

Alcohols and alcohols mixtures as liquid biofuels: a review of dielectric properties.

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Abstract

Oils, pure alcohols and alcohols mixtures have a complicated dielectric behavior. The strong electric field of the ions affects intensively the molecular interaction of solvents. Microwave heating resides in the characterization of dielectric properties. Classified as biodiesel precursors, advances in microwave technology of alcohols have a significant potential in improving the biodiesel production. In this context, this review provides basic knowledge on the dielectric properties theory and the heating phenomenon in the microwave fields. The main goal of the paper is to provide an organized summary of the main chemical and physical properties of alcohols and links them to their corresponding research studies dealing with dielectric properties measurements. The review covers the dielectric constant and loss factor variations observed with temperature and frequency, the relaxation time and the tangent loss of various mixtures found in the literature. Moreover, the review provides an updated database for organic solvents and alcohols to account for their abilities to couple in microwave radiation. The aim of the work is building a rigid bridge between chemico-physical and dielectric properties so it can make an essential step towards improving biofuels production. This review opens new perspectives for further investigation of dielectric properties that are interesting for microwave heating studies.

Keywords: dielectric properties, Alcohols, alcohols mixtures, liquid biofuels.

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Table of acronyms

Nomenclature	Definition
ΔH^*	Molar Enthalpy
ΔS^*	Molar Entropy
1PN	Propan-1-ol
2M2BAOH	2-methyl-2-butanol
3M1BAOH	3-methyl-1-butanol
BOH	Butanol
BuOH	Butanol
BZLOL	Benzyl Alcohol
CHP	Combined Heat and Power
CO ₂	Carbon Dioxide
Dp	Penetration Depth
EB	Ethyl benzoate
EGMPE	ethylene glycol mono phenyl ether
EtOH	Ethanol
f_b	Bruggeman factor
FCC	Federal Communications Commission
Freq.	Frequency
gf	Kirkwood correlation factor
H-bond	Hydrogen bond
HF	High Frequency
K	Time Constant
MB	Methyl benzoate
Melm	Methylimidazole
MeOH	Methanol
NaOH	Sodium

PrOH	Propanol
Ref.	Reference
RTC	Relative Temperature Coefficient
$\tan \delta$	Loss tangent
Temp.	Temperature
x	Volume fraction of the dispersed phase
X_1	Volume of solvent 1
X_2	Volume of solvent 2
α	Distribution parameter acting on the relaxation time
β	Parameter acting on the relaxation time
ϵ	Complex relative permittivity
ϵ_{mix}	Permittivity of the mixture
ϵ'	Dielectric constant
ϵ''	Loss factor
ϵ_{∞}	Permittivity at frequency greater than the universe
ϵ_r'	Relative dielectric constant
ϵ_r''	Relative loss factor
ϵ_s	Permittivity in static field
τ	Relaxation time
τ_1	Relaxation time of solvent 1
τ_2	Relaxation time of solvent 2
τ_{mix}	Relaxation time of the mixture
ω	Angular frequency

1. Introduction

Energy is a vital input for social and economic development [1]. Fuel is the ultimate necessity for assuring people's need of living and heating [2]. Both, the growing world population combined with the fast depleting reserves of fossil fuels have encouraged researchers to find alternative fuels to diesel [3]. This issue becomes essential with the

diminishing petroleum resources and its continuous cost increase associated with the alarming pollution levels [4]. The combined heat and power (CHP) biogas technology used widely in Europe is being converted to biomethane upgrading in many European countries such as France, Germany, Sweden and Netherlands [5]. In a serious consideration of the environmental problems associated with the conventional fuels usage based on petrochemical [6], the research of alternative sources is progressing towards the renewable bioresources available in the farms in form of biomass to be converted into liquid biofuels [7]. Interestingly, the overall carbon intensity of energy systems can be reduced by the deployment of carbon negative renewable energy technologies that involve biomass as input and offset the carbon emissions from conventional fossil-fuel-based energy technologies [8]. In this context, Budzianowski and Budzianowska [9] provided a study presenting the legislative goals of novel carbon indicators as effective control instruments for designing the post-Kyoto Protocol climate change mitigation law. Moreover, various solvents of low environmental impact and fast absorption rate required for Carbon Dioxide (CO₂) capture were analyzed and reviewed [10].

An increased number of developed countries have witnessed biofuels importance for their capability to replace the petroleum fuels [11]. Biofuels are the major key to reduce the foreign oil reliance and lower the toxic emissions [12]. Compared with syngas, hydrogen and natural gas, biofuels are rated to be the most environmentally friendly. So, worldwide's production of biofuels is expecting a significant increase in the future coming years, considering they are renewable, biodegradable and that they generate an acceptable exhaustion of gases, biofuels became the favorable choice for fuel consumption [7].

Predominantly produced from biomass, biofuels are solid, liquid and gas fuels. This paper is focused on liquid biofuels, which are presented by biodiesel and by bio-alcohols such as ethanol, butanol and methanol [13]. In the heat and power generation field, liquid products such as bio-oils are candidates to replace petroleum fuel [14]. Thus, the paper tackles several types of oils that were under dielectric investigation. The largest space was occupied by the alcohols and alcohols mixtures that were the most researched for their dielectric properties in the last decades.

In 2011, the dielectric permittivity of binary mixtures of anisole with methanol was reported [15]. Another experimental study was conducted for the properties of ethanol and methanol mixtures using the cavity perturbation technique [16]. A new conducting polymer based on glyoxal and p-phenylenediazomethine was synthesized and carried out in different solvents among which is the methanol [17]. Using open ended coaxial methods, dielectric properties measurements of soybean oils, alcohols and catalyst mixtures prove their dependence with frequency and temperature [18]. Recently, Ramesan and his coworkers studied the properties of the poly (vinylalcohol) and found that the dielectric constant and loss of the composites were higher than those of the pure blend [19]. Same conclusion was brought by Das and his coworkers in 2015 who observed that in comparison with pure PVA film, the dielectric constant of composite film were higher and fitted in the Cole-Cole equation [20].

In this concern, the application of dielectric heating on alcohols and alcohols mixtures is highly addressed in previous research works. Dielectric spectroscopy is a method proposed to determine the electric properties of alcohols and alcohols mixtures and thus ensure the compliance of produced biofuels with legislation [21]. For any process in microwave design and control of microwave heating, a major role is designated to the knowledge of dielectric properties of materials. In fact, predicting electromagnetic field distribution and temperature profiles for the reaction and understanding the overall mechanism of microwave dielectric heating depend immensely on the dielectric properties [18].

The review collects the essential knowledge about dielectric spectroscopy and summarizes the concept of microwave heating. It reviews the basic chemical properties of alcohols and alcohols mixtures from density, viscosity to vapor pressure and moisture content, focusing on their dielectric properties effects in terms of dielectric constant, loss factor and relaxation time. From the available studies, the review builds a linkage between chemical properties and dielectric characterization of alcohols and alcohols mixtures as major liquid biofuels representative for an improved production.

2. An overview of microwave dielectric heating

In the early 1950s, the classic work of Von Hippel and his coworkers [22] provided a valuable theoretical basis for technological developments with a precious database of dielectric properties on food stuff, common substances and materials. Recently, more effort has been redirected towards the measurements of dielectric properties which contributed in the expansion of the database [23]. Dielectric or microwave heating has been developed by numerous researchers [24]. In microwave heating, the electromagnetic energy is transformed into heat directly within the material [25] where microwaves penetrate the material and deposit energy so the heat is produced throughout the volume of the material. Depending on its frequency, a microwave system is considered reasonable with an overall efficiency of 80-85% [26]. Compared with other conventional heating techniques, microwave can provide rapid selective heating [27].

Microwave dielectric heating has been widely used in industrial field scopes. It is known to be a well-established procedure in processing of food and other materials such as ceramics, rubbers and plastic [26]. In synthetic chemistry this method has become a well established procedure. Microwave applications have been designed for the volumetric heating of rubber, wood, agricultural products and the inclusion of waste materials into glasses [28]. Material selective heating is one of the unique abilities of microwave heating; according to the dielectric properties of the material, the microwave will absorb differently [29].

An important database of dielectric properties has been provided by Von Hippel and his coworkers in the 1950s [22]. More work has been directed towards the dielectric properties measurements of biological material with the expansion of the technological rise [23,30].

Dielectric or microwave heating has been developed by many researchers [25]. In this type of heating, the electromagnetic energy is transformed into heat directly within the material [24]. In dielectric heating, the produced heat is propagated throughout the volume of the material rather than a core volumetric heating as an external source [27, 31, 32]. Compared with conventional heating techniques, this provides rapid and selective heating with an overall reasonable efficiency going up to 80.5% depending on frequency [26].

In the past decade, microwave pyrolysis has offered several advantages over other methods [33] and succeeded in being an efficient way to convert biomass into bioproducts including switchgrass [34], wheat straws [35,36], rice straws [37,38], corn stover [39,40], algae [41], coffee hulls [42,43], oil palm shell [44] and various types of wood [45-48].

Since the data measurement and processing is simple, the development of impedance sensors for highly resistive non aqueous industrial fluids reveals is pretty interesting theoretically [49]. Another equivalent approach aiming to achieve dielectric spectroscopic analysis that consists on simple optimization of measuring cell factors is considered as well by DeSouza [50]. The dielectric constant and electrical resistivity were evaluated in this approach presented in terms of impedance complex plane conductivity and dielectric constant spectra.

Whether extracted from biomass or conventional fossil, biofuels are essentially and constantly examined for quality assurance. The reactor type, the temperature, the presence of a catalyst and other operational conditions are distinct quality parameters affecting the upgrading process of pyrolysis liquids [51].

Compared to conventional heating, microwave dielectric heating has several advantages. First of all because the microwave energy is capable to produce much higher heating rates when introduced with at least one component that is capable of coupling strongly with microwaves. When it comes to introducing remotely the microwave energy, no direct contact occurs between the source of energy and the reacting chemicals. Thus, this will lead to an alternative distribution of chemical products and to a different profile temperature. Moreover, the chemicals do not interact equally with the microwave frequencies used which allows selective heating so the microwave energy can pass through the walls to heat the reactants only. Microwave dielectric heating is considered as an ideal method to accelerate the chemical reactions under increased pressures. Moreover, increasing the temperature of a reaction in organic solvents up to 100°C is possible using simple apparatus. These advantages have been investigated extensively in the last years with hundreds of papers published in this field. However, most of the work was empirical and qualitative and not all the available data is available to the chemical community. The use of wideband swept frequency instrumentation made it easier to obtain dielectric data of a variety of chemicals [28].

3. An overview of Dielectric properties characterization

A material that contains either permanent or induced dipoles acting as a capacitor when placed between two electrodes is known to be a dielectric material [52]. This means that charge is allowed to be stored with no observation of DC conductivity. The rotation of dipoles in the electric field and the finite displacement of charges lead to the polarization of dielectrics. The physical rotation of molecular dipoles and the distortion of the distribution of the electron cloud within the molecule are both processes that are involved by polarization. Irrespectively of the sample's dimensions, the capacity of charge storing in a specific material is described by the permittivity [23,53]. Permittivity is a description of a material's ability to absorb, transmit and reflect electromagnetic energy [16]. The dielectric constant (ϵ') reflects the ability of the material to store electric energy; its value is related to both chemical structure and intermolecular interaction [54]. The chemico-physical properties of the major pure alcohols and the alcohols mixtures found in literature are presented in tables 1 and 2 respectively.

The rotations of the polar molecules in the liquid will begin to lag behind the electric field oscillations when the frequency of the electromagnetic radiation is pushed up into the microwave region. The product component of the loss and the current will be in phase with the electric field. This phenomenon producing resistive heating occurs resulting in energy absorption from the electric field and is described as dielectric loss. The dielectric loss (ϵ'') influences the conversion of electromagnetic energy into thermal energy.

Table 1. Chemical Properties of alcohols.

Alcohol	Temp. (°C)	Energy Density (MJ/L)	Vapor Pressure (KPa)	Motor Octane number	Boiling Point (°C)	Freezing Point (°C)	Air fuel Ratio	Density ρ (g/mL)	Viscosity η (mNsm ⁻²)	Ref.
Methanol	20	16	12.8	97-104	64.5-65	-97 to -97.6	6.5	0.787		[55-58]
	30								0.013	[54]
	45								0.012	[54]
	60								0.010	[54]
	34							0.784	0.517	[15]
	35							0.786	0.510	[15,58,59]
Ethanol	20	19.6	7.6	102	78	-114 to -114.5	9.0	0.785	10.800	[15,58,59]
	30								0.200	[54]
	45								0.100	[54]
	60								0.130	[54]
	75								0.080	[54]
Propanol	30							0.799		[54]
	36							0.805	1.739	[15]
	37							0.803	1.731	[60,61]
Butanol	20	27-29.2	0.5	78	117-118	-89.3 to -89.5	11.2	0.810		[55-58]

The ability of the solvent to absorb energy in a microwave cavity which is reflected by the loss tangent ($\tan\delta$) of the solvent depends on the relaxation times of the molecules. Dielectric relaxation is usually described as a function of frequency in terms of the permittivity. The response of a medium to an external electric field of microwave frequencies is referred to as dielectric relaxation [16]. The functional group and the volume of the molecule affect critically the relaxation time, especially those with strong hydrogen bonding capabilities. With temperature of the solvent increasing, relaxation time of solvent decreases [18]. The Maxwell displacement current named after the author of electromagnetic theory is known to be the re-orientation of the dipoles and displacement of charge. When the dielectric is ideal, the oscillating electric field is 90° out-of-phase with the variations of the alternating voltage and no lag exists between the orientation of the molecules and the variations of the alternating voltage. Hence, the voltage current product is zero. No heating occurs for a dielectric material where the molecules can keep pace with the field changes [28].

Table 2. Chemical Properties of alcohols mixtures.

Fuel type and Alcohol mixture	Temp. (°C)	Density ρ (g/mL)	Moisture (%)	Ash (%)	Fixed Carbon	Molar enthalpy (ΔH^*)	Molar entropy (ΔS^*)	Dipole moment (Debye)	Ref.
Methyl benzoate	31	1.0787							[59]
Ethyl benzoate	32	1.0421							[59]
Propan-1-ol in Methyl benzoate						30.453	0.0636		[62]
Propan-1-ol in Ethyl benzoate						23.903	0.0417		[62]
1-Butanol	25							1.73	[59]
3-Methyl-1-butanol	25							1.72	[59]
2-Methyl-2-butanol	25							1.80	[59]
Benzyl alcohol	25							1.90	[59]
1BOH+BZLOL liquid mixture		0.8040							[59]
2M2BAOH+BZLOL liquid mixture		0.8050							[59]
3M1BAOH+BZLOL liquid mixture		0.8050							[59]
Benzene	33	0.8684							[59]
Coal			3.73	18.2	48.39				[55]

When applying a static electric field to a solution that contains polar molecules, the molecules will be aligned in the direction of the external field. They will not take a randomized orientation unless the field is switched on. Thus, the relaxation time indicates the time needed by the molecules to achieve this state of randomization [28]. The relaxation time, related to a time constant K , is temperature dependant. Thus, the enthalpy and entropy can be calculated from the relaxation time through an Arrhenius analysis.

The relaxation time (τ) of the molecules determines the loss tangents of the solvents which is related to the energy absorption ability in a microwave cavity [28]. The ratio of loss factor to dielectric constant gives rise to the loss tangent that determines the attenuation of the microwave power in the material and results in heating [63].

Resistance and capacitance are considered to be the simplest measurable dielectric properties in dielectric characterization. By ruling out the effect from the associated geometrical factor, these measurements can be converted to dielectric constant and electrical resistivity or conductivity respectively. Indeed these are the intrinsic properties of the materials [50]. Generally, oily substances have very low conductivity values that can go to 10^{-12} S/cm which make them very poor conductors of electricity. This property that might be due to their low charge mobility justifies their broad use as insulators in many electrical apparatus [64]. This also might explain the reason behind not considering the conductivity of diesel, biodiesel blends as assessment of biodiesel content. Although the materials properties might be altered due to thermo-degradation, Schilowitz [65] proposed a provisional solution approach that relies on making measurements at temperatures above 50°C.

According to Koehler et al. [66] and Tomlinson [67], a linear correlation between dielectric constant and biodiesel content could be achieved through the equivalent formalism of electric modulus for data analysis. In parallel, Perez and Hadfield measured the complex dielectric constant of oil detecting its quality using a similar sensorial approach [67]. Another commercial dielectric properties based fuel composition sensor was projected to quantify gasoline/alcohol fuel blends; the work aimed to characterize quantitatively diesel-biodiesel blends of several types and focused on determining the fuel composition in vehicles through a practical use) [69,70]. Apart from the investigations targeting fuel and biofuel, dielectric spectroscopy was proposed as a characterization method for the analysis of oils. For instance, Perini et al. [71] reported recently that the presence of water in water in oil emulsions could be possibly identified through dielectric properties.

Experimental methods of dielectric properties characterization are either based on reflection or transmission techniques. They can be executed using resonant or non-resonant, open or closed structures depending on the nature of the material samples. Closed resonant cavity, and open resonant structures are examples of resonant structures techniques. While free space transmission and open ended coaxial line and waveguide are classified under open structures, closed structure techniques hold other technique quietly used such as coaxial line and waveguides where each of these is designed for an appropriate frequency range [52].

4. Dielectric properties data

4.1. Dielectric Constant

4.1.1. Temperature

4.1.1.1. Oil

According to Elshami et al. [72], and Sorichetti [73], dielectric constant of soybean oil decreases with the temperature increase. This result was approved by Muley and Boldor [18] as well where the dielectric constant was considered to be virtually consistent with

respect to temperature. The minor difference in the results of both investigations was attributed to the low frequency ranges covered (0.01 KHz to 1 GHz) compared with the high investigation frequency range of Muley and Boldor [18]. With the temperature increase, molecular motion and molecule to molecule interaction increase as well [72,74]. Taking into consideration the change in the applied electric field, the polarization process that is associated with the orientation of molecules will be opposed by both of these phenomena [73]; which will contribute in the reduction of the dielectric constant. In 2014, the Brazil nut oil was studied at various temperatures from 0.3 to 13 GHz by Campos and his coworkers [75]. The dielectric constant values exhibited by Brazil nut oil are seen to be considerably low when compared with ethanol or other polar solvent; this was attributed to their non-polar nature. Table 3 gives some representative values for the oil dielectric properties found in literature.

Table 3. Dielectric properties of oil.

Alcohol Catalyst Mixture	Freq. (GHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Dipole moment Debye	Viscosity millipoise	Ref.
Brazil nut oil	0.915	30	2.98	0.19				[75]
	0.915	40	3.00	0.19				[75]
	0.915	50	3.24	0.26				[75]
	0.915	60	3.08	0.28				[75]
	0.915	70	3.08	0.28			10.10	[28][75]
	2.45	30	2.87	0.18			5.45	[28][75]
	2.45	40	2.88	0.18			10.80	[28][75]
	2.45	50	3.11	0.21			20.00	[28][75]
	2.45	60	2.96	0.23			17.70	[28][75]
	2.45	70	2.95	0.25			22.70	[28][75]
Soybean Oil	0.915	30	2.90	0.23	0.079			[18]
	0.915	45	2.97	0.28	0.096			[18]
	0.915	60	2.99	0.28	0.094		33.50	[18, 28]
	0.915	75	2.85	0.21	0.075			[4]
	2.45	30	2.86	0.10	0.035	1.67	10.80	[30-31]
	2.45	45	2.85	0.14	0.052		1.360	[18, 28]
	2.45	60	2.95	0.14	0.049			[18]
	2.45	75	2.81	0.11	0.04			[18]
	2.45	60	13.01	7.32	0.562			[18]
	2.45	75	14.98	6.20	0.413			[18]

4.1.2. Alcohol

For alcohols the dielectric constant decreases at a smaller rate with temperature increase. At high temperature, molecules have higher kinetic energy which makes them response faster to the change of electric field. Moreover, the molecules are further separated resulting in a smaller viscosity and contributing to the realignment process. For this, the dipole rotation of molecules increases which affects the dielectric constant of the material

at high temperatures compared with lower ones. With temperature increasing, the frequency at which dielectric constant starts to drop is shifted. In fact, the dipolar rotation becomes prominent with temperature rising which causes a shift in the location at which the dielectric constant starts to decrease. This behavior is one of the polar molecule characteristics [76]. Similar trends were observed for ethanol and methanol [18]. However, the dielectric constant values of methanol were considerably higher than those of ethanol. At 512 MHz, the highest value of 31.0 was scored compared with 18.0 the lowest value of methanol at 4500 MHz. Consequently, the difference between the highest and lowest value of dielectric constant (31-18) is also higher than that of the ethanol for the lowest temperature of 30°C. It is also notable that the dielectric constant rate of decrease with frequency is smaller for methanol than for ethanol. This could be attributed to the number of CH₂ groups in R-OH chains. This number is inversely proportional to the dielectric constant; when it increases, the dielectric constant decreases. In fact, the bonding of a hydrogen atom with an oxygen atom is accompanied with an alteration in the newly formed molecule. Although the carbon and hydrogen combination is non-polar, the polarization is changed due to the dipole moment induction. Moreover, methanol is able to rotate and realign faster than ethanol because it is considered to be more polar. First, because it has a smaller molecular size and second for the smaller distance between its poles [18].

According to Chmielewska et al. [77], after measuring the relative permittivity of binary alcohols at 15, 20, 25, 30 and 35°C over the whole composition range, it is possible to place the relative permittivity of pure alcohols in order of their molecules as such Eq. 1:

$$\epsilon_{\text{MeOH}} > \epsilon_{\text{EtOH}} > \epsilon_{\text{1-PrOH}} > \epsilon_{\text{i PrOH}} > \epsilon_{\text{i BuOH}} > \epsilon_{\text{1 BuOH}} > \epsilon_{\text{s BuOH}} > \epsilon_{\text{t BuOH}} \quad (1)$$

When the size of the molecules increases, the value of the permittivity decreases. Same goes for the type of alcohol since the primary alcohol has the largest value and the smallest value is found to be for the tertiary alcohol. The fact that values obtained for permittivity are greater for the smaller molecules and primary alcohols can be connected with steric hindrances. In other words, this can be related either to the association of molecules to each other or with the alcohol ability to create intermolecular hydrogen bonds of the linear type. Values of permittivity obtained for methanol and ethanol and reported by Sengwa et al. in 2008 [78], using the capacitive measurement methods agree well with the data obtained by Chmielewska [77]. Values collected for methanol and ethanol are presented in tables 4 and 5 respectively.

In order to describe the dielectric properties of alcohols, Durov and Shilov [79] used the quasi-chemical models of chain-like and chain-like plus cyclic aggregation of methanol. These methods prove to perform well in a broader temperature range. The dielectric constant shows a significant dependence with pressure at a constant temperature.

4.1.3. Alcohol-catalyst

Muley and Boldor [18] added Sodium (NaOH) as catalyst to the alcohols. The amount of NaOH added corresponds to 0.091g of catalyst in 10.235 ml of methanol and to 0.066 g of catalyst in 19.3 ml of ethanol which corresponds to 0.18% by the weight of oil for transesterification. Although the quantity is considerably small, it had spectacular effects on the dielectric properties.

In fact, the dielectric constant may stay constant or decrease depending on many factors such as the solvent properties, the association and dissociation of ions and the ions concentration. In Muley and Boldor study, the dielectric constant values recorded for the alcohol-catalyst mixtures are smaller than those of the pure alcohol by about 20%. The reason behind this decrease can be attributed to ion salvation [80]. In response to ion's electrostatic field, the solvent polar molecules orient towards the ion and so salvation takes place. A molecular salvation shell is formed around each ion, thus this association with ions stabilizes the system. Because they cannot orient easily by the applied electric field, the solvent molecules that are bound in this shell do not generate effective dipole moment. This will result in decreasing polarization and reducing the dielectric constant [18]. By inhibiting the free rotation of the solvent molecules, the interactions between ions and solvent dipoles lead to dielectric saturation of solvent molecules in the ion's electric field [80]. Table 6 presents the data found on the various mixtures collected among which the ethanol and Sodium catalyst mixture.

Table 4. Dielectric properties of methanol.

Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Ref.
13.56		35.10	0.40	0.011		[28]
27.12		35.00	0.50	0.014		[28]
433.9		34.20	4.44	0.13		[28]
900		32.10	8.49	0.265		[28]
915	30	30.87	6.48			[28]
915	40	29.80	5.14			[75]
915	50	28.51	4.17			[75]
915	60	27.10	3.25			[75]
915	30	29.51	6.55	0.222		[18]
915	45	28.34	4.63	0.163		[18]
915	60	26.84	3.30	0.123		[18]
915	30	29.51	6.55	0.222		[18]
915	45	28.34	4.63	0.163		[18]
915	60	26.84	3.30	0.123		[18]
2450	30	24.02	12.53			[75]
2450	40	24.87	10.75			[75]
2450	50	24.92	9.37			[75]
2450	60	24.65	7.64			[75]
2450	30	23.03	11.56	0.502		[18]
2450	45	24.33	9.13	0.375		[18]
2450	60	24.25	6.95	0.286		[18]

Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Ref.
2450		21.90	14.60	0.665		[28]
2450				0.799	562	[28]
2450		21.90	14.60	0.665		[28]
2450	30	23.03	11.56	0.502		[18]
2450	45	24.33	9.13	0.375		[18]
2450	60	24.25	6.95	0.286		[18]
2450	-20	14.75	12.59		40.80	[28]
2450	10	17.85	14.25		34.40	[28]
2450	0	20.90	16.46		28.80	[28]
2450	10	22.63	15.32		26.60	[28]
2450	20	20.06	11.77		170.00	[28]
2450	30	24.49	12.52		112.87	[28]
2450	40	24.19	10.43	1.260	340.00	[28]
2450	50	23.95	8.62	1.350	760.00	[28]
2450	60	19.42	6.10	1.170	1150.00	[28]
	20	33.70		0.659	332.00	[28]
	30				459.00	[18]
	45				376.00	[18]
	60				273.00	[18]
	25	32.60				[81]
900		3.96	2.25	0.568		[28]
2.45		3.43	1.17	0.341		[28]
13.56		8.00	0.70	0.088		[28]
27.12		9.30	0.90	0.097		[28]
433.9		5.16	3.62	0.702		[28]
900		3.96	2.25	0.568		[28]
2450		3.43	1.17	0.341		[28]
	20	32.80				[28]
	30	31.42	1.80			[15]
	10	38.51	3.55		49.080	[83]
	10	36.53	3.07		47.450	[83]
		32.70				[82]
		32.66				[84,85]
		32.78				[86]
		32.63				[87]
		32.70			49.600	[88]
		31.65	1.76			[77-82]

4.1.4. Mixture

The permittivity studies have been investigated by many works for alcohol mixtures from pure alkanols or mixtures of alkanols with water or nonpolar components. These investigations were executed with various methods of measurements [89]. In 2011, Rana

et al. [15] observed that the effective number of dipoles in the mixture is decreased by the interaction between the different molecules in the mixture. Thus, the static permittivity of the mixture will decrease non-linearly. Whenever the mixture is liquid, the molecular interactions between the constituents are very wide from hydrogen bonding to molecular association, dipole-dipole and dipole induced dipole interactions. The ideal behavior of dielectric constant deviates with the variation of concentration in the mixture constituent due to these interactions.

For Rana and his coworkers [15], the composition of the mixture plays a functional role in the character change of the static permittivity. In lower concentrations of anisole with methanol or ethanol, the excess permittivity is found to be positive indicating that the unlike molecules interact in a manner causing the effective dipole to increase. Effectively, unlike species interacts similarly to Hydrogen bond (H-bond) “structure makers” which will increase the dipole moment. On the other side, the excess permittivity is negative in higher concentrations of anisole indicating that the two liquids interact in a manner reducing the total number of effective dipole produced by the mixture constituent interaction [54]. No interaction between the molecules of the mixture will lead to a null value of the excessive permittivity. With orientation of the some of the neighboring dipoles in opposite directions, one of the constituents in a binary mixture act as a structure breaker for the other constituent hydrogen bonded structure. In the case of their experiments, it was the Anisole playing over methanol and propanol. A systematic change in static dielectric permittivity was reported for binary mixtures [15].

In 2010, Yang et al. [16] have also recorded the non-linear variation of the dielectric constant with the change in the volume fraction of methanol in ethanol which again recalls the intermolecular association taking place in the binary system and pointed by Rana et al. [15]. Experiments have shown that the permittivity is increasing with increasing temperature and with increasing methanol volume as well.

Regarding the interaction between the compounds in a mixture, an important dielectric parameter is the corrective Kirkwood correlation factor (g_f). This correlation factor takes into account the dipole moment of the molecule, the number of its molecules in a unit volume and the highly directional nature of the hydrogen bonds [28]. g_f should be equal to unity for an ideal interacting mixture. The magnitude of deviation of this factor from unity reflects the strength of the interaction between the compounds [90]. Values of g_f are more dependent on concentration than on temperature [91].

4.1.5. Binary mixtures

Among several equations corresponding to the estimation of mixture dielectric properties, many have been applied in the preceding literatures with success. In 1936, Onsager [92] has modeled the dielectric constant of liquids though a very successful method that was improved significantly by Kirkwood in 1939 [93]. Another equation to determine the dielectric constant equation for a dilute dispersion of spherical inclusions is based on electrostatics and is stated in Eq. 2 [94].

$$\left(\frac{\epsilon_{\text{mix}} - \epsilon_1}{\epsilon_2 - \epsilon_1}\right)\left(\frac{\epsilon_2}{\epsilon_{\text{mix}}}\right)^{1/3} = 1 - x \quad (2)$$

where 1 and 2 are subscripts referring to the two solvent components respectively and x denoting the volume fraction of the dispersed phase. The values of dielectric constant obtained by Yang et al. are calculated from the equation above.

4.1.6. Mixture of alcohol and polar liquids

For the binary systems (1PN+MB), Mohan and his coworkers [59] have determined the permittivity values of dielectric constants for various mole fractions at different temperatures. The results prove that regardless of the temperature, there is no linear variation of dielectric constant with mole fraction. Similar results were also obtained by Kroegers for alcohols and polar liquids mixtures [95]. This necessarily suggests strong interactions between the compounds. For both systems with low benzoate concentrations (MB and EB), weak inter-molecular interactions are marked between the compounds with values of g_f close to unity. g_f values deviate from unity when the concentration of benzoate increases which indicates strong hetero-interaction occurrence between the compounds.

Table 5. Dielectric properties of ethanol.

Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Ref.
0.59	10	7.05	5.81		55.20	[28]
0.8	20	7.49	6.46		48.80	[28]
1.19	30	8.05	7.06			[28]
1.53	40	8.95	7.39			[28]
2.03	50	10.11	7.28			[28]
2.88	60	11.15	6.76			[28]
3.26	70	11.71	6.35			[28]
3.26	80				419.00	[28]
3.26	90				370.02	[28]
3.26	100				230.80	[28]
3.26	110				171.10	[28]
2.45				0.571	644.00	[28]
2.45				1.300	1950.00	[28]
0.915	30	17.41	9.71			[75]
0.915	40	18.8	8.25			[75]
0.915	50	19.26	6.78			[75]
0.915	60	19.24	5.01			[75]
0.915	70	18.65	3.81			[75]
2.45	30	8.91	8.00			[75]
2.45	40	10.36	8.81			[75]
2.45	50	11.8	8.89			[75]
2.45	60	13.63	8.11			[75]

Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Ref.
2.45	70	14.68	7.31			[75]
0.915	30	15.85	9.54	0.602		[18]
0.915	45	17.68	7.57	0.428		[18]
0.915	60	18.22	5.06	0.278		[18]
0.915	75	18.35	3.63	0.198		[18]
2.45	30	8.21	6.83	0.831		[18]
2.45	45	10.02	7.63	0.762		[18]
2.45	60	13.01	7.32	0.562		[18]
2.45	75	14.98	6.20	0.413		[18]
0.915	30	15.85	9.54	0.602		[18]
0.915	45	17.68	7.57	0.428		[18]
0.915	60	18.22	5.06	0.278		[18]
0.915	75	18.35	3.63	0.198		[18]
2.45	30	8.21	6.83	0.831		[18]
2.45	45	10.02	7.63	0.762		[18]
	20	25.70		0.123	170.00	[28]
	25	24.35				[77]
	25	24.34				[84]
	25	24.55				[85-96]
	25	24.35				[87]
	30				158.00	[18]
	45				103.00	[18]
	60				66.90	[18]
	75				42.40	[18]
		24.50			162.00	[54]
		22.81	0.91		166.00	[97]

4.2. Frequency

4.2.1. Oil

For soybean oil, the dielectric constant remained approximately stable through the frequency range measurement (280 to 4500 MHz). Regarding the high frequency investigated by Muley and Boldor [18], dielectric constant decrease was relatively small. Its values are considered to be significantly low with 3.2 being the highest value scored. Since the dielectric constant of a polar solvent such as water reaches 80.10 [95], this low value can be due to the non-polar structure of oil [18]. Low values obtained by Muley and Boldor [30] were quite similar to the ones obtained in older studies where the dielectric constant reaches 2.91 at 915 MHz and 30°C [72-74]. In 2008, Hu and his coworkers [98] noted a substantial decrease in the dielectric constant values with frequency increase whenever the frequency range adopted is much lower: 0.01 KHz to 1 MHz.

This difference can be explained by the inertial effects. In fact, the process of reorientation is accelerated by the viscosity of the medium. With the inertial effects and the frequency rise, the alignment becomes harder causing the decrease in the dielectric constant [74]. Another explanation of the low values obtained in the fatty acid composition of oil. Hu and his coworkers [98] reported a value ranging between 3.104 and 3.127 for the linoleic acid class at a frequency range of 0.1 KHz to 0.5 MHz and this value decreased when frequency was rose to 1 MHz; soybean oil is classified under this fatty acid category. On the other hand, with the changing electric field, the electron rich double bond has a negative charge and tends to oscillate to a certain extent, this phenomenon is called unsaturation. The increase in the degree of unsaturation is noted to be accompanied with increase in the dielectric constant. For Brazilian nut oil, the values of the dielectric constant remained approximately unchanged throughout the frequency range from 0.3 to 13 GHz. Only a slight decrease was noticed was the frequency increase [75].

4.2.2. Alcohol

Knowing that ethanol is a polar solvent with a permanent dipole, its dielectric constant is therefore frequency dependant [74]. It has an obvious decreasing pattern with the frequency increase. The data presented by Muley and Boldor [18] shows the decreasing trend of the dielectric constant with the frequency increase which confirms with Debye's equation [22]. Similar results were obtained by Pace et al. [74] as well in 1968.

4.2.3. Alcohol-catalyst

Similarly to the pure alcohol, the dielectric constant for alcohol-catalyst mixture decreased with increasing the frequency. Whenever the frequency was fixed at a specific value, the dielectric constant was increasing with the temperature rise [18].

4.2.4. Mixture

Recently in 2015, Liu and Jia [97] have used dielectric relaxation spectroscopy in a wide frequency range of 20 MHz to 20 GHz at 25°C to study the dielectric permittivity of 1-methylimidazole (MeIm) mixtures. The excess dielectric model has been used to estimate the type of dipolar ordering and the strong effect of the H-bonds on the molecular interactions. A deeper understanding of the relaxation processes and the interaction aspects of molecules is revealed by four various models: the excess dielectric model, the Bruggeman mixture formula, the Basesy-Fisher model and the Luzar model. In fact, the dielectric constant of a MeIm-ethanol mixture decreases in a rapid manner with the increase in frequency and with the decrease in mole fraction of MeIm. Results come out to show that dielectric constant is strongly dependent of the mole fraction continuously in a simple manner. For this, the dielectric constant of the mixture was rising with the increase in MeIM.

The excess permittivity of the MeIm-ethanol mixture was found to be positive for the various concentrations. As recalled for the anisole mixture [24] (and cited in [19]) this

indicates that the constituents of binary mixture are interacting as H-bonded “structure makers” with parallel dipolar alignments in the same direction. Hence, the effective number of aligned dipoles will enhance the mixture polarization. On the other hand, an opposite negative trend was observed in the case of water-MeIm mixture, which indicates that one of the mixture constituents is acting as a “structure breaker” for the other constituent H-bonded structure with orientation of some of the neighboring dipoles in opposite directions. Thus, the total number of parallel aligned effective dipoles contributing to the mixture dielectric polarization is decreased. The smaller the value of the magnitude, the weaker is the H-bond molecular connectivity and vice versa. The evidence of the stoichiometric ratio of a stable adduct in the mixture is reflected by the molar ratio corresponding to the pronounced maximum deviation from ideality in the versus mole concentration [78]. Recently, Fakhar et al. [54] came out with positive values of the binary mixtures of the 2-methyl-2-butanol over the entire range of solute mole fraction at 25°C. The parallel aligned effective dipoles contributing to the mixture of dielectric polarization is increased by the constituents of this binary mixture acting as Hydrogen-bonded structure makers. Moreover, intermolecular reaction between the aromatic alcohol and the aliphatic alcohol is revealed by the plots of Bruggeman factor (f_b) deviating from linearity. The structural rearrangement of molecules led to a volume modification [54].

5. Loss Factor

5.1. Temperature

5.1.1. Oil

When compared with the loss factor of a polar solvent such as water (6.0 at 460 MHz), the dielectric loss of oil was considered to be negligible for the whole frequency range applied. It scored a maximum of 0.366 at 468 MHz. At a constant temperature, the loss factor has slight variations with the temperature increase from 30°C to 45°C and 60°C. With further increase to 75°C, the dielectric loss factor was notably decreasing. Pace and his coworkers [74] described a similar behavior of the dielectric loss factor. At a low temperature (30°C), this could be explained by the high viscosity which extends the relaxation time period and therefore increases the loss values [18]. On the opposite side, for high temperatures, the relaxation periods are smaller and the losses are diminished. Table 7 presents the major properties obtained for water molecules.

5.1.2. Alcohol

Both methanol and ethanol have a dielectric loss that is temperature dependant. With the temperature increase, the loss factor peak was shifted towards the higher frequency value. While the peak of the loss factor at 30°C was recorded between 3000 and 4000 MHz for methanol, the loss factor peak of ethanol was reached at about 100 MHz [18]. Conformingly with Gabriel and his coworkers who found out that the loss factor peak of methanol at 20°C was observed at 3000 MHz, the peak in Muley and Bolder’s study looks to fall outside the measured range. At the lowest operating temperature of 30°C, the

highest values of loss factor were recorded. Liao et al [99]. have similar results which confirm the dependence of the loss factor on temperature.

5.1.3. Alcohol-catalyst

When changing temperature, a relevant difference was noticed in the dielectric factor of methanol and ethanol mixtures. While a peak was observed in the case of methanol and ethanol pure alcohol, the loss factor was decreasing monotonously with frequency for the alcohol catalyst. Moreover, the value of the loss was much higher for the mixture in comparison with pure alcohols for a particular frequency [18]. At lower frequencies till 2450 MHz, loss factor was decreasing with temperature for the ethanol-catalyst mixture. Going above 2450 MHz, loss factor increases with temperature. On the other hand, the loss tangent values are higher for the methanol catalyst mixture than for the ethanol catalyst mixtures. Higher heating rates are ensured by higher loss tangent values [74].

At low frequencies, the conductivity was increased by the addition of electrolyte which will increase the dielectric heating immensely. More effective microwave energy absorption and conversion of energy into heat is known to occur in solutions with higher alkali concentration. Generally, a system with higher NaOH concentration is expected to exhibit more ionic conduction in response of microwave energy due to the thermal effect of ionic conduction in microwave processes. In Muley and Boldor's study [18], the increase in the loss factor was quite significant despite the low NaOH concentration. Although studies on the alcoholic electrolytic solutions have been performed, literature on the dielectric properties of NaOH alcoholic solutions is not available [80]. In reality, the behavior of dielectric constant in water solvent is similar to Muley and Boldor's study. However, the loss factor was reported to rise with increase of frequency and NaOH concentrations [100,101].

Table 6. Dielectric properties of various alcohol mixtures.

Type/Alcohol mixture	Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Dipole moment Debye	Viscosity millipoise	Ref.
EtOH + NaOH (catalyst)	915	30	13.57	11.04	0.814				[18]
		45	15.76	10.25	0.650				[18]
		60	16.5	8.41	0.509				[18]
		75	16.32	6.92	0.424				[18]
	2450	30	7.03	6.95	0.988				[18]
		45	8.97	7.96	0.888				[18]
		60	11.39	8.06	0.707				[18]
		75	13.04	6.89	0.528				[18]
Soybean+ EtOH	433	23	16.50						[76]
		30	16.50						[76]
		40	16.20						[76]
		50	15.80						[76]
	915	23	13.80						[76]
		30	13.80						[76]

Type/Alcohol mixture	Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Dipole moment Debye	Viscosity millipoise	Ref.
		40	14.00						[76]
		50	14.10						[76]
	2450	23	8.70						[76]
		30	8.70						[76]
		40	9.00						[76]
		50	9.60						[76]
	433	23	8.40						[76]
		30	8.60						[76]
		40	8.50						[76]
		50	8.00						[76]
	915	23	7.40						[76]
		30	7.70						[76]
		40	7.70						[76]
		50	7.80						[76]
	2450	23	5.40						[76]
		30	5.30						[76]
		40	5.30						[76]
			5.40						[76]
	433		10.56	6.35					[76]
	915		6.89	5.37					[76]
	2450		4.66	2.67					[76]
	433		24.74	13.54					[76]
	915		17.16	9.84					[76]
	2450		10.60	5.42					[76]
	433		3.11	0.07					[76]
	915		3.86	0.06					[76]
	2450		3.35	0.02					[76]
	433		12.59	5.09					[76]
	915		9.27	0.19					[76]
	2450		5.67	3.49					[76]
	433		23.69	12.25					[76]
	915		16.95	8.51					[76]
	2450		11.05	4.90					[76]
	433		3.16	0.02					[76]
	915		3.04	0.23					[76]
	2450		2.95	0.00					[76]
	5800	20	9.25	11.23					[18]
	5800	30	10.46	10.96					[18]
	5800	40	11.21	12.89					[18]
	2450	20	20.25	12.51					[18]
	2450	30	22.03	12.17					[18]
	2450	40	24.22	9.04					[18]
	915	30	15.78	11.55					[18]

Type/Alcohol mixture	Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Dipole moment Debye	Viscosity millipoise	Ref.
- NaOH (Oil catalyst)	915	45	12.23	6.90					[18]
	915	60	11.19	3.38					[18]
	915	75	8.13	1.58					[18]
	2450	30	8.38	7.65					[18]
	2450	45	6.98	5.70			1.84		[18-28]
	2450	60	8.74	3.93			1.70		[18-28]
	2450	75	7.94	2.77			1.69		[18-28]
Oil + MeOH + NaOH (Oil catalyst)	915	30	18.61	21.03			1.68		[18-28]
	915	45	19.84	26.40			1.66		[18-28]
	915	60	10.55	19.43			1.66		[18-28]
	2450	30	21.03	12.38					[18]
	2450	45	26.40	14.28					[18]
EOH + NaOH	915	30	13.57	11.04	0.814				[18]
	915	45	15.76	10.25	0.650			9450	[18-28]
	915	60	16.5	8.41	0.509				[18]
	915	75	16.32	6.82	0.424				[18]
	2450	30	7.03	6.95	0.988				[18]
	2450	45	8.97	7.96	0.888				[18]
	2450	60	11.39	8.06	0.707				[18]
	2450	75	13.04	6.89	0.528				[18]
MeOH+NaOH	915	30	23.34	27.12	1.162				[18]
	915	45	21.84	30.42	1.392				[18]
	915	60	20.8	34.18	1.643				[18]
	915	75				25.4			[28]
	2450	30	17.99	16.24	0.903	28.1			[4-5]
	2450	45	19.10	16.32	0.854	29.2			[18,28]
	2450	60	19.22	16.74	0.871				[18]
2450	75								
1BOH+ BZLOL liquid mixture		25	17.55						[54]
2M2BAOH + BZLOL liquid mixture		25	5.82						[54]
3M1BAOH + BZLOL liquid mixture		25	15.22						[54]

5.2. Frequency

5.2.1. Oil

The dielectric loss factor of oil was not varying significantly for the overall frequency range as well. Results indicate only a slight decrease with the frequency increase. However, when the temperature was maintained constant, the dielectric constant had a sharp decrease with frequency change. The non-polar and non-ionic molecules that have

weak interaction with the field are prevented from reorientation at these frequency values due to the high viscosity and inertial effects [18]. Contrary, Sorichetti [73] shows an increase in the loss factor and loss tangent of oil with increasing frequency from 10 to 1000 MHz. For the frequency range going from 0.3 to 1.3 GHz, the dielectric loss of the Brazilian nut oil is recorded by Campos et al. [75] to be negligible and almost constant. A slight change in the dielectric properties is noticed when sulfuric acid was added to the mixture; at frequencies below 1 GHz the changes were more pronounced. Despite the high acid concentration in the mixture and the high value of the dielectric loss in the sulfuric acid, the dielectric loss of the mixture was enhanced but remained negligible. In 2007, Kaatze [100] suggested obtaining more accurate values of the dielectric properties by using cyclohexane instead of water as reference liquid. Although the similar trend was observed, measurements exhibited lower values with cyclohexane [75]

5.2.2. Alcohol

In order to build a design process, the optimum frequency of operation needs to be chosen among the ones permitted by the Federal Communications Commission (FCC) that allows only certain microwave frequencies of operation for industrial, medical and scientific applications (915 and 2450 MHz). In order to optimize the heating process, Muley and Boldor [18] collected data during their study that provide the exact behavior of alcohols at different temperatures and selects the most suitable frequency at which heating rates are maintained throughout the temperature range. Since the equipment is usually built for 915 and 2450 MHz, a practical selection should fall within that range.

Both methanol and ethanol have a dielectric loss that is frequency dependant. With increasing the frequency, loss factor increases until it reaches a peak where its starts decreasing gradually. At frequencies lower than 1000 MHz, loss factor values of methanol were lower than those of ethanol. With frequency increase, the decreasing values for ethanol become smaller than those of the methanol. For the frequency range adopted by Muley and Boldor [18], the values of loss factors for ethanol were too small to reach their peaks.

For a given substance, the frequency at which the loss factor is the highest is defined to be the relaxation frequency [18]. At the lower temperature of 30°C, the relaxation frequency was recorded to be 3463 MHz and 1005.6 MHz for methanol and ethanol respectively. The relaxation frequency increases very fast with temperature increase. Therefore, for a frequency considered to be a low working frequency (below 2000 MHz) dielectric heating will be higher for ethanol at lower temperatures. On the other side, at high working frequency (above 2000 MHz) and higher temperatures, the conversion of electromagnetic energy will be dominant. According to Muley and Boldor [18], the loss factor of ethanol is higher than that of methanol at frequencies lower than 1500 MHz. Therefore, ethanol is considered to cause better heating at 915 MHz compared with methanol. Pace et al. [74] have similar results which confirm the dependence of the loss factor on frequency. Because the relaxation frequency depends on the viscosity of the material, the viscosity of methanol and ethanol is calculated by Muley and Boldor [18]

according to Eq. 1 and values obtained show a variance with methanol [103] but are in close agreement with the standard viscosity data of ethanol.

5.2.3. Alcohol-catalyst

The effect on the added ions (catalyst) on the alcohol was prominent in Muley and Boldor's experiment. The loss factor had a significant increase accompanied with a change in the frequency dependence. In fact, the loss factor was decreasing asymptotically with the frequency increase.

Table 7. Dielectric properties of water molecules H₂O.

Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time δ (ps)	Ref.
2450	20			0.757	538.00	[28]
	0	87.85			17.67	[88]
	5	85.86			14.91	[88]
	10	83.92			12.68	[88]
	15	82.02			10.83	[88]
	20	80.16			9.36	[88]
	25	78.35			8.27	[88]
	30	76.57			7.28	[88]
	35	74.84			6.50	[88]
	40	73.15	0.99		5.82	[85, 88-97]
	50	69.89			4.75	[88]
	60	66.78			4.01	[88]
13.56		78.30	0.10	0.001	4.75	[28-88]
27.12		78.40	0.10	0.001	4.01	[28-88]
433.9		78.50	1.70	0.022	8.25	[28-88]
900		78.60	3.51	0.045	8.98	[28-88]
2450		77.40	9.48	0.122		[28]
	20	80.40		0.941	237.00	[28]

6. Loss Tangent and Relaxation Time

6.1. Alcohols

Alcohols molecules are able to form intermolecular hydrogen bonds; they are viewed as organic radicals with pendant hydroxyl group and are significantly miscible in water. Their dielectric properties are very close to those of water. In fact, dipole moments of aliphatic alcohols have close similarities to water as well. The relaxation time of an alcohol becomes longer with the chain length increase. A linear relationship exists between the volume and the viscosity of the calculated molecule from one part and the relaxation time from another part. In fact, the relaxation process having place in the microwave region is the result of the restricted rotation of the whole molecule with except for the benzyl case. Since isomeric alcohols like propanols and butanols have

similar relaxation times, data obtained by Gabriel et al. [28] suggested that OH group in the molecules does not influence the relaxation time significantly. On the other hand, when a phenyl ring is adjacent to the CH₂OH fragment or when a hydrogen carbon chain involves a double bond, the relaxation time decreases significantly. In such rigid molecules, it is quite possible for a more localized rotational process to be observed [28].

6.2. Aromatic compounds

The chloro-bromo and iodo-derivatives have very similar dipole moments. As the volume of the substituent increases, a progressive increase in the relaxation time is observed. The longest relaxation times are the ones recorded for nitrobenzene and benzonitrile. Because of the larger dipole moments associated with them, the intermolecular forces between molecules containing these constituents are larger which will lead to a longer relaxation time [28].

6.3. Polyalcohols

Alcohols having several OH groups attached to the carbon backbone are known to be polyalcohols. Because of their high viscosity, these compounds are able to hydrogen bond extensively which correlated with the higher relaxation time. Although they benefit from high loss tangents associated to them, they are not widely used as solvents for synthetic procedures based on microwave dielectric heating. The relaxation process for polyalcohols reaches 50-130 KJ/mol which is considerably extended compared with water and simple aliphatic alcohols having values of 15-20 KJ/mol and 16-23 KJ/mol respectively [28]. Table 8 presents the data of the polyalcohols available in the literature classified in alphabetical order as aromatic compounds, glycols, methoxy-benzine amines or aliphatic alcohols.

6.4. Water-alcohol

The interactive mixture formed is mainly characterized by its dispersion with parameters varying continuously between the parameters of the components [28]. Their dispersion may be predicted by the Debye model Eq. 3.

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau^{(1-\alpha)}} \quad (3)$$

Where ϵ , ϵ_{∞} and ϵ_s refer to the complex permittivity, the permittivity at frequencies greater than the universe and the static field permittivity respectively, ω the angular frequency α is the distribution parameter acting on the relaxation time τ .

On the mathematical level, the broadening of the dispersion can be equivalent to multiple Debye dispersions that span a distribution of relaxation times. Davidson and Cole [104] presented another model in Eq. 4 to describe the frequency dependence of some sugars and alcohols (For $\beta=1$, it reverts to Debye equation).

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau^{\beta}} \quad (4)$$

In 2012, Shcherbakov and Artemkina [88] considered a wide temperature range to measure the conductivity of water, methanol, ethanol and propanol at limiting high frequency. With the temperature increasing and reaching its critical value, both permittivity and relaxation time of the polar solvents were decreasing monotonically. However, their ratio that is referred to as the limiting high frequency goes through a maximum. The relative temperature coefficient (RTC) of static permittivity and the dipole relaxation time are strongly temperature dependant which can explains this maximum ratio. For this, the dipole relaxation time and the relative temperature coefficient (RTC) are correspondent to the maximum on the temperature dependence of the limiting HF conductivity. It is noted also that the temperature dependence of the polar solvents and ion product of water also pass through a maxima in the temperature range corresponding to the maximum limiting HF conductivities of water and alcohols [104].

The correlation of the analogous data obtained by Akhadov in 1981 [105] and by Shcherbakov and Artemkina [88] show that the discrepancy between the values obtained for the relaxation time do not exceed 3.5%.

Recently in 2014, Chaube et al., [83] have reported dielectric data of methanol after applying the CNLS fits of the spectra. When comparing their results with the literature given by [106-108], a small deviation is observed. The difference in the results may be due to the various models and methods used to obtain dielectric parameters.

Table 8. Dielectric properties of polyalcohols.

	Family Type	Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Volatile matter	Ref.
1,3-Propanediol	Glycols	2450				0.456		31.6	[28]
1,4-Butanediol	Glycols	2450				0.206		36.6	[28]
1,5-pentanediol	Glycols	2450				0.41		1215.6	[28]
1,7-Heptanediol	Glycols	2450				0.282		26.1	[28]
2-Butoxyethanol	Glycols	2450				0.651		269.8	[28]
2-Ethoxyethanol	Glycols	2450				0.276		43.6	[28]
2-Methoxyethanol	Glycols	2450				0.301		35.5	[28]
2-Methylpropan-1-ol	Aliphatic alcohols	2450				0.669		170	[28]
3 methyl-but-2-en-1-ol	Aliphatic alcohols	2450						884	[28]
Acetone	Polar solvent		20	21.4				51.5	[28]
	Polar solvent			20.7				3.2	[85]
Benzene	Aromatic compound		20	2.3					[28]
Benzyl alcohol	Aliphatic alcohols	2450						442	[28]
Bromobenzene	Aromatic compound					0.459			[28]
Carbon tetrachloride	Polar solvent		20	2.2					[28]
Chlorobenzene	Aromatic compound	2450				0.589		25.8	[28]

	Family Type	Freq. (MHz)	Temp. (°C)	ϵ_r'	ϵ_r''	Tan δ	Relaxation Time τ (ps)	Volatile matter	Ref.
Chloroform	Polar solvent		20	4.8				9.04	[28]
Di (ethylene glycol) butyl ether	Glycols	2450						78.4	[28]
Di (ethylene glycol) ethyl ether	Glycols	2450				0.303		104.0	[28]
Di (ethylene glycol) methyl ether	Glycols	2450				0.325		133.8	[5]
Dimethyl sulfoxide	Polar solvent			47.1				19.4	[88]
Dimethylacetamide	Polar solvent			38.6				15.0	[88]
Dimethylformamide	Polar solvent			37.1				13.1	[88]
Ethyleneglycol	Glycols	2450				0.783		33.55	[28]
Formamide	Polar solvent			109.5				36.9	[88]
Glycerol	Glycols	13.56		42.5	3.70	0.087			[28]
	Glycols	27.12		42.1	8.30	0.197			[28]
	Glycols	433.9		11.4	9.87	0.866			[28]
	Glycols	900		8.41	6.39	0.759			[28]
	Glycols	2450		6.33	3.42	0.54			[28]
Iodobenzene	Glycols	2450				0.31			[28]
	Aromatic compound					0.337			[28]
m-Methoxybenzylamine	Methoxy benzine amines		20	7.4					[28]
Nitrobenze	Aromatic compound	13.56		35.1	0.20	0.006			[28]
	Aromatic compound	27.12		35.2	0.40	0.011			[28]
	Aromatic compound	433.9		35.3	3.98	0.113			[28]
	Aromatic compound	900		33.7	7.73	0.229		199.0	[28]
	Aromatic compound	2450		25.2	14.70	0.584			[28]
	Aromatic compound								
	Polar solvent	27.12		78.4	0.10	0.001			[28]
N-Methylformamide	Polar solvent	433.9		78.5	1.70	0.022			[28]
	Polar solvent	900		78.6	3.51	0.045			[28]
	Polar solvent	2450		77.4	9.48	0.122			[28]
	Polar solvent			181				123.0	[85]
o-Methoxybenzylamine	Methoxy benzine amines		20	7.2					[28]
p-Methoxybenzylamine	Methoxy benzine amines		20	7.2					[28]
Propylene carbonate	Polar solvent			64.9				42.2	[88]
Trans-Hex-2-en-1-ol	Aliphatic alcohols	2450						548.0	[28]

6.5. Mixture Solvents

For binary mixtures, the relaxation time is a non-linear reciprocal function of the volume fraction of ethanol. When the volume fraction of ethanol increases, the relaxation time decreases. Highest values of relaxation time are recorded at the lowest experimental

temperature (20°C). The same decreasing pattern is observed at 30°C and 40°C with smaller values [16].

The Debye expression has brought some interesting indications related to the relaxation properties of mixture of solvents especially for the implication of volumes and the nature of the mixing process. Many attempts were executed to build into the Debye equation parameters taking into account the molecule tendency to aggregate, its varying shape and the directional nature of the hydrogen bonding interactions [23]. When the solvents mix well at the molecular level and are chemically similar, a single relaxation time is exhibited at an average position. The molar ratio of the components is reflected by the average position at which the relaxation occurs. In the case the solvents do not mix well at the molecular level, two different relaxation times will appear with values that are very close to the molar ratios of the pure solvents. Hence, the possible interpretation is that pure solvents are aggregated in micro assemblies without experiencing average environments. For this, the relaxation times are not significantly different from pure solvents and the relaxation volumes are larger than the molecular volumes. Davies [53] concludes that the relaxation processes occurs with molecules aggregation. In 1997, Lou and his coworkers [109] proposed a mixing formula for the relaxation time τ at a constant temperature, Eq. 5.

$$\ln \tau_{mix} = x_1 \ln \tau_1 + x_2 \ln \tau_2 \quad (5)$$

Where τ_{mix} denotes the relaxation time of the mixture, x_1 and x_2 denote the volumes of the two solvents 1 and 2 respectively and τ_1 , τ_2 denote the relaxation times of the two solvents 1 and 2 respectively.

In 2015, Liu and Jia [97] measured the water-MeIm mixtures in 2015. The dielectric relaxation is highly sensitive about the H-bond structures of the unlike molecules in the mixture, therefore simple mole fraction mixture law cannot reflect precisely the peak of static dielectric relaxation time. In the analysis of interactive mixtures, the presence of organic molecules may affect the water in the system so it can be referred to as bound water.

7. Results and discussions

The experiments presented through the review are a proof that the magnitudes of the dielectric constant and loss factor and their frequency dependence are essential for the interpretation of the dielectric heating phenomenon. They are considered to be fundamental parameters because they control the extent to which a substance is capable to couple with microwave radiation [28]. The relaxation time, dielectric constant and loss factor for a range of organic molecules has been discussed. The following results could be drawn out from the results

1- Temperature and Frequency

Dielectric properties were dependant on both temperature and frequency. Dielectric constant and loss factor of non polar material such as oil were not affected by temperature and frequency. Throughout the frequency range, dielectric constant values of methanol were higher than those of ethanol. Same applies for the loss factor that was higher for methanol at frequencies above 1000 MHz and lower at lower frequencies. The excess permittivity can be ordered by the temperature variation reflecting more effective dissociation of hydrogen bonded networks with temperature increase; the smallest excess permittivity value is recorded at the highest temperature.

2- Intermolecular interactions

It is very complex to analyze the behavior of the dielectric properties of an electrolytic solution such as the transesterification of Brazilian nut oil under acidic conditions. The molecular interactions between the solvents and the solute are affected by the presence of ions with their strong electric fields. In a reaction mixture, many parameters such as density, volume temperature, concentration of reactant and products are submitted to continuous changes with the proceeding of the reaction. Thus, the analytical calculation of the dielectric properties of reaction mixtures is complex due to the variety of factors to be taken into consideration. However, the knowledge of the dielectric properties of the reaction mixture facilitates the design of the microwave cavities operating at an optimum frequency [75].

Due to dipole-dipole interactions and hydrogen bonding, it is fundamental to understand the intermolecular interactions in the binary mixtures. Being a macroscopic property, the permittivity is capable of carrying information about the association of molecules. Its variation with temperature holds knowledge about the dynamics of microstructures. Regarding the alcohols mixtures, the dipole moment of the OH group generates the dipole moments of all alcohol molecules and they are nearly the same. Thus, intermolecular interactions are the main reason behind the changes of relative permittivity.

Results show that for binary mixtures of ethanol and methanol, the permittivity gradually increases with methanol concentration increasing in ethanol. On the other hand, the relaxation time decreases with increasing the concentration and temperature. These results confirm that molecular interactions with H-bonding decrease the number of effective parallel-aligned dipoles with the formation of 1:1 complexes in liquid ethanol +methanol mixtures. Moreover, the classic Debye equation requires some modification in order to calculate the dielectric properties of binary mixtures [16].

For binary mixtures, a non-linear increase of static permittivity occurs with increment of the alcohol such as methanol. In fact, a large possibility of molecules interactions may occur between the constituents. Molecular association, dipole—dipole, dipole induced interactions and hydrogen bonding are example of the common interactions that result in deviating from ideal behavior of static permittivity according to the variation in the concentrations of the mixture constituents [90].

3- Ion Salvation

For alcohol-catalyst mixture, the ion salvation effect was clearly observed which made the dielectric properties of the methanol catalyst mixtures higher than those of the ethanol catalyst mixtures throughout the frequency range. In order to develop numerical models for this microwave assisted biodiesel production process, such results should be used for better improvement and optimization [18].

4- Dipole moment

Because the ability of the dipoles to re-orientate in an applied dielectric field affects the dielectric polarization, it is noteworthy that compounds having large permanent dipole moments end by having large dielectric constants. In the contrary, due to the exposition of the material to electromagnetic radiation and rapid reverse of the electric field component, the values of the dielectric constant decrease because the smallest molecules are no longer able to rotate at a significant amount [28].

Since they don't have a permanent dipole moment, non-polar solvents don't have relaxation process in the microwave region so they become transparent to microwaves. They can be still used as coolants for removing excess heat from a microwave cavity but not as effective as microwave solvents.

As a matter of fact, the loss factor will reach its peak value when the dielectric constant reaches half of its declining value between the permittivity in a static field ϵ_s and the permittivity at frequencies greater than the universe ϵ_∞ . Since $\tan\delta$ is defined to be the ratio of the loss factor is the dielectric constant, the maximum of the tangent loss will be reached at frequencies that are slightly higher than those of the loss factor.

5- Hydrogen Bonding

From the various experiments and studies cited earlier, one can conclude that due to the hydrogen bonded aggregations and the quasi-chemical approach based on dielectric, the conventional interpretation methods of the existing experimental techniques should be more sensitive to the long correlations. However, data obtained is considered to be efficient in reconstructing the supra-molecular structure of methanol at its fluid state in the whole thermodynamic space. The measurements of the dielectric properties of ethanol close to the critical point do not reveal an anomalous behavior similar to the methanol that showed dramatic increase in density fluctuations [110]. In addition, the distribution of molecules over the number of hydrogen bonds, the size and the structure distribution of methanol aggregates which present the precise supra-molecular structural characteristics of methanol are still under debate for the present time. This should be evaluated in the future experiments and theoretical studies. More complex supra-molecular species such as branch species and rings of various sized can be included using a more strict thermodynamic treatment of the aggregation process.

The Cole-Cole model describes the dielectric spectra very well and reveals the existence of two types of H-bonds in the mixtures. The bonding energy in ethanol-ethanol pair is 19% bigger than the corresponding value in methanol ethanol pair. Moreover, the static permittivity for a binary mixture, as indicated by Bruggeman mixture formula, cannot be compared to the simple mole fraction mixture law. The Basesy-Fisher model can be used to identify the solute of water and ethanol. The type of polar ordering that depends on the extent of substitution and the average H-bond strength is given by the Luzar model. The synthesis of various models can enlighten the different aspects of the molecular interaction which contributes to a better understanding of the relaxation behavior [97].

6- Conductivity

The maximum values of the temperature dependence of limiting HF conductivities of the solvents are observed in concurrence with the solutions and solvent highest values conductivities. These results obtained by suggest a strong relationship between the conductivity of electrolyte solutions and the dielectric properties of a solvent. The nature of this relationship and its essence requires further investigation. Moreover, salts addition is increasing the conductivity of the solvents. Thus, salts addition on solvents influence dramatically their heating rates.

7- Catalysts

Microwave dielectric properties are strongly dependant on temperature and frequency. They are also significantly affected by the addition of catalysts. Muley and Boldor [18] have indicated that the mixture of oil, alcohol and catalyst results differently at room temperature before heating or when heated at a pre-determined temperature before mixing. Such a result is essential in the design of a transesterification system based on microwave.

8- Mole Fractions

Chaube et al. [83] have demonstrated a non linear decrement with increment in methanol concentration. Since the binary liquid mixture of ethylene glycol mono phenyl ether (EGMPE) and methanol have distinct relaxations, their single primary relaxation as binary mixture displayed suggests that their molecules in the liquid phase are not reacting individually to the external field but rather in a strongly co-operative way. On the other hand, the high molecular weight of the molecules of the first salvation shell (triglycerides) of the Brazilian nut oil affects significantly the low mobility of the counterions. This fact combined with the electric field high frequency led to the non-variance of the dielectric constant and loss factor of the Brazilian nut oil although the higher acidic concentrations additions.

9- Relaxation Process Time

Some important exceptions are involved in the association of the relaxation process in the microwave region with rotation of the whole molecule. First of all, as the mass of the

compound increases, the relaxation time increases particularly for solvents with significant hydrogen bonding. A more localized rotational process is possible to be observed for relatively large rigid molecules with pendant substituent. Bond rotations are observed in many compounds that contain phenyl groups. For example, the benzyl alcohol molecular volume suggests a relaxation time of more than 1000 ps for complete molecular rotation whereas its relaxation time does not exceed 188ps [28].

A relaxation time of 65ps corresponds to the standard microwave frequency for dielectric heating at 2.45 GHz. Therefore, all the alcohols having a relaxation time between 51.5 and 800 ps are considered as effective solvents for dielectric heating. In fact, their relaxation properties enable them to couple effectively with this fixed microwave frequency [18]. Having a permanent dipole moment, polar solvents have relaxation processes in the microwave regions and can be suitable candidate's solvents for microwave dielectric heating. Having a sufficiently large loss tangent, the solvent is capable of acting as effective medium for dielectric heating.

The temperature is factor that affects significantly the relaxation time of a solvent. It decreases when temperature increases. The randomized position of the molecules is enabled by their larger translational motions more quickly when the electric field is switched off. Therefore, if an organic solvent has a relaxation time that is greater than 65 ps, it will have a loss tangent that increases with temperature and more of the microwave energy is converted into thermal energy. Thermal runaway is a description of this phenomenon. Because the majority of the organic solvents have relaxation times greater than 65 ps, it won't be surprising that many organic solvents superheat in microwave cavity. This phenomenon was discussed in Baghurst and Mingos [111].

10-loss tangent

Water with 0.1 value of loss tangent at 2.45 GHz is considered to be enormously useful in food processing industry which makes all the solvents with loss tangent greater than 0.1 good bets for microwave dielectric heating experiments [112].

Changing the frequency of the microwave radiation leads to a decrease in the loss tangent of water and other organic solvents such as methanol and nitrobenzene. However, a much larger loss tangent is observed at 433.9 MHz. Hexanol and glycerol have longer relaxation times. Therefore, solvents with higher relaxation times have some advantages to use alternative microwave frequencies that are initially designed for electric heating [111].

11-High Heating Rate

High heating rates of the whole mixture could be obtained by the addition of small amounts of a polar solvent. A rapid energy transfer occurs between the polar molecules coupling with the microwave and the majority of non-polar solvent. Therefore, an

effective mechanism for introducing non-polar solvents as coupling agents into a microwave cavity is provided.

8. Conclusions

Investigating the various literatures found on the chemico-physical properties of alcohols and coupling then with appropriate dielectric properties is an indispensable task for an improved biodiesel production. Dielectric properties were dependant on both temperature and frequency. The permittivity is a macroscopic property carrying much information about the molecules associations which makes the evaluation of intermolecular interactions residing in the essence of chemical properties. The mole fraction composition, their conductivity, hydrogen bonding and ions salvations are contributors of dielectric properties determinations. Although various mathematical models were used through the literature review to determine dielectric properties variations, a single one proves not to serve for precise elaborations and only more analyzed synthesis of the existing models can lead to deeper come outs. Results of the review can be used as well for the optimization and numerical models development of biodiesel productions. The review provides a ready access database from which much information can be drawn out from the records. The classified data in the review can lead to the design a microwave heating experiment based on the dielectric parameters. This review opens new perspectives for further investigation of dielectric properties that are interesting for microwave heating studies.

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