Monitoring and control system for tuneable high frequency microwave assisted chemistry

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Abstract. Microwave chemistry is an established technique in the synthesis of organic compounds at a frequency of 2.45GHz. This is considered to be a result of the development of microwave ovens, rather than an objective solution, which maximises efficiency through careful selection of the operating frequency. To obtain a frequency for a dielectric, the complex permittivity should be determined as a function of frequency. If the correct heating frequency is found, superheating can occur when a liquid solvent reaches its boiling point and exceeds it. This paper presents sensor diodes and temperature sensors used in a mono-mode reactor, with computer control of an E-H tuner, frequency and incident power to control temperature and power, experimental results showing heating and reactions using ethanol are reported.

1. Introduction
Microwave chemistry has become increasingly more prominent in laboratories over the last decade, and has become a standard technique in the synthesis of organic compounds alongside more traditional heating methods [1,2]. Since the work of Gedye in 1986 [3] there have been over 1000 publications in the area of microwave synthesis with the majority of experiments carried out at a frequency of 2.45GHz. The development and commercial success of the domestic microwave oven has resulted in the availability of cheap magnetrons operating at this frequency. Therefore, it has become the standard operating frequency for carrying out experiments. For many solvents used in reactions, the frequency of 2.45GHz does not correspond to the best frequency, which gives the highest dielectric loss, and therefore results in inefficient dielectric heating [4]. By using an optimum frequency that provides a higher loss for a solvent, heating can be maximised by coupling microwave energy more efficiently. Superheating is a phenomenon associated with microwave dielectric heating and can be observed in a standard microwave oven during the heating of water [5]. Superheating is described as the increased temperature that can be achieved above the stated boiling point of a liquid. Superheating arises in the absence of nucleation sites on the vessel wall, resulting in the inability for bubbles to form, and therefore the inability to initiate boiling. The temperature rise above the boiling point of a liquid is generally quite a small increase at atmospheric pressure; however, the amount of superheating is related to how much energy can be coupled into the solvent. A small increase in temperature above the boiling point by only 10°C is also seen to dramatically increase reaction rates, and by pharmaceutical standards, the production of specific chemicals could be doubled [6]. A control system can be implemented in order to optimise microwave coupling by controlling cavity tuning, and also temperature control to maintain a required temperature or a superheated state.
2. Microwave Heating Mechanisms

The largest contributing factor to microwave dielectric heating is the dipole moment of charged particles exposed to an alternating electric field \([7]\). The total polarity of a charge \(a_t\) is the sum of other mechanisms that contribute to the overall heating process, as shown in equation 1. It is important to note that each component has varying contributions to the overall polarity of the charge, and therefore the proportion of heating that occurs \([8]\).

\[
a_t = a_e + a_s + a_d + a_i
\]  

(1)

The component \(a_e\) is due to the displacement of electrons relative to the nucleus of the particle, and \(a_s\) is a result of movement of a number of nuclei relative to each other. Both of these heating methods only contribute a very small amount to the overall heating process at frequencies in the microwave region due to displacement of these particles following the electric field component of the wave almost perfectly. Component \(a_d\) also has a small effect on heating. This is a result of polarization between interfaces in a heterogeneous liquid. The \(a_i\) component is a result of the alignment of polar molecules in the dielectric material and their attempt to follow the electric field as the field changes. Materials with a permanent dipole attempt to align with an applied electric field, however an instant reaction to the field is difficult for the molecule to achieve due to the presence of other molecules in its vicinity. Very low frequencies will therefore result in dipoles following the electric field almost perfectly, however not much energy is lost. Conversely, very high frequencies will result in a change of electric field orientation in such a short time frame as to induce no movement of the dipole. Therefore a medium frequency between these two extremes will induce the most heating. This frequency is low enough as to allow the dipole to follow the field, but high enough for a phase difference to exist between the applied field and the orientation of the dipole, and therefore causing collisions that causes a loss of energy in the dipole and a temperature rise in the dielectric material. Homogeneous materials have their dielectric properties completely described by the complex dielectric constant \((\varepsilon^*)\). This number is represented by the sum of both the real and imaginary parts, as shown in equations 2-3.

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]  

(2)

The real part of this complex term shows the ability of a dielectric material to be polarised by an external electric field. At DC and very low frequencies (<100MHz). This represents the whole of the complex dielectric constant, and there is no imaginary term present. This is due to the ability of the dipole to perfectly follow the alternating field. As there is an increase in frequency acting upon the dipole, it fails to follow the field exactly, and therefore a lag is created. This phase difference is represented in the imaginary part of the complex term \((j\varepsilon'')\), which the loss of the material and thus the amount of heating. \(\tan\delta\) is a term that can also be used to quantify the dielectric loss of a material. This is defined as the ratio between \(\varepsilon'\) and \(\varepsilon''\), as shown in equation 3.

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(3)

The Debye model \([9]\) can be used to find the most effective frequency to provide the most heating to a dielectric where \(\varepsilon'\) and \(\varepsilon''\) can be expressed as shown in equations 4 and 5.

\[
\varepsilon' = \varepsilon_m + \frac{(\varepsilon_s - \varepsilon_m)}{(1 + \omega^2 \tau^2)}
\]  

(4)

\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_m)\omega\tau}{(1 + \omega^2 \tau^2)}
\]  

(5)
Here, $\varepsilon_s$ is the dielectric constant in a static field, and $\varepsilon_\infty$ the dielectric constant at high frequencies considered to be infinite in this case. $\tau$ is the relaxation time. This is the time period taken for a dipole to orient itself with an applied electric field. Using the Debye equation it is possible to calculate the value of $\tau$, as shown in equation 6.

$$\tau = \frac{4\pi \eta r^2}{kT} \quad (6)$$

Where $\eta$ is the viscosity, $r$ is the molecular radius, $k$ is Boltzman’s constant, and $T$ is temperature in Kelvin. $\eta$, $r$, and $T$ are all likely to change under heating as the temperature rises. Figure 1 shows the change in $\varepsilon'$ and $\varepsilon''$ for water as a function of frequency from a static field to greater than 100GHz based on equations 4 and 5. The point at which $\varepsilon''$ is at its greatest, and therefore most lossy is seen be in the order of 20GHz.

![Figure 1. Graph showing real and imaginary part of the complex permittivity as a function of frequency](image)

Microwave ovens use a frequency of 2.45GHz as a method to overcome the limited skin depth of higher frequencies such as 20GHz (An optimum frequency to provide high dielectric loss in the water content of food) when penetrating into a large volume of food. Ethanol is another very common solvent in organic synthesis. Therefore the frequency at which ethanol is most lossy should be considered, and is reported to be between 1GHz and 2GHz at 25°C. The complex permittivity does however change as a function of temperature making the most efficient operating frequency rise to 8GHz at 78°C. Because of this change, it is important to continually tune the cavity in order to keep it operating at its most efficient.

3. Experimental Setup

A Marconi Microwave Test Set 6200A was used to provide a frequency source in the range of 8-20GHz. A coaxial cable was connected to this and to a Varian 40dB travelling wave tube amplifier with a maximum output of 15W. Waveguide is then used to direct the microwaves into a reaction cavity via a circulator, which is used to direct any reflected power into a match load. Two -30dB cross couplers are used before and after the circulator to monitor forward and reflected power. Each of the cross couplers are connected to sensor diodes which are input via coaxial cable into the Microwave Test Set, which is used to display both the forward and reverse power. A quartz test tube containing the chemicals to be heated is placed into the reaction cavity. A diagram and photograph of the system setup is shown in figures 2 and 3 respectively.

A GPIB interface is used to connect the test set to the PC were online monitoring and control software has been written and used to display the forward and reflected power of the system, the operational
frequency, and the temperature of the chemicals. An optical fibre probe is located within the reaction vessel to take temperature readings at each second interval. The probe has a resolution of 0.1°C, and a maximum operating temperature of 250°C. The temperature is read by the PC via RS232, and this also is displayed by the software. The system is fully operational under atmospheric conditions. The software was developed using Delphi, with a GUI interface for ease of use. The software is able to change frequency and output power of the system in real-time while an experiment is being carried out. A proportional integral derivative (PID) controller is implemented to allow a pre-determined temperature to be held for any duration of time, allowing controlled reactions to take place. Careful selection of the P, I, and D terms is important as to avoid overshoot of the target temperature and avoid bumping due to microwave superheating effects. A screenshot of the software created is shown in figure 4.

The cavity is tuned using an EH tuner, which is automatically adjusted to give minimum reflected power and ensure that the maximum amount of power is coupled into the liquid. The EH tuner is computer controlled via RS232, allowing continual tuning of the cavity during the heating process.

4. Automatic Cavity Tuning
The reaction cavity is automatically tuned using an EH tuner with stepper motors attached to the “E arm” and the “H arm” of the tuner. Using a PIC microcontroller, the stepper motors are controlled via pulses generated by the PIC, which is controlled by PC using RS232. An algorithm is implemented based on the reflected power obtained using GPIB from the Marconi Test Set, which changes the
position of the E, and H plungers to attempt to obtain a lower reverse power reading, and therefore improve cavity tuning. The EH tuner is shown in figure 5. The stepper motors are attached to studding, which when rotated, allows a plunger inside the waveguide to move. This acts as a variable short circuit in each arm of the tuner, changing the dimensions of the cavity, and therefore tuning it. The algorithm used to tune the cavity is a reflection of how a user would manually tune such a system. Assuming there is no local minima in the system that is not the optimum position for each plunger, it can be regarded that any minima found in reverse power for a particular position of both plungers is regarded to be as good or better than any other minimum that could be found. Based on this, each plunger is moved to a central neutral position, and moved in turn in each direction, to find a lower reverse power reading. As the reverse power drops to a lower value, the plunger is continually moved in this direction until it begins to rise again, implying that a minimum in reverse power has been found on this plunger, for the current position of the other plunger. The other plunger can then be adjusted to attempt an improvement on the current reverse power reading. This process is continually repeated until the system is switched off. This is due to the dynamic nature of the dielectric constant as a function of temperature (see Microwave Heating Mechanisms), causing continual tuning of the cavity in real time to be required.

5. Results
Experiments were carried out initially using only ethanol heated at various frequencies to determine the optimum frequency at which the highest rate of ethanol heating occurred. Figure 6 shows the heating of 6ml of ethanol using 6W of microwave power. The frequency was varied automatically between 12 GHz and 16GHz and the temperature plotted against time. The experiment was run for 600s. Figure 6 shows that there is an increase in the rate of temperature rise at a frequency of 12.5GHz; however, the rate then decreases as the frequency increases.

![Figure 6](image_url)

**Figure 6.** Graph showing the heating rates of ethanol at various frequencies

Because certain frequencies afford a higher rate of heating of the ethanol solvent, it is clear that this frequency should be chosen to provide the optimum heating conditions during reactions. A number of organic reactions were also carried out in order to see if the accelerated heating rates obtained in the previous experiments would result in quicker conversion time in a reaction. An experiment consisting of the reaction of 2-bromonitrobenzene with 2.5 equivalents of piperidene, see figure 7. It was concluded that the quicker reaction nears completion quicker at 12GHz and shows the same trend as that for the heating experiments for ethanol.
6. Conclusion

For a particular dielectric there is a frequency, which is best suited to provide maximum heating due to maximum power absorption and minimum reflection. It has been shown that for water this is around 20GHz at 25°C, and this varies as a function of temperature, so constant tuning of a heating system is important. Ethanol is considered to have a much lower optimum frequency, and as a result the conversion rate increases by approximately 25 minutes for 80% conversion with a frequency 12GHz compared to 13GHz for the reaction of 2-bromonitrobenzene and piperidene. Frequency selection based on knowledge of a dielectric to be heated is clearly important to give maximum heating and most efficiency. Control of cavity tuning is required as the as the dielectric properties change during the heating process.

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