CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756296

Dielectric Properties for Extraction of Orthosiphon Stamineus (Java Tea) Leaves

Mohd Johari Kamaruddin*[,a,b], Mohamad Sukri Bin Mohamad Yusof[a,b], Norzita Ngadi[b], Zaki Yamani Zakaria[b], Agus Arsad[b], Kamarizan Kidam[a,b]

[a]Centre of Hydrogen Economy (CHE), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
[b]Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia.
mjohari@cheme.utm.my

A dielectric properties study was performed at ISM frequencies and a range of temperatures (25 – 45 °C) on the extraction of Orthosiphon Stamineus (Java Tea) leaves system in order to relate their dielectric properties to microwave heating mechanisms and design of microwave applicator quantitatively. The main results concluded that the heating mechanism of the extraction mixture in an electromagnetic field was controlled by the dielectric properties of solvent (water), where the solvent was the major component (> 90 % v/v) as well as the component with highest dissipation factor (tan δ). The penetration depths of extraction mixture at ambient temperature (25 °C) are 3.8 cm, 3.2 cm and 1.4 cm at ISM frequencies of 0.433 GHz, 0.915 GHz and 2.45 GHz. These tiny penetration depths limit the potential to achieve the successful scale up of a microwave-assisted extraction of Orthosiphon Stamineus leaves in batch mode at ISM frequencies. This will lead to inhomogeneous bulk temperature distribution within the extraction mixture and irreproducible extraction yield without sufficient stirring and stirrer compatible with microwave system. A fast heating rate based on a high value of tan δ of the extraction mixture revealed that the microwave heating technique has a great potential in reducing the processing time especially at heating up stage compared to conventional thermal heating technique in extraction of Orthosiphon Stamineus leaves. The dielectric properties of extraction mixture are worth to be considered to certify the consistency and reproducibility of the microwave-assisted extraction at large scale production.

1. Introduction

Orthosiphon stamineus (OS), or commonly known as Java tea, is a traditional herb that is widely grown in tropical areas. In Southeast Asia, OS is used for the treatment of eruptive fever, epilepsy, gallstone, hepatitis, rheumatism, hypertension, syphilis and kidney stone. In Malaysia, the tea from the leaves is taken as supplement drink to improve health and for treatment of kidney stone, bladder inflammation, gout and diabetes (Akowuah et al., 2005). OS has been used to treat urinary lithiasis, edema, influenza and jaundice (Akowuah and Zhari, 2010). OS contains several chemically active components, such as terpenoids (diterpenes and triterpenes), polyphenols (lipophilic flavonoids and phenolic acids), and sterols. The three main polymethoxylated flavones in OS leaves are sinensetin (SEN), eupatorin (EUP), 3'-hydroxy-5,6,7,4'-tetramethoxyflavone (TMF) and the major phenolic acid is rosmarinic acid (RA) (Akowuah et al., 2005). In industry, OS leaves are typically extracted by conventional, indirect heating with an external heat source such as steam or heating oil. This conductive/convective heating is a comparatively (with non-conventional heating) slow and inefficient process because it depends on the thermal diffusivity and heat transfer properties of the heating coil, reactor surface and herbs mixtures to transfer energy into the system (Meredith, 1998). To overcome these problems, non-conventional extraction such as super critical fluid extraction, ultrasonic assisted extraction and microwave-assisted extraction processes are introduced. In general, microwaves could offer selective heating, rapid and high efficiency energy transfer, short processing time and compactness of equipment (Ahmad Zaini and Kamaruddin, 2013).

Please cite this article as: Kamaruddin M.J., Yusof M.S.B.M., Ngadi N., Zakaria Z.Y., Arsad A., Kidam K., 2017, Dielectric properties for extraction of orthosiphon stamineus (java tea) leaves, Chemical Engineering Transactions, 56, 1771-1776 DOI:10.3303/CET1756296

From the laboratory assessment studies of microwave-assisted extraction on OS leaves that had been carried out by the authors, the microwave heating produced reliable results and comparable yields to the conventional thermal heating. Microwave-assisted extraction has been reported to have a great potential as an alternative to the conventional extraction method in the aspects of time and energy consumptions. However, the lack of dielectric property data related to this herb, solvents and mixtures involved in the processing makes microwave-assisted-processing system difficult to design, reproduce, control and operate at an industrial scale. The aim of this study was to quantify the dielectric properties of OS leaves, solvent and the extraction mixture within the microwave frequency range and temperature by using coaxial probe techniques.

1.1 Dielectric Properties of Material

All materials include OS leaves, solvent and the extraction mixture has an exclusive set of electrical characteristics that are reliant on its atomic structure. Dielectric properties are not constant and change with frequency, temperature, density, orientation, composition, pressure, and molecular structure of the material (Agilent, 2006). Knowledge of dielectric data is essential in the design of microwave heating systems because it enables estimates to be made of the power density and associated electric-field stress and also the penetration depth (D_p) microwave energy into the material.
The fundamental electrical property through which the interactions are described is the complex relative permittivity of the material, ε*. It is mathematically expressed as Eq(1) (Stuerga, 2006):

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

Where, ε' = dielectric constant and ε" = dielectric loss or loss factor.
The ε' is equal to the relative permittivity (ε_r) or the absolute permittivity (ε) compared to the permittivity of free space (ε_o). The ε' is a measure of how much energy from an external electric field is stored within a material through polarisation mechanisms. The imaginary part of permittivity (ε") is called the dielectric loss and is a measure of how dissipative or lossy a material is to an external electric field (Galema, 1997). The word "loss" is used to indicate the amount of input microwave energy that is lost to the sample by being dissipated as heat. The ε" is always greater than zero and is usually much smaller than ε' (Agilent, 2006).
Dissipation factor or tan δ is another important term in and details how efficiently microwave energy is converted into thermal energy. It is defined mathematically as the ratio of ε" to ε' (Chan and Reader, 2000) as shown in Eq(2):

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\text{Energy lost per cycle}}{\text{Energy stored per cycle}} \tag{2}$$

The dielectric properties of materials are determined by the static permittivity (ε_s), optical permittivity or permittivity at high frequency (ε_∞) and relaxation time (τ) of the materials. The behaviour of *ε´* and *ε"* for most pure and homogeneous materials (especially polar liquids) obey the Debye equation as shown in Eq(3) and Eq(4) (Gabriel et al., 1998):

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{3}$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{4}$$

Where, ε_s = static permittivity or dielectric constant at low frequencies, ε_∞ =optical permittivity or dielectric constant at very high frequencies, ω = the angular frequency (ω=2πf) and τ = the dielectric relaxation time.
The quantity of the oscillator strength (ε_s-ε_∞) is important in the analysis of dielectric property data in terms of molecular structure. For example, the different between ε_s and ε_∞ gives the idea about polar or non-polar of a material. In addition, these values give the measure of the strength of the relaxation process as well as ability of the materials to store, absorb and dissipate microwave energy into heat.
In order for effective microwave heating to occur, the energy should penetrate as deeply as possible into the dielectric material. If this does not occur, then heating is limited to the surface of the material (as in conventional heating). The depth at which the available power in the material has fallen to 1/e (0.368) of its surface value is known as the penetration depth. The penetration depth, D_p is a function of both the ε' and ε", and can be expressed by the following equation (Meredith, 1998):

$$D_p = \frac{\lambda_o}{2\pi\sqrt{(2\varepsilon')}} \frac{1}{\sqrt{\left[\left\{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right\}^{0.5} - 1\right]}} \tag{5}$$

where, λ_o = wavelength (m) and ε' = dielectric constant.
For dielectric materials with ε" ≤ ε', Eq(5) can be simplified to Eq(6), with the estimation error up to 10 %:

$$D_p = \lambda_o\sqrt{\varepsilon'}/2\pi\varepsilon'' \tag{6}$$

The D_p is a very important parameter for a sample to be heated under microwave energy because it gives an immediate first-order indication of the heat distribution within it (Meredith, 1998). Based on Eq(6), it is interesting to note that, at constant ε' the D_p decreases with the ε". Meanwhile, the D_p increases with the ε' when the ε" value is keep constant.

1.2 Relationships between Microwave Heating and Dielectric Properties of the Material

An understanding of the relationships between power dissipation and dielectric properties will reveal how the desired results are achieved in microwave heating. There is a direct relationship between the frequency and the wavelength Eq(7) (Collins 2002).

$$C = \lambda\ x\ f \tag{7}$$

Where C = speed of light in a vacuum (3.0 x 10^8 m/s), λ = wavelength (m) and f = frequency (Hz).
Additionally, there is a relationship between power density, frequency and loss factor Eq(8) , as well as penetration depth in Eq(6) (Metaxas and Meredith, 1983).

$$P_d = 2\pi f\varepsilon_o\varepsilon'' E_i^2 \tag{8}$$

Where P_d = power dissipation density (Watts/m^3), f = frequency (Hz), ε_o = permittivity of free space (8.85 x 10^{-12} F/m), E_i = the electric field strength inside the material, V/d (Volts/m) and ε'' = the dielectric loss or loss factor of the material.
Based on Eq(6) to Eq(8), the relationships can be summarised as follows (Gallawa, 2001):

a. By assuming ε" is always constant, the higher the frequency, the faster the material or load will heat, but the depth to which the microwave energy penetrates will be proportionally less.
b. By assuming ε" is always constant, the lower the frequency, the deeper the microwave energy will penetrate, but the sample or load will heat proportionally more slowly.
c. The higher ε" of material or load, the more efficient the material converts microwave energy into thermal energy, and thus, the faster the temperature will increase, though at the same time the penetration depth of the microwave energy will proportionally decrease.

In practice the value of ε" of the material or load is not constant and varies not only with frequency, but also with temperature, moisture content, physical state (solid or liquid) and composition. All these may change during processing, so it is important to consider ε" and ε' as variables during the process and knowledge about the dielectric properties of the material to be heated under relevant process conditions is crucial.

2. Materials and methods

2.1 Sample Preparation

OS leaves with about 500 (±50) microns in size and distilled water (solvent) were obtained from Centre of Lipids Engineering and Applied Research (CLEAR), Universiti Teknologi Malaysia. The standard extraction procedure was as follow:
About 10 g of OS leaves was introduced into a 250 mL conical flask with 200 mL of distilled water for 1 : 20 sample to solvent ratio. This ratio was selected regards to the normal practice extraction mixture systems (1 : 20 v/v of sample to solvent ratio) which are the optimised ratio for the most herbs extraction studies reported. This mixture was mechanically stirred until the mixture was homogeneous, then the mixture was heated to measure the temperature (i.e. 25 - 45 °C) by using an oil bath.

2.2 Dielectric Properties Measurement

The dielectric properties of the OS leaves and its extraction mixtures for this study were measured using the coaxial probe technique. This measurement system consists of computer, network analyser (Agilent 8753 ES VNA, 0.2 GHz–20 GHz), a cable and an open-end coaxial probe. The probe was capable of operating up to 60 °C. The coaxial probe method requires calibration prior to collection of the data to account for any systematic errors and a detailed explanation of calibration procedures can be found in Kamaruddin et al. (2011). The dielectric properties of OS leaves and its extraction mixtures were measured by immersing the probe into the samples. During the measurements, the S_{11} signal was collected by the VNA and the data stored on a dedicated PC before the data automatically transformed into ε' and ε" values using software provided by Agilent.

3. Results and Discussion

3.1 Dielectric Properties of OS leaves, Water and Extraction Mixture

In order to get the information on how the dielectric properties of the OS leaves extraction mixtures behave in relation to their solid and solvent, the ε' and ε" of extraction mixtures were plotted together with the properties of OS leaves and water (solvent). Figures 1 (a) and (b) show the dielectric properties of OS leaves, water and the extraction mixture (OS leaves with water). This analysis was conducted at room temperature (25 °C). In general, the dielectric properties of OS leaves were very low compared to the dielectric properties of water. This indicates that, OS leaves (without any solvent added) are behaved as low loss material with low interaction with microwave energy in the applied electromagnetic field.

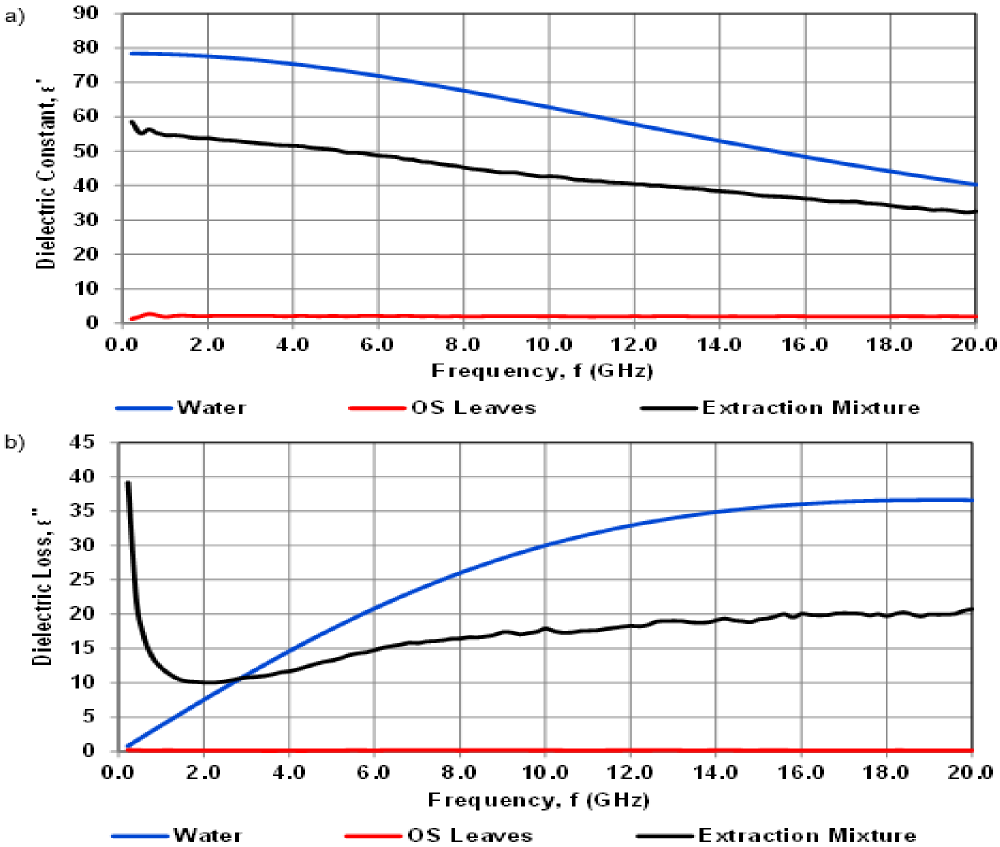

Figure 1: Graph of (a) dielectric constant (b) dielectric loss against frequency of OS leaves, water and extraction mixtures

The ε' and ε" values of extraction mixture are in between of water and OS leaves values at the frequencies measured except the ε" of mixture at frequencies lower than 3.0 GHz. This indicates that when OS leaves was mixed with water (solvent), there was an enhancement in ε' and ε" of the OS leaves. This improvement in reading of dielectric properties of extraction mixture was due to the amount of water as the portion of mixture used was 20 times higher than OS leaves (1:20 v/v of OS leaves to solvent ratio). Water as polar solvent with higher dielectric properties in the mixture clearly influenced ε' and ε" values of the mixtures.

The higher values of ε" of extraction mixture at frequencies measured below 3.0 GHz may be due to shifting of relaxation frequencies of water (19.2 GHz) to a lower frequency (less than 0.2 GHz) when the OS leaves dispersed within the water. When the relaxation frequency shifted to frequency lower than 0.2 GHz, the right curve of relaxation (ε" versus f) which is gives high values of ε" at 0.2-3.0 GHz and reducing with further increasing of frequencies as depicted in Figure 1(b).

The key finding of this survey is that the component that will dominate the dielectric properties of the extraction mixture at extraction temperature is the solvent (water). Its response is the single most significant of all the precursors and the dielectric properties of the total mixture are shown to be significantly influenced by the solvent. The dependency of the dielectric response of the extraction mixtures with solvent as depicted in Figures 1(a) and 1(b), can be interpreted as follow:

a. The dielectric response of the extraction mixtures during the progress of extraction may be dominated by the change of mixture/solvent temperature

b. The heating rate and penetration depth (D_p) of the extraction mixtures under microwave field depends significantly on the dielectric properties of solvent. So further understanding of the solvent dielectric properties behaviour through a dielectric relaxation analysis is necessary.

c. The extraction system can heat readily in a microwave field dominated by dipole polarisation (low frequency) mechanism at ISM frequencies measured.

3.2 Dielectric Properties and Penetration Depth of Extraction Mixture at ISM Frequency and Temperature

The penetration depth (D_p) of OS leaves extraction mixture is a very important parameter in microwave heating since it gives an immediate indication of the heat distribution within the bulk of mixture. In order for effective microwave heating to occur, the energy should penetrate as deeply as possible into the mixture. If this does not occur, then microwave heating is limited to the surface of the mixture. The values of D_p of extraction mixture at ISM frequency, 0.433 GHz, 0.915 GHz and 2.45 GHz from ambient (25 °C) to extraction temperature (45 °C) were determined and shown in Table 1.

Table 1: Dielectric properties and penetration depth of OS leaves mixture at selected ISM Frequencies (0.433, 0.915 and 2.45 GHz)

Frequency (GHz)	Temperature (°C)	ε'	ε''	Tan δ	D_p (cm)
	25	55.21	21.74	0.39	3.8
	30	61.30	25.40	0.41	3.4
0.433	35	50.79	21.83	0.43	3.6
	40	61.25	21.07	0.34	4.1
	45	61.83	20.84	0.34	4.2
	25	54.64	12.10	0.22	3.2
	30	60.12	13.85	0.23	2.9
0.915	35	49.49	11.70	0.24	3.1
	40	60.25	11.60	0.19	3.5
	45	61.15	11.34	0.19	3.6
	25	53.18	10.13	0.19	1.4
	30	58.36	11.01	0.19	1.4
2.45	35	47.90	8.93	0.19	1.5
	40	58.82	9.45	0.16	1.6
	45	59.81	9.16	0.15	1.6

From Table 1, The D_p values of OS leaves mixture at 2.45 GHz were calculated to be approximately 1.4 cm (25 °C) increasing to 1.6 cm at 45 °C. This means that a reactor with a diameter of 2.8 cm which is double the value of D_p (considered microwave energy come from surrounding of the reactor) can be utilised for the OS leaves extraction for efficient microwave heating with the minimum temperature gradient inside the bulk of the mixture. This short D_p suggests that direct scale-up of microwave-assisted extraction in batch mode at frequency 2.45 GHz is limited due to the limitation of the microwave energy to penetrate deeply into the bulk of extraction mixture. Scale-up of the process to larger volumes might benefit from use of a lower frequency such as 0.433GHz where D_p is about 4.2 cm at 45 °C. However, microwave heating at 2.45 GHz could be benefited by the fast heating rate achievable due to higher power density at higher frequency, where the tan δ of the extraction mixture is considered as lossy material.

Based on a high value of tan δ at ISM frequencies measured of the extraction mixture revealed that the microwave heating technique has a great potential in reducing the processing time especially at heating up stage compared to conventional thermal heating technique in extraction of OS leaves. The dynamic change in dielectric property with temperature as shown in Table 1 at ISM frequencies measured suggested that the microwave-assisted extraction system particularly in the continuous mode of processing needs to a dynamic impedance matcher and on-line process control and monitoring system in order to control and monitor the extraction temperature, input power, progress of extraction and yield of extraction.

4. Conclusion

From the measurement of dielectric properties of OS leaves, solvent (water) and mixture of OS leaves with water, it was found that the solvent, water is the dominant component in the extraction mixture system in terms of its ability to heat when exposed to microwave energy at a ISM frequencies (0.433 GHz, 0.915 GHz and 2.45 GHz). The work in this study which centred on the influence of the reactor geometry upon the outcome of a microwave heated extraction has identified that the main challenges of the design of successful microwave-assisted extraction of OS leaves are; the limitation of the microwave power flux penetration depth, D_p and the variation of dielectric properties of the extraction mixtures as the extraction progresses. The extractor/applicator size should be comparable with the D_p of extraction mixtures to obtain sensible yield enhancement as shown in most laboratory scale study.

Acknowledgments

The research was financially supported by the Ministry of Education (MOE), Malaysia and Universiti Teknologi Malaysia (UTM) through University Grants, VOT No. 07J47, 05H99 and 15H84

Reference

Agilent, 2006, Application Note: Basics of Measuring the Dielectric Properties of Materials, Agilent Technologies Inc., United States of America.

Ahmad Zaini M.A., Kamaruddin M.J., 2013, Critical issues in microwave-assisted activated carbon preparation, Journal of Analytical and Applied Pyrolysis 101, 238-241.

Akowuah G.A., Ismail Z., Norhayati I., Sadikun A., 2005, The effects of different extraction solvents of varying polarities on polyphenols of Orthosiphon stamineus and evaluation of the free radical-scavenging activity, Food Chemistry 93, 311-317.

Akowuah G.A., Zhari I., 2010, Effects of extraction temperature on stability of major polyphenols and antioxidant activity of Orthosiphon stamineus leaf, Journal of Herbs, Spices and Medicinal Plants 16, 160-166.

Chan T.V.C.T., Reader H.C., 2000, Understanding Microwave Heating Cavities, Artech House, Boston, USA.

Collins M.J., 2002, Introduction to Microwave Chemistry, Microwave Synthesis Chemistry at the Speed of Light, Brittany L.H. and Matthews N.C., CEM Publishing, 11-28.

Gabriel C., Gabriel S., Grant E.H., Grant E.H., Halstead B.S.J., Mingos D.M.P., 1998, Dielectric parameters relevant to microwave dielectric heating, Chemical Society Reviews 27(3), 213-224.

Galema S.A., 1997, Microwave chemistry, Chemical Society Reviews 26, 233-238.

Gallawa J.C., 2001, The Complete Microwave Oven Service Handbook: Maintenance, Troubleshooting and Repair, Microtech Production, Florida, US.

Kamaruddin M.J., El Harfi J., Dimitrakis G., Nguyen N.T., Kingman S.W., Lester E., Robinson J.P., Irvine D.J., 2011, Continuous direct on-line reaction monitoring of a controlled polymerisation via dielectric measurement, Green Chemistry 13,1147-1151.

Metaxas A.C., Meredith R.J., 1983, Industrial Microwave Heating, Peter Peregrinus Ltd., London, UK.

Meredith R., 1998, Engineers' Handbook of Industrial Microwave Heating, The Institution of Electrical Engineers, London, UK.

Stuerga D., 2006, Microwave-material Interactions and Dielectric Properties, Key Ingredients for Mastery of Chemical Microwave Process, Microwaves in Organic Synthesis Loupy A., Wiley-VCH Verlag Gmbh & Co. KGaA, Weinheim, 1-57.