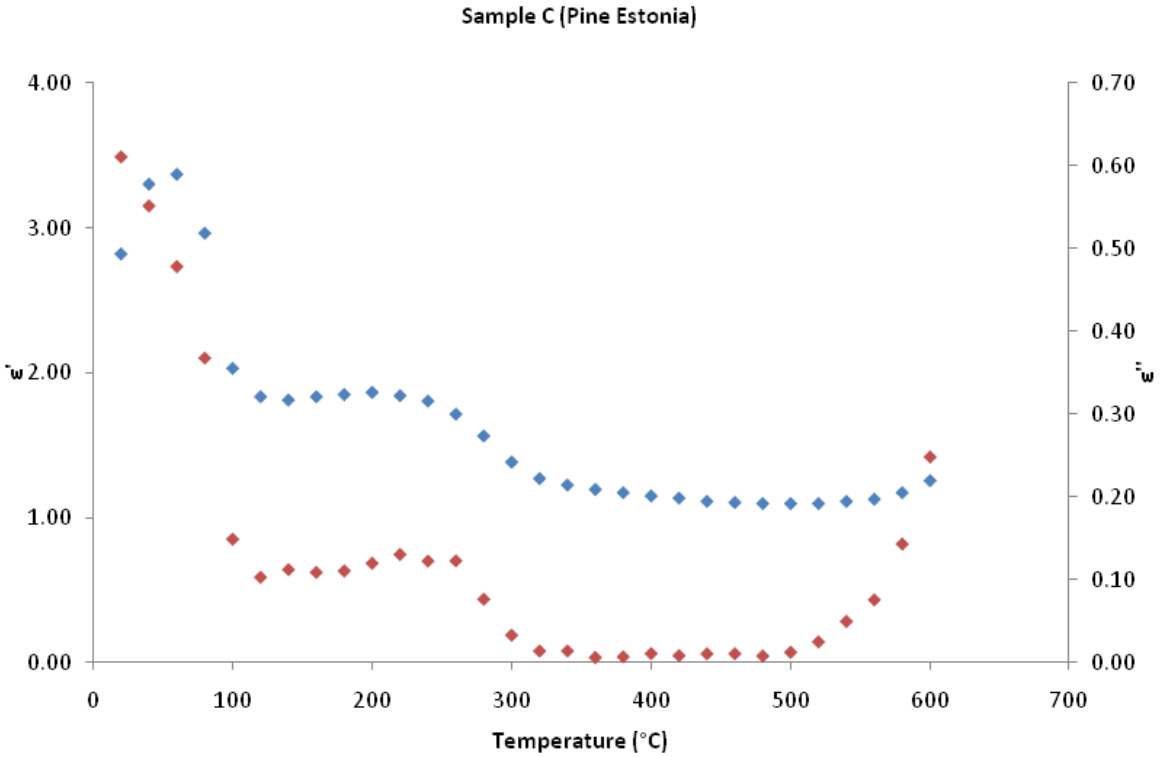


Figure 7:- Dielectric Properties of sample C in air at 2.47 GHz

The dielectric properties of Sample D follow similar trends to Sample C, and the same temperature regions exist for both samples. Data for Sample D are shown in Figure 8 and Figure 9.

Both datasets (Figures 5-9) give an insight into the effects of temperature and the likely bulk heating response that will occur due to microwave treatment. However, the exact values of ε′ and ε″ are not correct due to a change in volume as the sample burns in the cavity perturbation apparatus. Exact values of ε′ and ε″ are critical to the successful design of a pilot scale microwave cavity that can be used for fast pyrolysis reactions, so a technique is required that can measure ε′ and ε″ without being affected by the volume change. This technique is described in detail in Section 2.2.

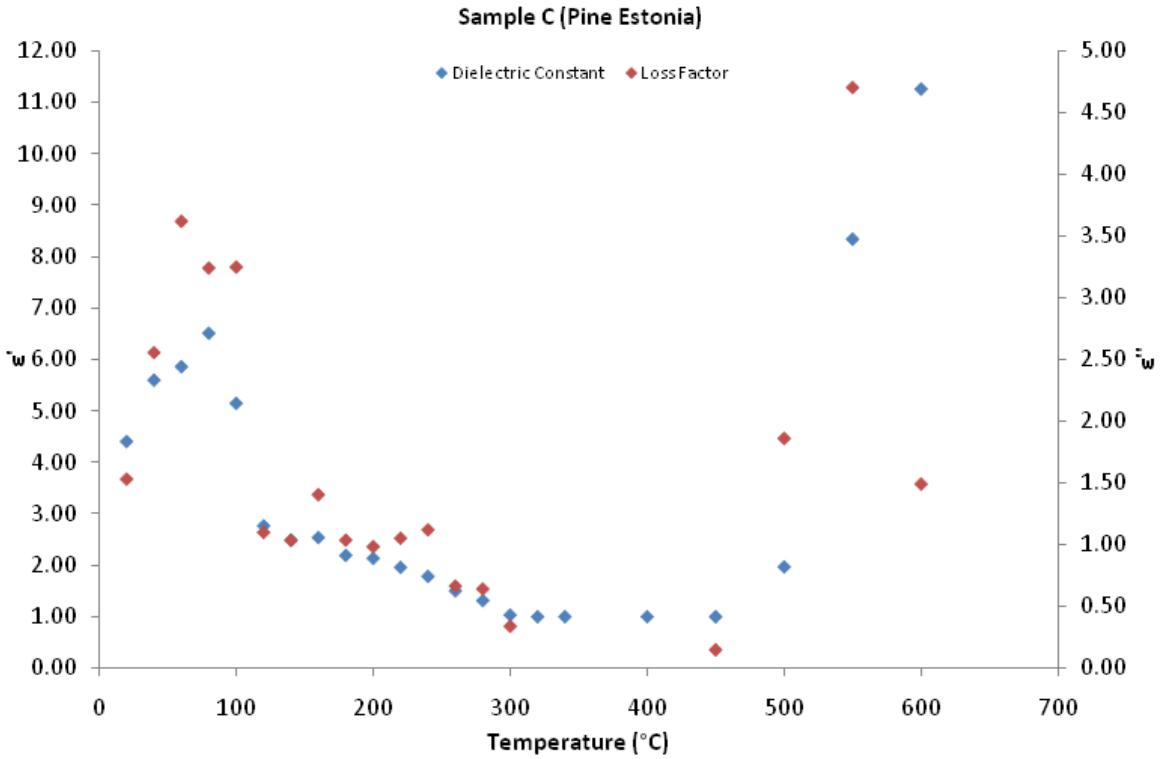


Figure 8:- Dielectric Properties sample D in air at 912 GHz

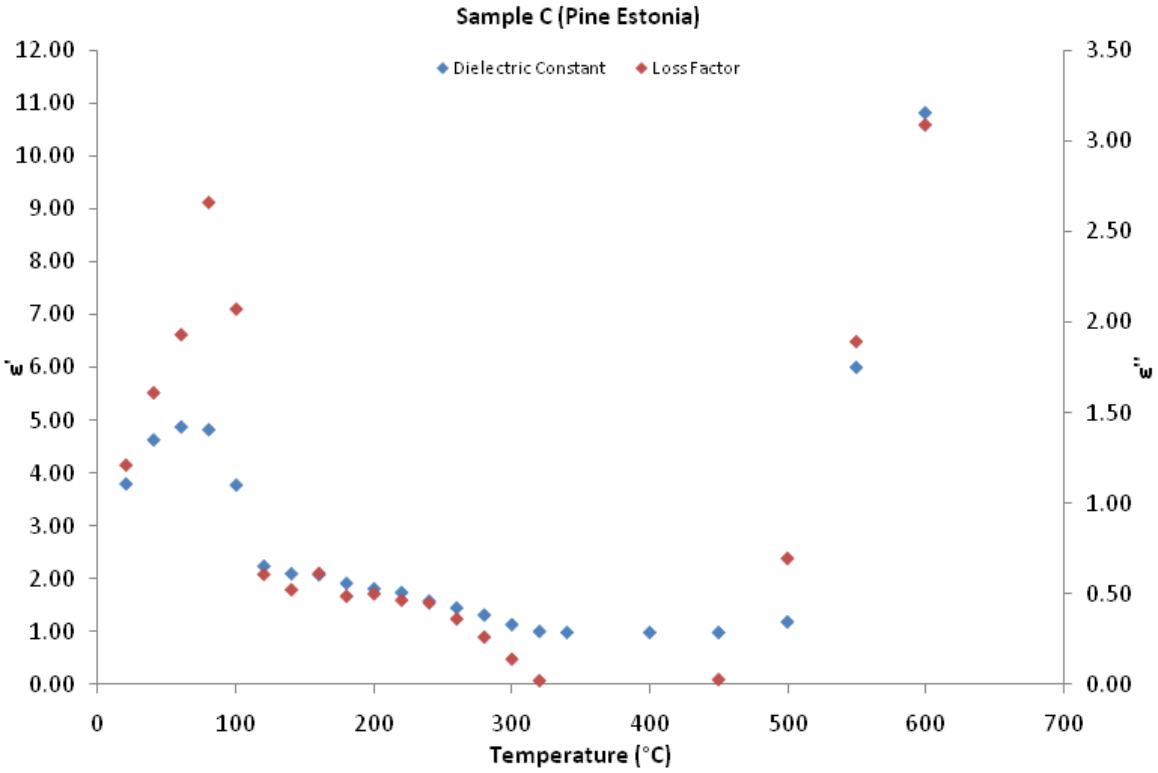


Figure 9:- Dielectric Properties of sample D in air at 2.47 GHz

5.2.2 Samples prepared in furnace flushed with Nitrogen (Procedure 2.2)

Figures 10-13 show the dielectric property data for samples J and C plotted against the apparent temperature using the procedure outlined in Section 2.2. In all cases the dielectric constant and loss factor remain very low at temperatures up to 600°C, much lower than the values in Figures 5-9, and in some cases, the loss factor is too low to be measured accurately. This is likely to be because the revised technique promotes greater water removal than the technique outlined in Section 2.1. The original technique contains the sample at the bottom of a long quartz tube, whereas the second technique utilises a flow of nitrogen over a larger mass of sample. The vaporisation of water will be promoted if a flow of inert gas introduced and this is the likely explanation for the much lower dielectric constant and loss factor at temperatures up to 600°C.

At apparent temperatures above 600°C the dielectric constant and loss factor increase sharply, and continue to increase at higher temperatures. This behaviour is to be expected since the remaining char is known to be a good microwave absorber due to its electronic structure. The values of dielectric constant and dielectric loss factor at high apparent temperatures in Figures 10-13 can be combined with the measurements at lower temperatures in Figures 5-9 to produce a complete dielectric property profile of each sample at temperatures from 20-800°C.

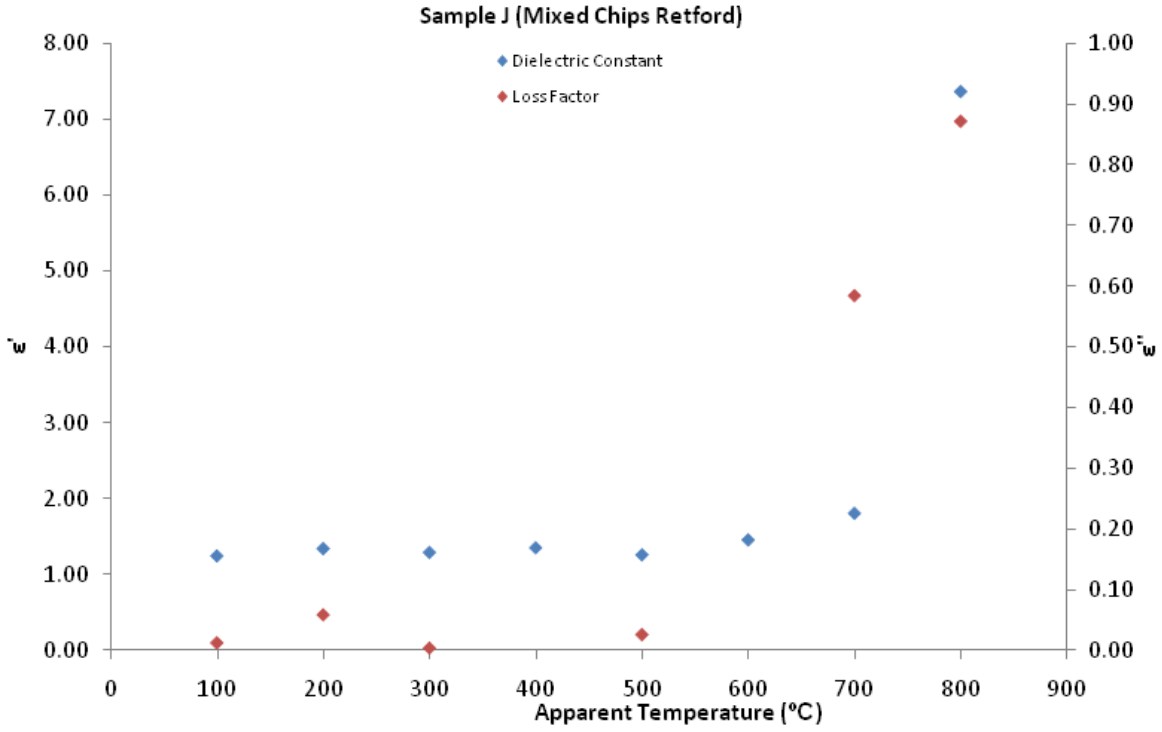


Figure 10:- Dielectric properties of sample J against apparent temperature at 912 MHz

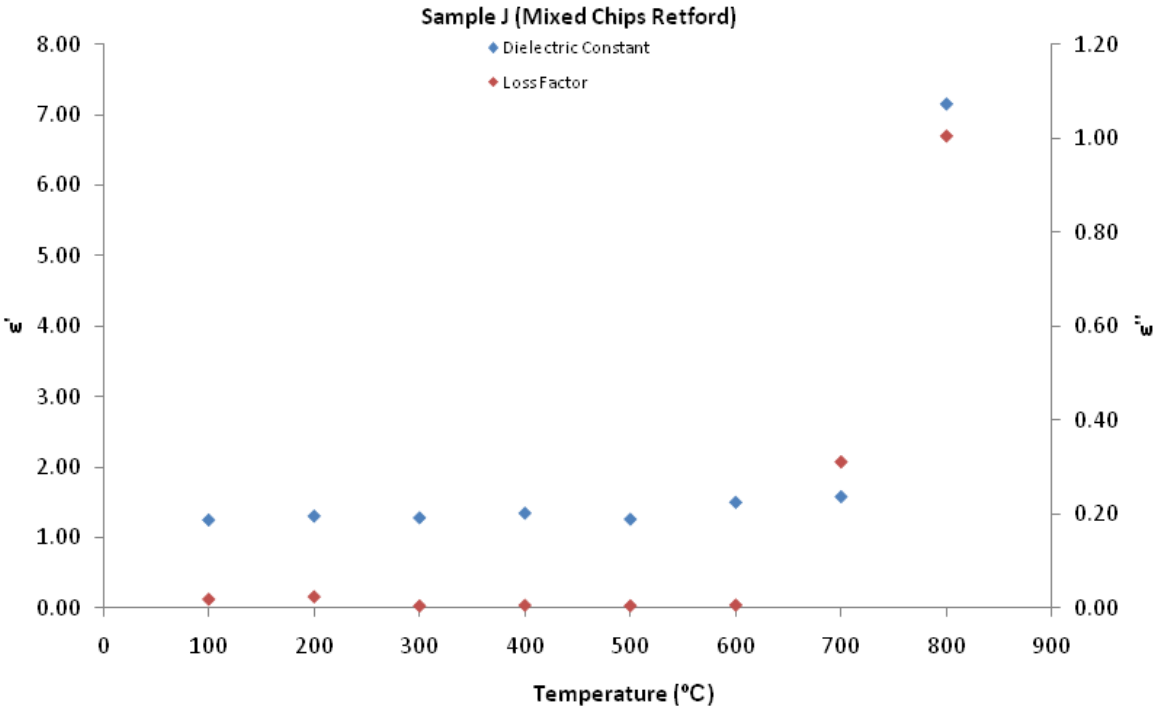


Figure 11:- Dielectric properties of sample J against apparent temperature at 2.47 GHz

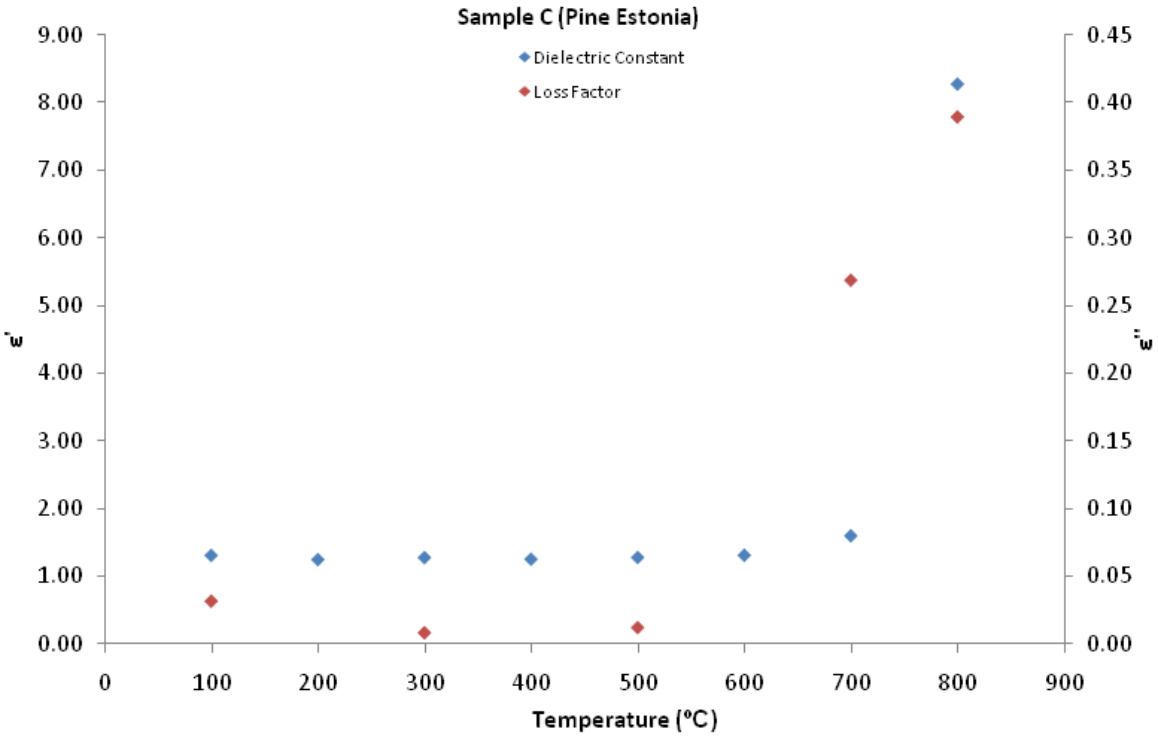


Figure 12:- Dielectric properties of sample C against apparent temperature at 912 GHz

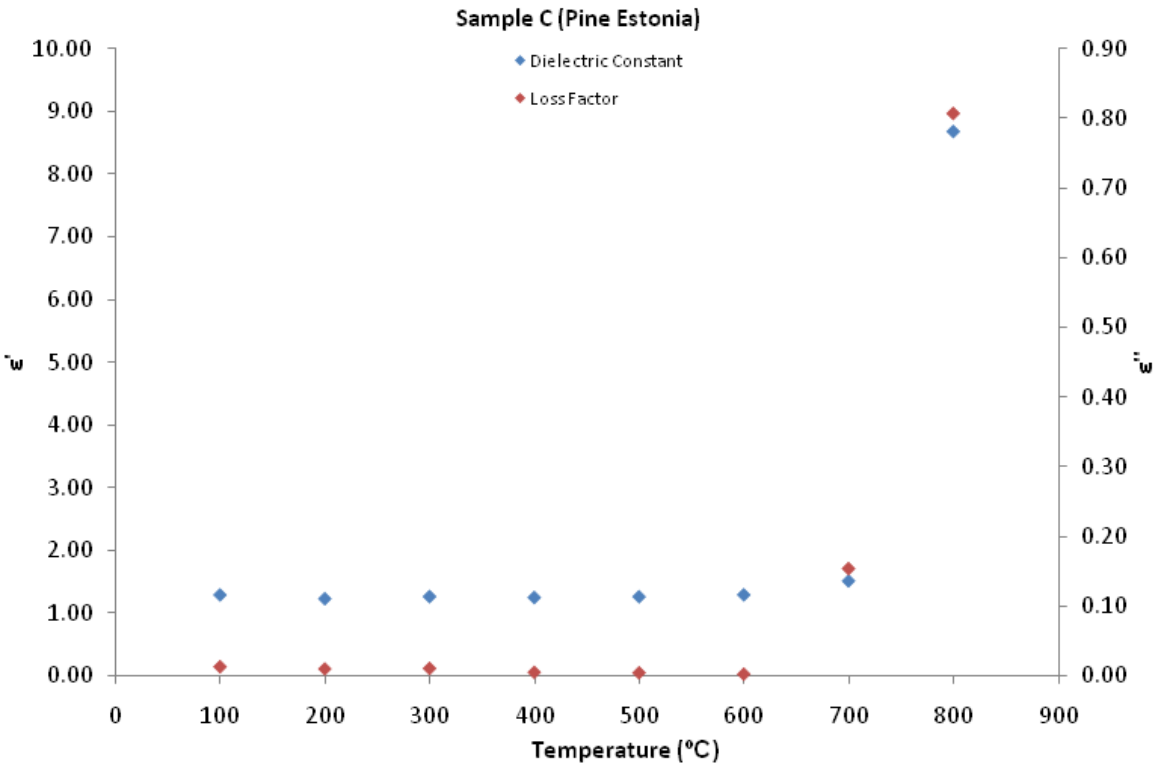


Figure 13:- Dielectric properties of sample C against apparent temperature at 2.47 GHz

6 DISCUSSION

Dielectric property measurements on supplied forest waste samples are reported. It can be seen be that this is a challenging material to measure and difficulties were encountered with the use of the cavity perturbation method. However, despite these difficulties several clear trends have been observed; slight increase in dielectric constant up to 100 degrees, followed by significant reduction until the carbonisation process takes place creating a strong microwave heater. It is also apparent (and further amplified in Figure 14) below that the microwave response of the material is a function of its water content. Figure 14 shows a plot of tan delta versus temperature for wet and dry wood. It can be seen that the main difference is the initial difference in values up to 100 degrees, after this point the values produced are almost identical.

Dielectric property data serves different purposes. As already stated, dielectric constant will influence of the effective wavelength of the electromagnetic signal inside an application and for this purpose a bulk value is required for the whole material in a form which is representative of the way that the material will be presented in the applicator (bulk density, PSD etc.). In addition it is important to consider the dielectric properties of the individual phases present within the material, this is certainly true in a selective heating application as presented here. This is shown in Figure 14, where the contribution of water can be clearly seen.

It is possible to conclude from the data that the water is the major microwave heated phase, therefore it will be expected that performance will be essentially independent of wood type and solely a function of water content and form. However, for completeness all measurements will be carried out.

Further measurements will be made and presented at the next project review meeting which will employ a waveguide type measurement which will allow the bulk properties of the material to be determined for the design of the applicators for testing.

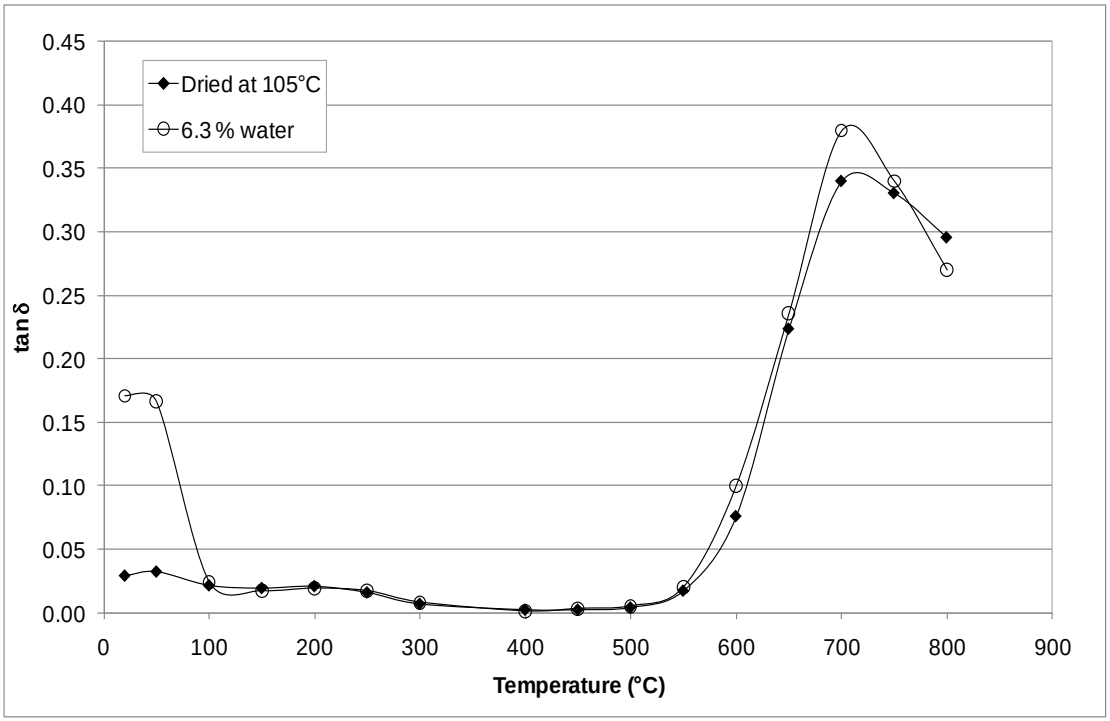


Figure 14:- Loss tangent of wet and dried wood at 2.47 Ghz.

7 CONCLUSIONS

The dielectric properties of two forestry waste samples have been characterised at two industrially-allocated frequencies and at temperatures from 20-800°C. Two measurement techniques have been used, based upon a cavity perturbation method to give accurate dielectric property readings at all temperatures. The dielectric constant and dielectric loss factor both vary significantly with temperature at both frequencies, and the behaviour is explained based on the water content and the degree of graphitisation due to combustion.

The forestry waste samples will absorb significant amounts of microwave energy at temperatures below 300°C and above 500°C. Between 300-500°C the samples are essentially transparent to microwaves, and this presents a significant challenge in the design of a microwave applicator for fast pyrolysis.

The measured values of ε' and ε'' obtained in this study can be used to inform the selection of appropriate scale-up concepts, simulation of the electric field strength and electric field distribution within a particular microwave applicator and the selection of the most appropriate cavity geometry during the design of the pilot scale system. However, further data which presents dielectric properties of the test materials in a more realistic form is required for the design of the process applicators in this project due to significant range of feed particles sizes expected in the material. This will be presented at the next review meeting.

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