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Solvent Selection in Microwave Assisted Extraction of Castor Oil

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Castor oil has various uses in the field of cosmetics, plastics, manufacturing of biodiesel, lubricants and medicine. The use of microwave-assisted extraction (MAE) of oils from plant materials has shown tremendous research interest and potential to overcome long extraction time and high solvent volume. This study aims to evaluate suitable solvents for MAE of castor oil because not all solvent molecules have the ability to absorb microwave energy for heating, and consequently effective extraction. The MAE operating conditions were fixed at 230 W power intensity, solvent to feed ratio (S/F) of 20 : 1 and 10 min extraction time using petroleum ether, water, hexane and ethanol. The castor oil was characterised according to yield and dielectric properties. Results showed that the mix of hexane-ethanol (5 % ethanol) was found to be the most stable and effective solvent for MAE of castor oil with 36 % yield. The characteristics of oil are comparable to that of conventional soxhlet method. The dielectric constant of hexane shows some alteration when small amount of ethanol was used as modifier to allow extraction to occur.

1. Introduction

Castor seeds are poisonous to humans and animals because of the elements ricin, ricinine and certain allergens in the seeds that are toxic (Ogunniyi, 2006). The extracted oil from seeds has more than 700 uses in the field of cosmetics, plastics, manufacturing of biodiesel, lubricants and medicine if taken in recommended quantities. Owing to the increasing demand of castor oil, new extraction methods were sought to obtain products with high quality and safety features. The conventional extraction methods such as soxhlet extraction and mechanical pressing are time consuming and laborious, and may lead to possible solvent contamination of final products. Microwave-assisted extraction (MAE) is comparable with other alternative modern extraction techniques due to its simplicity and low cost of equipment. It has fast extraction ability with a small amount of solvent consumption and less risky for thermolabile constituents (Vivekananda et al., 2007). By comparing MAE with conventional methods, MAE produces a better yield and highly pure products within less than an hour. Less solvent amount required, extraction time reduces drastically and extractions at relatively lower temperature are added values to this technique (Danlami et al., 2014). The MAE is an original combination of microwave heating and extraction. The process efficiency of MAE is depending on the operating conditions selected. The selection of solvent used is the most important factor that affects the MAE process (Veggi et al., 2013). Hexane is a widely used solvent in oil extraction due to its low boiling temperature and low corrosiveness (Radziah et al., 2011). Other polar and non-polar solvents such as petroleum ether (Ajiwe et al., 1994), pentane, isopropanol, toluene, ethyl acetate, cyclohexane, acetone, chloroform, ethanol (Zarnowski and Suzuki, 2004) is also used in oil extraction. The extraction solvent in MAE cannot be selected simply based on conventional extraction. The selection of solvent for MAE must take into consideration the ability of solvent to absorb microwave energy so that the extraction becomes effective (Routray and Orsat, 2011). The present study aimed to evaluate the effectiveness of solvents, namely hexane, ethanol, petroleum ether and water in MAE of castor oil. The findings were discussed based on the oil yield, dielectric properties and attempts of extraction using mixed polar and non-polar solvents.

2. Materials and methods

2.1 Samples

Castor beans were purchased from Ancient Greenfield Pvt. Ltd, India. The encased seeds were air dried for 24 h. The shells were then separated from the nib by lateral airflow. The cleaned seeds were further dried for 5 h until a constant weight was achieved. The dried materials were crushed, and separated by a vibrator sieve to a nominal particle size of 2 mm. The particles were stored in a refrigerator at −4 °C before extraction. All chemical solvents used in oil extraction are of analytical grade reagents, and were purchased from R & M Chemicals, U.K.

2.2 Extraction procedures

The oil from castor seeds was extracted by soxhlet method. A sample of 15 g of crushed seeds was extracted using 300 mL of petroleum ether, water, hexane, ethanol, and a mixture of hexane-ethanol as solvents, for 2.5 h. The solvent was then recovered using a rotary evaporator (model Hei VAP Value, Heidolph) to obtain the oil yield. The microwave-assisted extraction (MAE) of castor oil was performed using a modified domestic microwave (Sharp R6460). A volume of 200 mL of solvent was added into a capped Teflon mould (1L) and placed inside the microwave. The mould is connected to a condenser outside the microwave using a PTFE tube. For each extraction run, 10 g of sample was used. The MAE was carried out at 230 W for 10 min. The microwave was turned off and the apparatus was allowed to cool. The solvent-castor oil mixture was transferred to a rotary evaporator for oil yield.

2.3 Dielectric properties

Open-ended coaxial probe (HP 85070D) was used to measure the dielectric properties of solvents and castor oil. This probe is attached to a computer controlled HP 8720B Vector Network Analyser (VNA). The dielectric properties were measured at room temperature, and the range of frequency from 0.2 to 10 GHz. The ability of the material to absorb and generate the heat on interaction with microwaves is defined by its dielectric properties, and is specified by complex dielectric constant (Ulaby et al., 2001). The relative complex permittivity (ε^*) of the material is given in Eq(1),

$$\varepsilon^* = \varepsilon' + i\,\varepsilon'' \tag{1}$$

where ε' is the real part of relative permittivity, the so-called dielectric constant that determines the behavior of material under microwave radiation, while ε'', is the imaginary part known as the loss factor that describes the conversion of absorbed microwave energy to heat. The loss tangent used in defining the ability of the material to convert the electromagnetic energy into heat at specific frequency and temperature, and is given in Eq(2) (Sacilik and Colak, 2010),

$$\tan\delta = \varepsilon''/\varepsilon' \tag{2}$$

3. Results and discussion

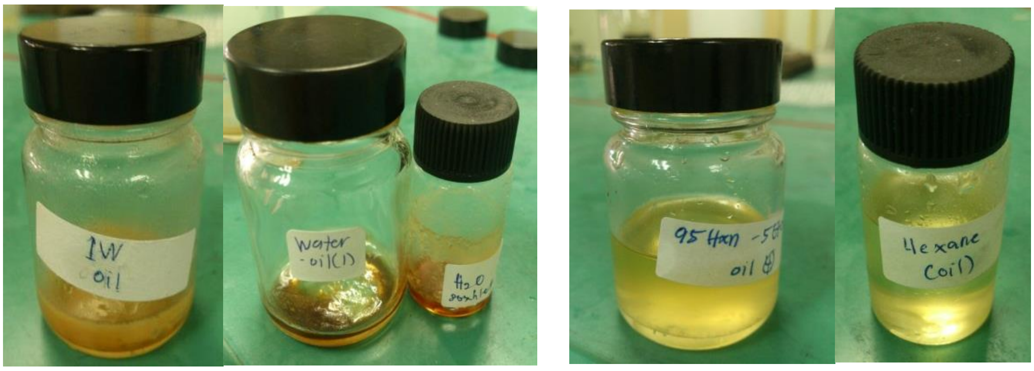
The castor oil yield by different solvents using soxhlet extraction and MAE techniques are shown in Table 1. The highest oil yield for soxhlet extraction was obtained by using ethanol as solvent. For MAE, the significant oil yield was achieved with a mixture of 5 % ethanol in hexane.

The polarity of solvent is important in extraction. Polarity is the ability of molecules to interact with other polar molecules (Barwick, 1997). From Table 1, it is obvious that the oil yield extracted by soxhlet technique using ethanol (a polar organic solvent) is higher than those using non-polar organic solvents (hexane and petroleum ether). Due to the hydroxyl group of ethanol which is hydrophilic, the solubility of ethanol becomes higher. Thus, fatty acids in castor oil that are also polar hydrocarbon would dissolve better in ethanol. However, the higher boiling point of ethanol compared to that of petroleum ether and hexane would also bring problems regarding the degradation of temperature-sensitive materials, and accelerated and side reactions during extraction and solvent recovery. Water is an inorganic polar solvent that was found to be ineffective to extract oil from castor seeds through soxhlet method. About 12.4 % of oil yield was obtained using water by MAE. Water produces an emulsion layer that may jeopardise the oil quality, and complicate the extraction procedures. As shown in Figure 1(a), the extracted castor oil with water (MAE) exhibits a darker colour compared to other solvents (Figure 1(b)). The dark colour may be due to the colouring matter in oil seeds, and could be related to the dipolar nature of water in microwave that produces undesirable reaction with ricinoleic acid in castor oil (Akaranta and Anusiem, 1996).

In MAE, it was found that the non-polar organic solvents may not be suitable for extraction of castor oil. Hexane and petroleum ether were not heated up by microwave radiation, and there was no sign of vapours formed in the condenser during microwave heating. No effective extraction occurs, and so no oil yield was recovered. However, with small amount of ethanol (5 %) added in hexane as modifier, castor oil was able to be extracted by MAE with 35.9 % yield, that is also better than that by soxhlet method (hexane) and ethanol alone by MAE. Ethanol is a good microwave absorber, while hexane is a good extraction solvent but not a good microwave absorber. By manipulating the presence of ethanol (polar solvent) in hexane (non-polar solvent), the MAE of castor oil can be done with higher yield.

Table 1: Castor oil yield (%) by different solvents and extraction techniques

Solvent type	Soxhlet	MAE
Water	12.36 ± 0.48	9.97 ± 0.11
Petroleum ether	30.28 ± 0.02	-
Hexane	34.71 ± 0.04	-
Ethanol	36.61 ± 0.08	20.45 ± 0.13
5 % ethanol - 95 % hexane	17.41 ± 0.23	35.94 ± 0.15
5 % water - 95 % petroleum ether	-	2.02 ± 0.03



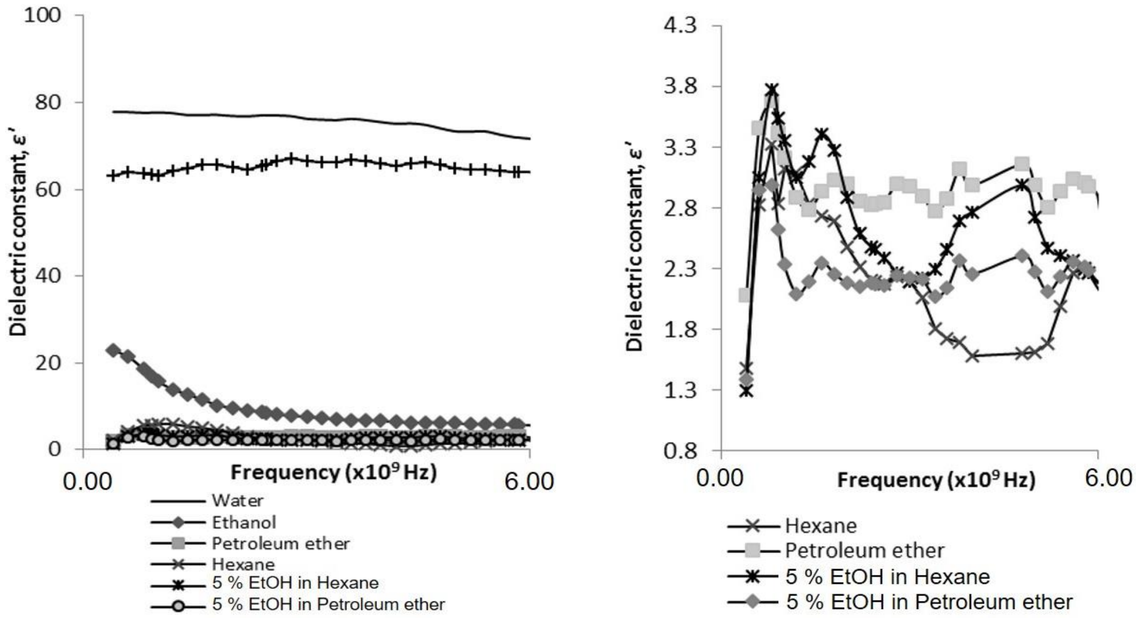
(a) (b)

Figure 1: (a) Castor oil using water as solvent; (b) Castor oil using other solvents

The dielectric properties of materials are important for predicting the heating rates and describing the behaviour of materials when applying a high-frequency or microwave electric fields in dielectric heating applications (Venkatesh and Raghavan, 2004). Figure 2 shows the effect of frequency on dielectric constant of different solvents, and Table 2 summarises the dielectric properties of different solvents at microwave frequencies.

Figure 2(a) obviously shows that water and ethanol are polar-type solvents. Solvents with dielectric constant lower than 5 could be classified as non-polar solvents. Interestingly, a modification of 5 % water in petroleum ether displays a significant change in the dielectric constant compared to petroleum ether alone. Although heating in microwave can be promoted by adding small amount of water (polar solvent) in non-polar solvents, it should be noted that water is not miscible in these solvents. Attempts to use water-mixed petroleum ether in MAE has resulted in aggressive and uncontrolled heating whereby the solvent was splashed beyond the condenser even with 5 % of water. The oil yield for this MAE extraction was recorded as 2.02 %. Figure 2(b) focuses on the selected solvents with dielectric constant values below 4.0. It reveals that by adding small amount of ethanol could change the dielectric behaviour of hexane and petroleum ether. It should be noted that ethanol is a polar organic solvent that is miscible in non-polar organic solvents, and the close boiling point of these solvents making the oil separation and solvent recovery simpler. Aggressive heating could happen in MAE if excessive amount of ethanol more than 30 % is used together with hexane and petroleum ether since ethanol is an excellent microwave absorber.

The loss tangent, $\tan \delta = \varepsilon''/\varepsilon'$ is an indicator of the ability of the material to convert the absorbed energy into heat. A good absorber has $\tan \delta \geq 0.1$, while that with $\tan \delta \leq 0.1$ is transparent to microwave. Materials with high loss factor (ε'') at the frequency of the incident radiation will heat at a faster rate from core to surface (Saxena and Chandra, 2014). Figure 3 illustrates that ethanol would absorb microwave energy faster than other solvents because it gives the highest loss tangent. It is widely accepted that non-polar solvents, like hexane and petroleum ether will remain transparent to microwaves; thus producing no heat (Alfaro et al., 2003). The presence of 5 % of ethanol in hexane will heat the solvent better under microwave irradiation compared to hexane alone.



(a) (b)

Figure 2: (a) Dielectric constant of solvents; (b) Dielectric constant below 4.0 for selected solvents

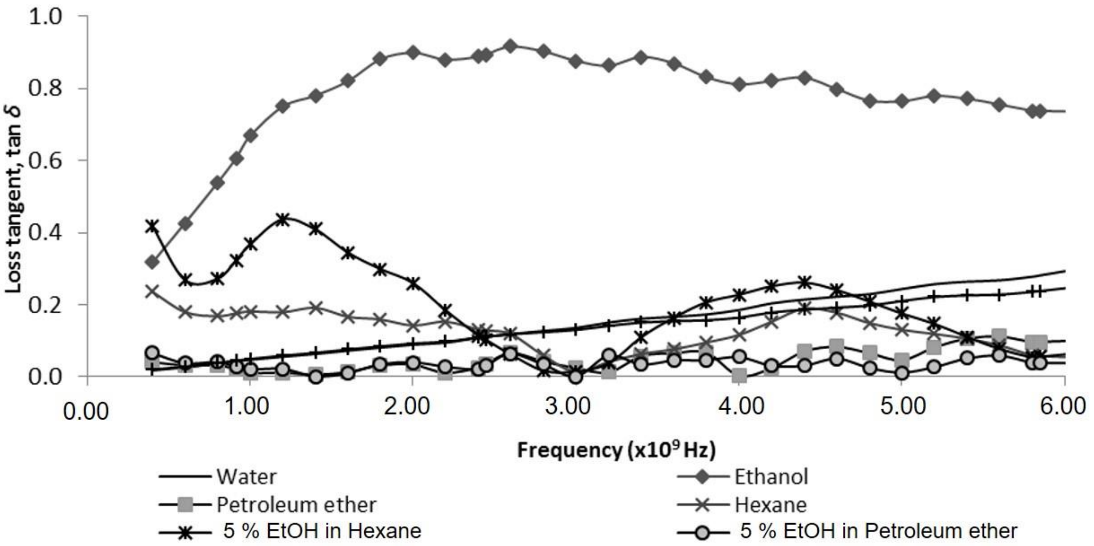


Figure 3: Loss tangent of solvents

Figure 4 shows the dielectric constant of extracted castor oil using different solvents. In general, the values of dielectric constant of castor oil are between 2 and 8. The dielectric constant that is lower than 8 indicates that the material is highly non-polar (Muley and Boldor, 2013). The patterns of ε' of castor oil are nearly uniform with varying frequency except for oil extracted using water by MAE. The fluctuated trend and slightly greater ε' may be due to the presence of remaining solvent (water) in oil (emulsion). This is owing to the difficulty of separating the water from the emulsion.

Table 2: Dielectric properties of different solvents at room temperature

Solvent type	915 MHz			2,450 MHz			5,800 MHz		
	ε'	ε"	tan δ	ε'	ε"	tan δ	ε'	ε"	tan δ
Water	77.69 ± 0.26	3.34 ± 0.35	0.04	77.09 ± 0.33	8.57 ± 0.41	0.11	72.03 ± 0.39	20.01 ± 0.37	0.28
Ethanol	16.98 ± 0.54	10.30 ± 0.46	0.61	8.54 ± 0.29	7.64 ± 0.48	0.89	5.79 ± 0.17	4.28 ± 0.47	0.74
Petroleum ether	3.41 ± 0.32	0.07 ± 0.02	0.02	2.83 ± 0.31	0.10 ± 0.08	0.04	3.01 ± 0.29	0.29 ± 0.05	0.09
Hexane	5.75 ± 0.14	1.01 ± 0.08	0.18	2.54 ± 0.18	0.33 ± 0.14	0.13	2.31 ± 0.16	0.14 ± 0.05	0.06
5 % ethanol in hexane	3.53 ± 0.39	1.14 ± 0.16	0.32	2.46 ± 0.42	0.25 ± 0.19	0.10	2.29 ± 0.40	0.12 ± 0.18	0.06
5 % ethanol in petroleum ether	2.62 ± 0.21	0.07 ± 0.11	0.03	2.18 ± 0.23	0.07 ± 0.12	0.03	2.32 ± 0.22	0.09 ± 0.11	0.04
5 % water in petroleum ether	63.36 ± 0.29	2.84 ± 0.23	0.05	65.72 ± 0.30	7.33 ± 0.17	0.11	64.10 ± 0.29	15.10 ± 0.22	0.24

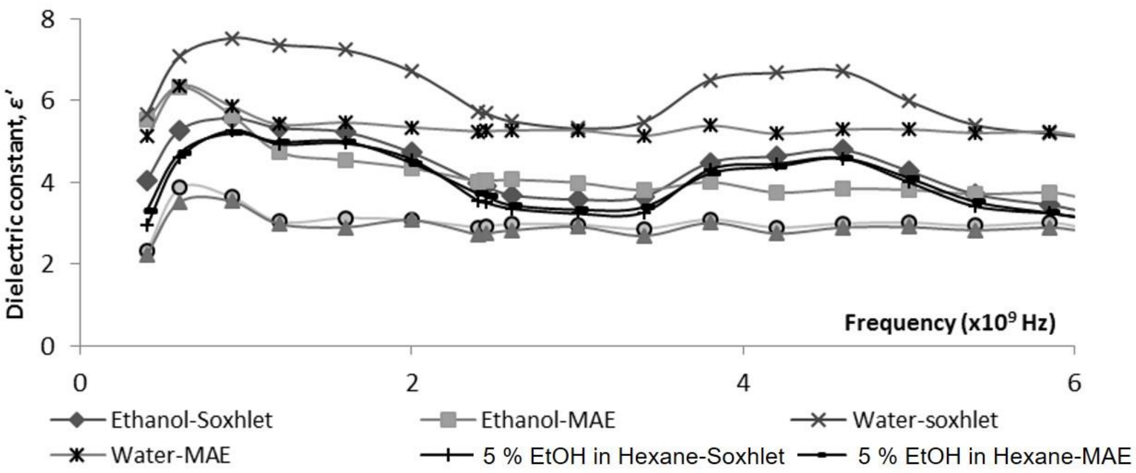


Figure 4: Dielectric constant of castor oil by soxhlet extraction and MAE techniques using different solvents

4. Conclusion

Solvents of low polarity (non-polar), such as hexane and petroleum ether are not effective for oil extraction by MAE. Polar solvents such as ethanol and water are highly suitable for MAE, but they possess higher boiling point that could bring problems associated with oil quality. Solvent with high tan δ is required for MAE. Adding a 5 % of ethanol in hexane could promote solvent heating in MAE, and has shown a remarkable yield of 36 % as compared to no yield by hexane alone. By selecting suitable solvent, MAE could extract castor oil from castor seeds with higher yield (36 % using 5 % ethanol in hexane), at shorter period, no significant change in the oil dielectric properties and comparable oil yield to that of soxhlet extraction using non-polar solvents.

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