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Alternative Methods for Fatty Acid Alkyl-Esters Production: Microwaves, Radio-Frequency and Ultrasound

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1. Introduction

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning every day because of the increase in the petroleum price and the environmental advantages (Mustafa, 2011).

Biodiesel is a mixture of mono-alkyl esters of long chain fatty acids, is an alternative fuel made from renewable sources as vegetable oils and animal fats. It is biodegradable, non-toxic, show low emission profiles and also is beneficial environmentally. (Fangrui and Milford, 1999).

Biodiesel is quite similar to petroleum-derived diesel in its main characteristics such as cetane number, energy content, viscosity, and phase changes. Biodiesel contains no petroleum products, but it is compatible with conventional diesel and can be blended in any proportion with fossil-based diesel to create a stable biodiesel blend. Therefore, biodiesel has become one of the most common biofuels in the world (Lin et al., 2011). There are four primary techniques for biodiesel production: direct use and blending of raw oils, micro-emulsions, thermal cracking and trans-esterification (Siddiquee and Rohani, 2011).

Direct use of vegetable oil and animal fats as combustible fuel is not suitable due to their high kinematic viscosity and low volatility. Furthermore, its long term use posed serious problems such as deposition, ring sticking and injector chocking in engine. Microemulsions with alcohols have been prepared to overcome the problem of high viscosity of vegetable oils. Another alternative way to produce biodiesel is through thermal cracking or pyrolysis. However, this process is rather complicated to operate and produce side products that have not commercial value. The most commonly used method for biodiesel production is trans-esterification (also known as alcoholysis) reaction in presence of a catalyst. Trans-esterification is the process of exchanging the alkoxy group of an ester compound with another alcohol (Lam et al., 2010).

Esterification is the sub category of trans-esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohols. Esterification reactions are acid-catalyzed and proceed slowly in the absence of strong acids such as sulfuric, phosphoric, sulfonic-organic acids and hydrochloric acid (Vyas et al., 2010).

The fatty acid methyl esters (FAME) are more used because of its facility of production, however, presents operating problems at low temperatures for its high content of saturated

fractions that crystallize and can block the filters of the engines. One of the alternatives to reduce the flow properties at low temperatures (FPLT) of methyl esters specially the obtained from oil palm is use alkyl esters, obtained through of trans-esterification with branched alcohols, that prevent the agglomeration and formation of crystals of these methyl esters.

Alkyl esters can be produced through trans-esterification of triglycerides, which are separated by immiscibility and higher density. (Marchetti et al., 2007; Ma and Hanna, 1999; Vicente et al., 2004)

Very few studies have been made with the aim to obtain alkyl esters and all are obtained by homogeneous catalysis (Lee et al., 1995). Yields of these reactions are very low by the high steric hindering that presenting the branched alcohols. To increase the conversion, in this work, we propose use assisted reactions by alternative methods.

The preparation of fatty acid alkylester using alternative methods, such as: electromagnetic radiation (microwave, radio frequency) and ultrasound, offers a fast, easy route to this valuable biofuel with advantages of a short reaction time, a low reactive ratio, an ease of operation a drastic reduction in the quantity of by-products, and all with reduced energy consumption.

In this work the revision of the relevant aspects of the production optimization, intrinsic effects and parameters more relevant in the synthesis and characterization of fatty acid alkylesters (biodiesel) using as alternative methods: Microwaves, Radio Frequency and Ultrasound is proposed.

2. Fatty acid alkylesters production assisted by microwaves

Electromagnetic radiation (EMR) is a form of energy exhibiting wave like behaviour as it travels through space. EMR has both electric and magnetic field components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation. Electromagnetic radiation is classified according to the frequency of its wave. In order of increasing frequency and decreasing wavelength, these are radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays (Serway and Jewett, 2004).

Microwaves belong to the portion of the electromagnetic spectrum with wavelengths from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz.

Within this portion of the electromagnetic spectrum there are frequencies that are used for cellular phones, radar, and television satellite communications. For microwave heating, two frequencies, reserved by the Federal Communications Commission (FCC) for industrial, scientific, and medical (ISM) purposes are commonly used for microwave heating. The two most commonly used frequencies are 0.915 and 2.45 GHz. Recently, microwave furnaces that allow processing at variable frequencies from 0.9 to 18 GHz have been developed for material processing (Thostenson and Chou, 1999). Microwave radiation was discovered as a heating method in 1946, with the first commercial domestic microwaves being introduced in the 1950s. The first commercial microwave for laboratory utilization was recognized in 1978 (Gedye et al., 1986; Giguere et al., 1986).

Over the last decade, microwave dielectric heating as an environmentally benign process has developed into a highly valuable technique, offering an efficient alternative energy source for numerous chemical reactions and processes. It has many advantages compared to conventional oil-bath heating, such as non-contact heating, energy transfer instead of heat

transfer, higher heating rate, rapid start-up and stopping of the heating, uniform heating with minimal thermal gradients, selective heating properties, reverse thermal effects (heating starting from the interior of the material body), energy savings and higher yields in shorter reaction time (Tierney and Lidstrom, 2005). Microwave heating is based dielectric heating, the ability of some polar liquids and solids to absorb and convert microwave energy into heat. In this context, a significant property is the mobility of the dipoles by either ionic conduction or dipolar polarization and the ability to orient them according to the direction of the electric field. The orientation of the dipoles changes with the magnitude and the direction of the electric field. Molecules that have a permanent dipole moment are able to align themselves through rotation, completely or at least partly, with the direction of the field. Therefore, energy is lost in the form of heat through molecular friction and dielectric loss (Loupy, 2002). The amount of heat produced by this process is directly related to the capability of the matrix to align itself with the frequency of the applied electric field. If the dipole does not have enough time to realign, or reorients too rapidly with the applied field, no heating occurs (Kappe, 2004).

The production of biodiesel via the conventional heating system appears to be inefficient due to the fact that the heat energy is transferred to the reactants through conduction, convection and radiation from the surface of the reactor. Hence, conventional heating requires longer reaction time and a larger amount of heat energy to obtain a satisfactory biodiesel. The replacement of conventional heating by microwave radiation for the transesterification process is expected to shorten the reaction time due to the transfer of heat directly to the reactants. The microwave radiation during the transesterification process is expected to create (i) an alignment of polar molecules such as alcohols with a continuously changing magnetic field generated by microwaves and (ii) molecular friction due to which heat will be generated (Yaakob et al., 2009).

The involvement of such heterogeneous catalytic systems under microwave conditions represents an innovative approach with processing advantages. These solid-state catalysts find scope in the context of green chemistry development as they are active in solvent free or dry media synthesis, with potential advantages in terms of separation, recovery post-reaction and recycling assays. The creation of hot spots, specific under MW conditions, is typically utilized for energy saving as improved yields and selectivities are recorded after shorten reaction times at lower nominal temperatures. These hot spots may induce a re-organization of the catalyst under microwave conditions and are probably responsible for reaction rates and selectivity enhancement (compared to conventional heating at the same nominal temperature) (Richela et al., 2011)

2.1 Esterification reactions assisted by MW

The esterification reaction is a slow equilibrium, and can be catalyzed by Brønsted acids such as sulfuric acid. The main problem is the generation of highly acidic waste causing a serious environmental problem, and to reduce this problem have been used alternative heterogeneous catalysts and microwaves as a heating source to promote and increase the yielding. Algunos catalizadores empleados son: scandium triflate and bismuth triflate (Socha and Sello, 2010), sulfated zirconia (Kim et al., 2011a), niobium oxide (Melo et al., 2010), entre otros.

The temperature presented a pronounced effect on the conversion, following an exponential dependence. The results for a distinct molar ratio of alcohol/fatty acid indicated that the

increase of this parameter lead to a decrease on the reaction conversion. In general, the esterification reaction under microwave irradiation yielded similar results to those obtained with the conventional heating but with very fast heating rates (Melo et al., 2009). The pulsed microwaves with repetitive strong power could enhance the efficiency of biodiesel production relative to the use of continuous microwave with mild power (Kim et al., 2011b). Electric energy consumption for the microwave heating in this accelerated esterification was only 67% of estimated minimum heat energy demand because of significantly reduced reaction time (Kim et al., 2011a).

For oils with a high content of free fatty acid FFA as palm oil, has been proposed obtain alkyl ester from crude palm oil (CPO), using microwaves like heating source, in a process of two stages by means of homogeneous and heterogeneous catalysis; the first stage (esterification), was made using sulfuric acid and Dowex 50X2, Amberlyst 15 and Amberlite IR-120 resin catalysts, to diminish the acid value of the oil, avoiding the soap formation and facilitating the separation of the phases. In these works has been reported the obtaining of alkyl ester using alcohols non-conventional such as: ethanol (EtOH) (Suppalakpanya et al., 2010a, 2010b), isopropyl (IsoprOH), isobutyl (IsobuOH), 2-butyl (2-BuOH) and Isopentyl (IsopentOH) alcohols (Mazo and Rios, 2010a; Mazo and Rios, 2010b), where was found that that the acidity order obtained for the catalysts is Dowex < Amberlite < Amberlyst, and the order for the alcohols: Methanol < isopropyl alcohol < isobutyl alcohol < 2-butyl alcohol < isopentyl alcohol, because Dowex microreticular resin presents the lowest divinylbenzene (2%), which has a lower cross-linking that produces a high expansion of the resin in a polar medium, and the resin can expand their pores up to 400%, enabling the income of the voluminous substrate (FFA) and its protonation. Amberlyst 15 macroreticular resin is activated due to its surface area, and the protons located on the outer surface seem that catalyse the esterification because the interiors are inaccessible due to high cross-linking. The reaction is favoured with the increasing of polarity of solvents.

Table 1 shows the work carried out for bio-diesel production by esterification of FFA under different conditions using microwave irradiation.

2.2 Transesterification reactions assisted by MW

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature and can be produced locally and in environmentally friendly ways. Edible vegetable oils such as canola and soybean oil in the USA, palm oil in Malaysia, rapeseed oil in Europe and corn oil have been used for biodiesel production and found to be good diesel substitutes. Non-edible vegetable oils, such as Pongamia pinnata (Karanja or Honge), Jatropha curcas (Jatropha or Ratanjyote), Madhuca iondica (Mahua) and Castor Oil have also been found to be suitable for biodiesel production (Yusuf et al., 2011).

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol (with or without catalyst) to form esters and glycerol. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side (Fangrui and Milford, 1999). Under Transesterification reaction with alcohol the first step is the conversion of triglycerides to diglycerides, which is followed by the subsequent conversion of higher glycerides to lower glycerides and then to glycerol, yielding one methyl ester molecule from each glyceride at each step (Hideki et al., 2001).

FFA	Catalyst	Catalyst amount (%)	Alcohol	Oil to alcohol molar ratio	Microwave reaction conditions	Ester conversion (%)	Ref.
Oleic Linoleic	- -	- -	MeOH EtOH MeOH	1:10	Synthos 3000-Anton Paar. 1400W. 30min, 200°C	51.8 31.5 49.6	(Melo et al., 2009)
Oleic	Sulfated Zirconia	5 wt	MeOH	1:20	Experimental MW heating system 20min, 60°C	90.0	(Kim et al., 2011a)
Oleic	Amberlyst 15 dry	10 wt	MeOH	1:20	Experimental MW heating system. Pulsed MW. 15min, 60°C	66.1	(Kim et al., 2011b)
Oleic	Niobium Oxide Sulfated Zirconia	5 wt	MeOH	1:10	Synthos 3000-Anton Paar. 1400W. 20min, 200°C	68.0 68.7	(Melo et al., 2010)
Linoleic Linoleic Oleic Oleic Myristic Myristic Palmitic Palmitic	$Sc(OT_f)_3$ $Bi(OT_f)_3$ $Sc(OT_f)_3$ $Bi(OT_f)_3$ $Sc(OT_f)_3$ $Bi(OT_f)_3$ $Sc(OT_f)_3$ $Bi(OT_f)_3$	1%mol	MeOH	48 eq	Biotage MW reactor. 1min, 150°C	97.0 98.0 100.0 88.0 98.0 90.0 100.0 99.0	(Socha and Sello, 2010)
FFA Palm Oil	H_2SO_4	2.5%wt Oil	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:8	Domestic MW 1000W 60 min, 60°C 60 min, 75°C 60 min, 105°C 60 min, 90°C 60 min, 115°C	99.8 99.8 96.2 95.5 90.8	(Mazo and Rios, 2010a)
FFA Palm Oil	H_2SO_4	4% wt FFA	EtOH	1:24	Domestic MW 800W 60 min, 70°C	87.7	(Suppalakpanya et al., 2010a and b)
FFA Palm Oil	Dowex 50X2	10%wt Oil	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:20	Domestic MW 1000W 60 min, 60°C 60 min, 75°C 60 min, 105°C 60 min, 90°C 60 min, 115°C	95.6 86.2 82.8 78.5 77.7	(Mazo and Rios, 2010b)
FFA Palm Oil	Amberlite IR120	10%wt Oil	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:20	Domestic MW 1000W 60 min, 60°C 60 min, 75°C 60 min, 105°C 60 min, 90°C 60 min, 115°C	91.3 85.1 81.4 74.8 74.1	(Mazo and Rios, 2010b)
FFA Palm Oil	Amberlyst15	10%wt Oil	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:20	Domestic MW 1000W 60 min, 60°C 60 min, 75°C 60 min, 105°C 60 min, 90°C 60 min, 115°C	91.4 84.7 80.6 66.8 73.5	(Mazo and Rios, 2010b)

Table 1. Microwave assisted esterification.

Several examples of microwave irradiated transesterification methods have been reported using homogenous alkali catalyst (Kumar et al., 2011; Azcan and Danisman, 2008), acid catalyst (Mazo and Rios, 2010a) and heterogeneous alkali catalyst (Patil et al., 2011), heterogeneous acid catalyst (Yuan et al., 2009) and enzymatic (Yu et al., 2010).

Microwave synthesis is not easily scalable from laboratory small-scale synthesis to industrial multi kilogram production. The most significant limitation of the scale up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another reason for rejecting microwave reactors in industry (Groisman and Aharon, 2008).

The preparation of biodiesel using a scientific microwave apparatus offers a fast, easy route to this valuable biofuel with advantages of a short reaction time, a low oil/methanol ratio, and an ease of operation. The methodology allows for the reaction to be run under atmospheric conditions; it is complete in a matter of a few minutes and can be performed on batch scales up to 3 kg of oil at a time (Leadbeater and Stencel, 2006).

The continuous-flow preparation of biodiesel using a commercially available scientific microwave apparatus offers a fast, easy route to this valuable biofuel. The methodology allows for the reaction to be run under atmospheric conditions and performed at flow rates of up to 7.2 L/min using a 4 L reaction vessel. Energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy-efficient than using a conventional heated apparatus (Barnard et al., 2007).

Few studies report the use of alcohols different to methanol. Alcohols more used are ethanol and butanol, and the latter is a versatile and sustainable platform chemical that can be produced from a variety of waste biomass sources. The emergence of new technologies for the production of fuels and chemicals from butanol will allow it to be a significant component of a necessarily dynamic and multifaceted solution to the current global energy crisis. Recent work has shown that butanol is a potential gasoline replacement that can also be blended in significant quantities with conventional diesel fuel (Harvey and Meylemans, 2011).

Table 2 shows the work carried out for bio-diesel production from various feedstocks, catalysis and alcohols under different conditions using microwave irradiation.

Oil	Catalyst	Catalyst amount (%wt)	Alcohol	Oil to alcohol molar ratio	Microwave reaction conditions	Ester conversion (%)	Ref.
Castor	50% H_2SO_4/C	5	MeOH	1:12	MAS-1 Shanghai Sineo MW 65°C, 60 min	94	(Yuan et al., 2009)
Castor	SiO_2/50%H_2SO_4 SiO_2/50%H_2SO_4 Al_2O_3/50%KOH	10 10 10	MeOH EtOH MeOH	1:6	Domestic MW 540W 60°C, 30 min 60°C, 20 min 60°C, 5 min	95 95 95	(Perin et al., 2008)
Jatropha	KOH	1.5	MeOH	1:7.5	Start Synth-Milestone 1200W 65°C, 2 min	99	(Shakinaz et al., 2010)
Waste frying	SrO $Sr(OH)_2$	1.5	MeOH	1:4 wt	Domestic MW 900W 60°C, 40 s	99 97	(Koberg et al., 2011)

Pongamia Pinnata	NaOH KOH	0.5 1.0	MeOH	1:6	Start Synth-Milestone 1200W 60°C, 7 min	95.3 96.0	(Kumar et al., 2011)
Rapeseed	NaOH KOH	1.0	MeOH	-	Start Synth-Milestone 1200W 60°C, 5 min	91.7 90.8	(Azcan and Danisman, 2008)
Soybean	Nano CaO	3.0	MeOH	1:7	ETHOS900 Milestone 900W 65°C, 60 min	96.6	(Hsiao et al., 2011)
Soybean	Novozym 435	3.0	MeOH	1:6	MCR-3 Shanghai JieSi 800W 40°C, 12h	94.0	Yu et al., 2010)
Canola	$ZnO/La_2O_2CO_3$	1.0	MeOH	1:1 wt	Biotage MW reactor. <100°C, 5 min	>95	(Jin et al., 2011)
Camelina	BaO SrO	1.5 2.0	MeOH	1:9 1:12	Domestic MW 800W 100°C, 4 min 60°C, 4 min	95 78	(Patil et al., 2011)
Camelina	NaOH KOH BaO SrO $BaCl_2/AA$ $SrCl_2/AA$	0.5 1.0 1.5 2.0 2.0 2.0	MeOH	1:9	Domestic MW 800W 60°C, 60 s 60°C, 60 s 60°C, 4 min 60°C, 4 min 60°C, 5 min 60°C, 5 min	95 85 95 95 27 20	(Patil et al., 2010)
Safflower	NaOH	1.0	MeOH	1:10	Start labstation-Milestone 60°C, 6 min	98.4	(Duz et al., 2011)
Soybean Rice Bran	NaOH	0.6	EtOH	1:5	ETHOS E-Milestone 73°C, 10 min	99.25 99.34	(Terigar et al., 2010)
Rapeseed	KOH	1.0	ButOH	1:4	MARS CEM Corp. 117°C, 30 min	100	(Geuens et al., 2008)
Soybean	H_2SO_4 KOH	5.0 1.0	ButOH ButOH	1:6	CEM Discover 300W CEM MARS 1600W 100°C, 15 min 120°C, 1 min	93 93	(Leadbeater et al., 2008)
Jatropha Waste frying	NaOH	1.0	MeOH	1:12	MW650 Aurora Instruments MW discovery 65°C, 7 min	89.7 88.63	(Yaakob et al., 2009)
Palm	H_2SO_4	3.0	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:30	Domestic MW 1000W 60°C, 5h 75°C, 5h 105°C, 5h 90°C, 5h 115°C, 5h	49.40 62.39 67.39 62.39 75.00	(Mazo and Rios, 2010a)

Palm	$NaOCH_3$	0.9	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:27	Domestic MW 1000W 60°C, 1h 75°C, 1h 105°C, 1h 90°C, 1h 115°C, 1h	 99.9 99.87 88.39 83.19 81.63	(Mazo and Rios, 2010a)
Palm	K_2CO_3	3.0	MeOH IsoprOH IsoBuOH 2-BuOH IsopentOH	1:20	Domestic MW 1000W 60°C, 3h 75°C, 3h 105°C, 3h 90°C, 3h 115°C, 3h	 8.63 49.51 67.59 52.00 54.59	(Mazo and Rios, 2010b)
Palm	KOH	1.5	EtOH	1:4	Domestic MW 800W 70°C, 5 min	97.4	(Suppalakpanya et al., 2010a)

Table 2. Microwave assisted transesterification.

2.3 Optimization production biodiesel under MW irradiation

Some examples about the obtaining of biodiesel making a response surface methodology (RSM) was used to analyze the influence of the process variables (oil to methanol ratio, catalyst concentration, and reaction time) on the fatty acid methyl ester conversion, are shown in Table 3, where is confirmed that the microwave energy has a significant effect on esterification and transesterification reactions.

Oil	Catalyst	Catalyst amount (%wt)	Alcohol	Oil to alcohol molar ratio	Microwave reaction conditions	Ester conversion (%)	Ref.
Dry algae	KOH	2.0	MeOH	1:12 (wt/vol)	Domestic MW 800W 60°C, 4min	64.18	(Patil et al., 2011)
Macauba	Novozyme 435 Lipozyme IM	2.5	EtOH	1:9	Synthos 3000-Anton Paar. 1400W. 30°C, 15min	45.2 22.9	(Nogueira et al., 2010)
Pongamia pinnata	Esterification: H_2SO_4 Transesterification: KOH	3.73 1.33	MeOH MeOH	33.83% (w/w) 33.4% (w/w)	Domestic MW 800W 60°C, 190s 60°C, 150s	87.4 89.9	(Venkatesh et al., 2011)

Table 3. Recent examples of optimization of reaction conditions a for production of biodiesel from various feedstocks using response surface methodology

3. Fatty acid alkylesters production assisted by radio frequency

Radio waves, whose wavelengths range from more than 104 m to about 0.1 m, are the result of charges accelerating through conducting wires. They are generated by such electronic devices as LC oscillators and are used in radio and television communication systems (Serway and Jewett, 2004).

Radio frequency (RF) heating is a promising dielectric heating technology which provides fast heat generation through a direct interaction between an RF electromagnetic field and the object being heated (Piyasena et al., 2003). Compared to microwave heating, a popular

dielectric heating technology, RF heating systems are simpler to configure and have a higher conversion efficiency of electricity to electromagnetic power (Wang et al., 2003). Moreover, RF energy has deeper penetration into a wide array of materials than microwave energy, increasing feasibility of RF heating for industrial scale applications.
Very few publications have been obtained by this alternative heating method, which use a RF heating apparatus (SO6B; Strayfield Fastran, UK). The distance between the two electrodes was fixed at 15 cm. A 150-mL conical flask coupled with a water-cooling reflux condenser was used as a reactor. Schematic diagram and photograph are shown in Fig. 1.

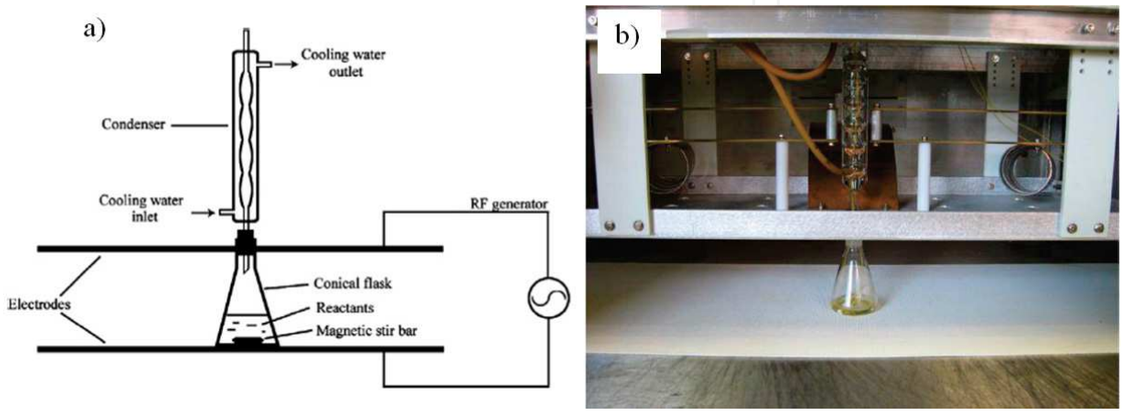

Fig. 1. a) Schematic diagram of RF heating apparatus (Lui et al., 2010) and b) Photograph of RF heating apparatus (Lui et al., 2008).

Applications to obtaining biodiese using different oils, reaction conditions and catalysts are described below:

3.1 Esterification reactions assisted by RF

Efficient biodiesel conversion from waste cooking oil with high free fatty acids (FFAs) was achieved via a two-stage procedure (an acid-catalyzed esterification followed by an alkali-catalyzed transesterification) assisted by radio frequency (RF) heating. In the first stage, with only 8-min RF heating the acid number of the waste cooking oil was reduced from 68.2 to 1.64 mg KOH/g by reacting with 3.0% H_2SO_4 (w/w, based on oil) and 0.8:1 methanol (weight ratio to waste oil). Then, in the second stage, the esterification product (primarily consisting of triglycerides and fatty acid methyl esters) reacted with 0.91% NaOH (w/w, based on triglycerides) and 14.2:1 methanol (molar ratio to triglycerides) under RF heating for 5 min, and an overall conversion rate of 98.8 ± 0.1% was achieved. Response surface methodology was employed to evaluate the effects of RF heating time, H_2SO_4 dose and methanol/oil weight ratio on the acid-catalyzed esterification. A significant positive interaction between RF heating time and H_2SO_4 concentration on the esterification was observed (Lui et al., 2010).

3.2 Transesterification reactions assisted by RF

Efficient biodiesel production from beef tallow was achieved with radio frequency (RF) heating. A conversion rate of 96.3% was obtained with a NaOH concentration of 0.6% (based

on tallow), an RF heating for 5 min, and a methanol/tallow molar ratio of 9:1. Response surface methodology was employed to evaluate the influence of NaOH dose, RF heating time, and methanol/tallow ratio. The alkaline concentration showed the largest positive impact on the conversion rate. Similar fast conversion from canola oil to biodiesel was achieved in our previous work, indicating that RF heating, as an accelerating technique for biodiesel production, had a large applying area (Lui et al., 2011).

3.3 Optimization production biodiesel under RF irradiation

Fast transesterification of canola oil and methanol for biodiesel production was achieved using radio frequency (RF) heating. The conversion rate of oil to biodiesel reached 97.3% with RF heating for 3 min, a NaOH concentration (based on oil) of 1.0%, and a methanol/oil molar ratio of 9:1. A central composite design (CCD) and response surface methodology (RSM) were employed to evaluate the impact of RF heating time, NaOH concentration, and molar ratio of methanol to oil on conversion efficiency. Experimental results showed that the three factors all significantly affected the conversion rate. NaOH concentration had the largest influence, with the effect being more pronounced at lower (0.2-0.6%, based on weight of oil) concentration. No evident interaction among the three factors was observed. RF heating efficiency was primarily related to the amount of NaOH and methanol. The scale of the experiment was increased by five times (from 20 to 100 g oil per batch) without decrease of the conversion rate, indicating the scale-up potential of RF heating for biodiesel production (Lui et al., 2008).

4. Fatty acid alkylesters production assisted by ultrasound

Sound waves are the most common example of longitudinal waves. They travel through any material medium with a speed that depends on the properties of the medium. As the waves travel through air, the elements of air vibrate to produce changes in density and pressure along the direction of motion of the wave. If the source of the sound waves vibrates sinusoidally, the pressure variations are also sinusoidal (Serway and Jewett, 2004).

Sound waves are divided into three categories that cover different frequency ranges

(1) Audible waves lie within the range of sensitivity of the human ear. They can be generated in a variety of ways, such as by musical instruments, human voices, or loudspeakers. (2) Infrasonic waves have frequencies below the audible range. Elephants can use infrasonic waves to communicate with each other, even when separated by many kilometers. (3) Ultrasonic waves have frequencies above the audible range. You may have used a "silent" whistle to retrieve your dog. The ultrasonic sound it emits is easily heard by dogs, although humans cannot detect it at all. Ultrasonic waves are also used in medical imaging (Serway and Jewett, 2004).

Sonochemistry is a branch of chemical research dealing with the chemical effects and applications of ultrasonic waves, that is, sound with frequencies above 20 kHz that lie beyond the upper limit of human hearing. The development of ultrasound in organic synthesis began on 1930 when Richards and Loomis, 1927, applied ultrasound (100-500 KHz) in organic synthesis for determine the effect on the solubility of gases for first time. Developments were very slow, then Luche and Damiano, 1980, reported metal activation reactions using ultrasound probes. Thereafter, reaction systems using US to speed up chemical reactions have been developed.

A low frequency ultrasonic irradiation could be useful for transesterification of triglyceride with alcohol. Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction (Singh et al., 2007). Ultrasonication increases the chemical reaction speed and yield of the transesterification of vegetable oils and animal fats into biodiesel. Ultrasonic assisted transesterification method presents advantages such as shorter reaction time and less energy consumption than the conventional mechanical stirring method, efficient molar ratio of methanol to TG, and simplicity (Ji et al., 2006; Siatis et al., 2006).

Many researchers have tried to solve the mass-transfer limitation problem in biodiesel synthesis using ultrasonic cavitation and hydrodynamic cavitation. Cavitation has been shown to efficiently speed up the transesterification reaction because it simultaneously supplies heating as well as the stirring effect as a result of jet formation on bubble collapse. Cavitation is basically the formation, growth, and implosive collapse of gas or vapour filled microbubbles and can be induced acoustically (using ultrasound) or hydrodynamically in a body of liquid. The collapse of these bubbles lead to local transient high temperatures (g 5000 K) and pressures (g 1000 atm), resulting in the generation of highly reactive species, such as OH•, HO_2•, and H• radicals in water. Cavitation effects also increase the mass and heat transfers in a medium and accelerate the reaction rates and yields (Mahamuni and Adewuyi, 2009).

Main factors that vary the yielding in the production of biodiesel using US are:

Effect of Ultrasonic Frequency on Biodiesel Yield. The frequency of the ultrasound has a significant effect on the cavitation process because it alters the critical size of the cavitation bubble, which in turn changes the intensity of the collapse of the cavitation bubbles.

Effect of Ultrasonic Power on Biodiesel Yield. It is well-known that as the ultrasonic power increases, the size of the cavitation bubbles increase leading to more intense collapse of bubble, which causes better emulsion formation of oil and methanol resulting into higher interfacial surface area for mass transfer and hence the higher biodiesel yield. The BD yield increased with increasing ultrasonic power from 150 to 450 W, but the ME content decreased at ultrasonic powers over 450 W. This is due to the decrease of the real irradiation time caused by the increase in the pulse interval required for tuning the temperature due to the extension of the irradiation power (Lee et al., 2011).

Effect of Catalyst Loading. As the amount of KOH increases, the concentration of methoxide anions, which are responsible for nucleophilic attack on the triglyceride molecules to produce biodiesel, also increase, resulting in higher biodiesel yield.

Effect of Oil/Methanol Molar Ratio. As oil and methanol are not miscible into each other, they form a heterogeneous reaction mixture and mass transfer between these two phases becomes important for the transesterification reaction. The presence of ultrasound can help increase the mass transfer between the two phases by the formation of a fine emulsion, which increases the interfacial area between the two phases. Ultrasound can also increase the mass transfer coefficient due to the presence of acoustic streaming and jet formations at the end of cavitation bubble collapse near the phase boundary between oil and methanol phases.

As shown in Fig. 2, the factors with more contribution to the production of biodiesel are ultrasonic power and catalyst loading, then oil/methanol molar ratio and finally, the frequency.

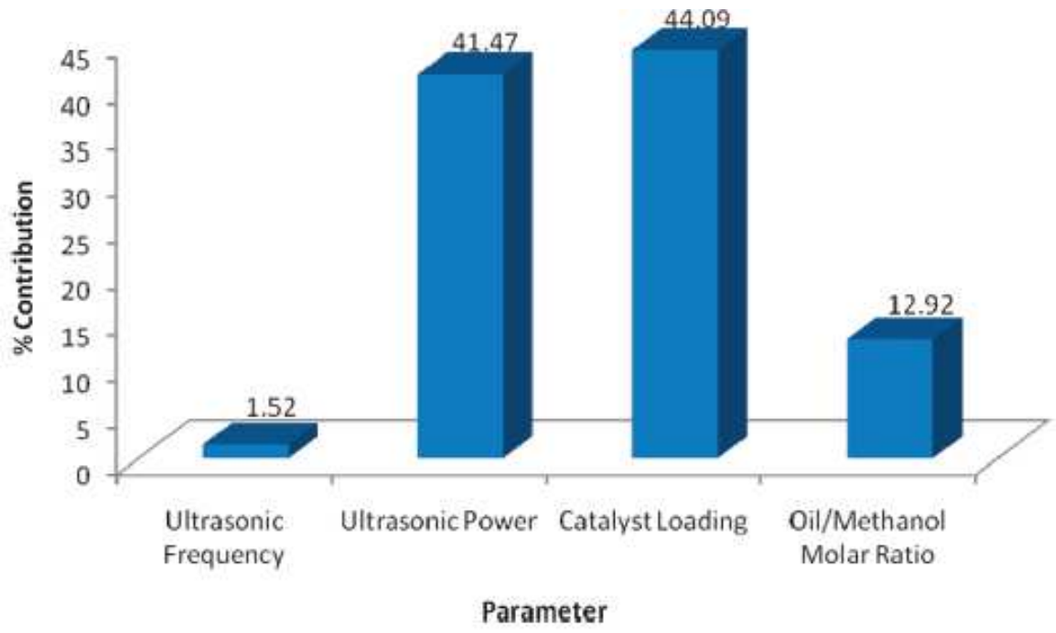

Fig. 2. Percentage contribution of the factors contributing to the production of biodiesel by ultrasound

4.1 Esterification reactions assisted by ultrasound

Not found reports of this methodology for the esterification reaction in the obtaining of biodiesel.

4.2 Transesterification reactions assisted by ultrasound

The works that use US in the transesterificatication reaction for the obtaining biodiesel use edible oils as soybean, triolein, palm, canola, fish and coconut. Also, use no edible oil as Jatropha, homogeneous basic catalysts as KOH, and heterogeneous basic catalysts as CaO, SrO, BaO, Na/SiO_2 and Novozym435 enzymes and lipase. Table 8 shows the work carried out for bio-diesel production from various feedstocks under different conditions using ultrasound irradiation.

The equipments used are conformed by transducer, cleaner and probe used in batch processes. In recent years, chemistry in flowing systems has become more prominent as a method of carrying out chemical transformations, ranging in scale from microchemistry up to kilogram-scale processes. Compared to classic batch ultrasound reactors, flow reactors stand out for their greater efficiency and flexibility as well as lower energy consumption. Cintas et al., 2010, developed a new ultrasonic flow reactor, a pilot system well suited for reaction scale up. This was applied to the transesterification of soybean oil with methanol for biodiesel production. This reaction is mass-transfer-limited initially because the two reactants are immiscible with each other, then because the glycerol phase separates together with most of the catalyst (Na or K methoxide). In our reactor a mixture of oil (1.6 L), methanol and sodium methoxide 30% in methanol (wt/wt ratio 80:19.5:0.5, respectively) was fully transesterified at about 45 C in 1 h (21.5 kHz, 600 W, flow rate 55 mL/min). The same result could be achieved together with a considerable reduction in energy

consumption, by a two-step procedure: first a conventional heating under mechanical stirring (30 min at 45°C), followed by ultrasound irradiation at the same temperature (35 min, 600 W, flow rate 55 mL/min). Our studies confirmed that high-throughput ultrasound applications definitively require flow reactors (Cintas et al., 2010). The detailed scheme of the system is showed in Fig. 3.

Oil	Catalyst	Catalyst amount (%wt)	Alcohol	Oil to Alcohol molar ratio	Ultrasonic reaction condition	Source of ultrasound	Ester conversion (%)	Ref
Soybean	KOH	0.5	MeOH	1:6	611kHz, 139W, 26°C, 30min	Multifrequency transducer UES300C sonochemist	90	(Mahamuni and Adewuyi, 2009)
Triolein	KOH	1.0	MeOH	1:6	40kHz, 1200W, 25°C, 30min	Honda electronic cleaner	99	(Hanh et al., 2008)
Soybean	Novozym 435	6.0	MeOH	1:6	40kHz, 500W (50%), 40°C, 4h 0.5%v/v tert-amyl alcohol/oil	Ultrasonic bath KQ500DV Kunshan	96	(Yu et al., 2010)
Soybean	NaOCH3	20g (30% in MeOH)	MeOH	1.6L:80g MeOH	21.5kHz,600W, 45°C, 1h Flow 55mL/min	3 transducer (21.5kHz)	90	(Cintas et al., 2010)
Jatropha	Na/SiO_2	3.0	MeOH	1:9	24kHz, 200W, 15min	UP200S Hielscher ultrasonic Gmblt	98.53	(Kumar et al., 2010a)
Canola Soybean Corn	KOH	1.0	MeOH	1:6	450W, 55°C, 30min	Probe type VCX-600	98 97 95	(Lee et al., 2011)
Jatropha	Lipase Chromobacterium viscosum	5.0	MeOH		0.7s, 100W/m3, 30min	UP200S Hielscher ultrasonic Gmblt	84.5	(Kumar et al., 2011)
Palm	KOH	20.0	MeOH		Petroleum ether Ethyl methyl ketone 47kHz, 340W, 60°C, 2h	Water bath Bransonic cleaner	75.2 60	(Boey et al., 2011)
Palm	CaO SrO BaO	3.0	MeOH		20kHz, 200W (50%), 65°C, 60min	Transducer and probe	77.3 95.2 95.2	(Mootabadi et al., 2010)
Waste frying	KOH	First stage 0.7 Second stage 0.3	MeOH		20kHz, 25°C, 5min	Horn transducer	81 99	(Thanh et al., 2010)
Fish	$NaOC_2H_5$	0.8	EtOH		35kHz, 20kHz, 20°C, 30min	Bath Probe	95 95	(Armenta et al., 2007)
Coconut	KOH	0.75	EtOH		24kHz, 200W, 7min	UP200S Hielscher ultrasonic Gmblt	98	(Kumar et al., 2010b)

Table 4. Ultrasound assisted transesterification

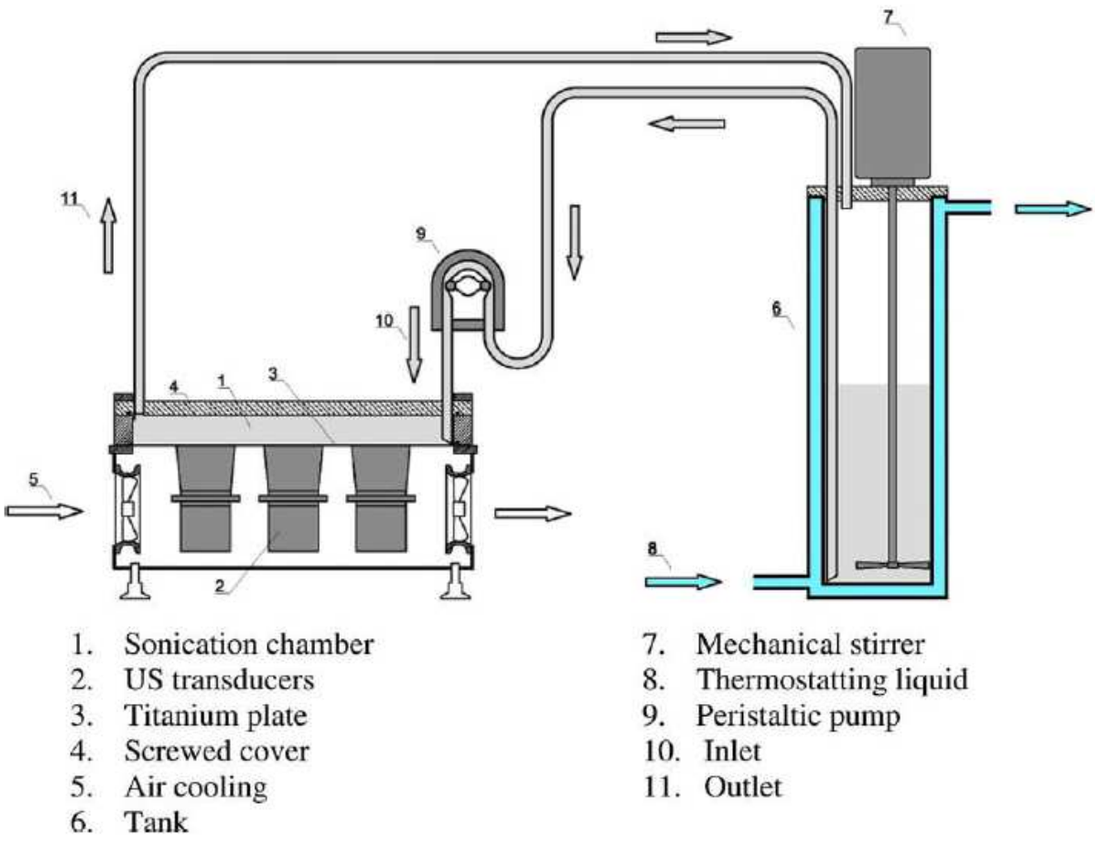

Fig. 3. Detailed scheme of the system for biodiesel production (Cintas et al., 2010).

4.3 Optimization production biodiesel under ultrasound

This paper utilizes the Taguchi optimization methodology (L9 orthogonal array) to optimize various parameters for the ultrasound-assisted, KOH-catalyzed transesterification of soybean oil with methanol. The statistical tool used in the Taguchi method to analyze the results is the analysis of variance (ANOVA). The optimum conditions are determined to be 581 kHz, 143 W, 0.75% (w/w) KOH loading at 1:6 oil/methanol molar ratio, resulting in more than 92.5% biodiesel yield in less than 30 min. Confirmation experiments have been performed to prove the effectiveness of the Taguchi technique after the optimum levels of process parameters are determined. (Mahamuni et al., 2010).

5. Future development

Most reports are aimed to the obtaining of biofuels of first-generation. However, these methodologies of synthesis are directed to the obtaining of fuels of second and third generation to promote sustainable chemistry and the use of renewable raw materials that not compete with foods.

The coupling of biotechnological processes with these new technologies would allow the improvement of existing processes, reducing time and increasing the production.

The development of additives that improve the properties of biodiesel would allow an improvement in cold flow properties for biodiesel from oils as palm, which can be obtained with these technologies.

Efforts must concentrate on developing these technologies at pilot and industrial levels, with continuous processes, low energy consumption, economic and insurance.

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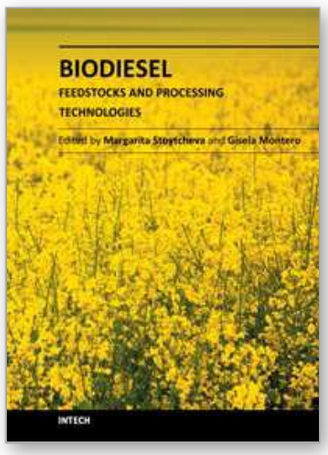

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The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate it processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

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