TRANSESTERIFICATION OF RAPESEED OIL WITH METHANOL IN THE PRESENCE OF VARIOUS CO-SOLVENTS

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SUMMARY: In this study, transesterification of rapeseed oil using various co-solvents (diethyl ether (DEE), dibutyl ether (diBE), tert-butyl methyl ether (tBME), diisopropyl ether (diIPE), tetrahydrofuran (THF), and acetone) was studied. The variables affecting the ester yield during transesterification reaction, such as catalyst content, methanol:oil molar ratio, methanol:co-solvent molar ratio, co-solvent type, catalysts type, agitation rate and reaction temperature were investigated. The process was monitored by gas chromatography, determining the concentration of the methyl esters. Biodiesel was characterized according to ISO norms. Among the studied co-solvents, the DEE and tBME take to the best results, however diIPE, diBE and acetone hardly improve the obtained results using only methanol. Within the range of studied variability, the rest of variables do not exercise a very significant influence. The best results are obtained with 0.7 % of KOH, a molar ratio methanol/oil of 9:1, a molar ratio co-solvent/methanol 1:1, an agitation rate of 700 rpm and a temperature of 30 ºC.

1. INTRODUCTION

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability, increasing emissions of combustion-generated pollutants, and their augmented costs will make biomass sources more attractive (Basha, Gopal et al., 2009; Demirbas, 2009; Singh and Singh, 2010).

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel, as an alternative fuel for internal combustion engines, is defined as a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C14–C22) esters of short-chain alcohols, primarily, methanol or ethanol (Ma and Hanna, 1999; Demirbas, 2009).

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Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are, at least, five reasons that justify its development:

- It provides a market for excess production of vegetable oils and animal fats.
- It decreases, although will not eliminate, the country's dependence on imported petroleum.
- Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced around 78% compared with petroleum-based diesel fuel.
- The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NOx).
- When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel (Gerpen, 2005).

Raw materials contribute to a major portion in the cost of biodiesel production. The choice of raw materials depends mainly on its availability and cost. Countries, such as USA and those belonging to European community, are self-dependent in production of edible oils and even have surplus amount to export. Hence, edible oils such as soybean and rapeseed are used in USA and European Countries, respectively. Similarly, countries with coastal area such as Malaysia and Indonesia have surplus coconut oil and that is utilised for the synthesis of biodiesel. Brazil, being the largest sugarcane producer in the world, produces ethanol which is used to run 40% of its fuel powered cars. India, even though with a vast land area including coastal area, does not produce enough edible oils and has to import them to meet food requirements. So, in Indian context, the raw materials used for the development of biodiesel have been the unutilised and underutilised materials (jatropha and karanja). Search for raw material for biodiesel production is not limited to vegetable oils only. In the United States, researchers are of the opinion that even surplus vegetable oils will not be enough to meet the future demand of biodiesel and so they have tried algae as a raw material for biodiesel production. Algae, in the presence of sunlight, convert carbon dioxide into sugars and proteins. But when they are starved of nitrogen, mainly oil is produced. A more viable method suggested, is the use of biofuels made from waste biomass or the use of degraded and waste land for their growth (Sharma and Singh, 2009).

Unlike diesel fuel, vegetable oil mostly consists of saturated hydrocarbons and those vegetable oils are triglycerides, consisting of glycerol esters of fatty acids. Vegetable oils have a different chemical structure. Up to three fatty acids are linked to a glycerin molecule with ester linkages. The fatty acids vary in their carbon chain length and in number of double bonds (Murugesan, Umarani et al., 2009).

Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline or acid catalysts. They also interfere with the separation of fatty acid esters and glycerol (Ma and Hanna, 1999).

The fatty acids and the fuel properties of rapeseed oils are summarized in Table 1 and 2, respectively. The flash point of rapeseed oil is much higher than that of diesel. It makes the ignition relatively difficult, but the transportation and handling is much safer. The calorific value is 10–15% less in comparison to diesel, but due to the higher density, the volumetric content of heat value is nearly about the same as that of diesel (Shahid and Jamal, 2008).

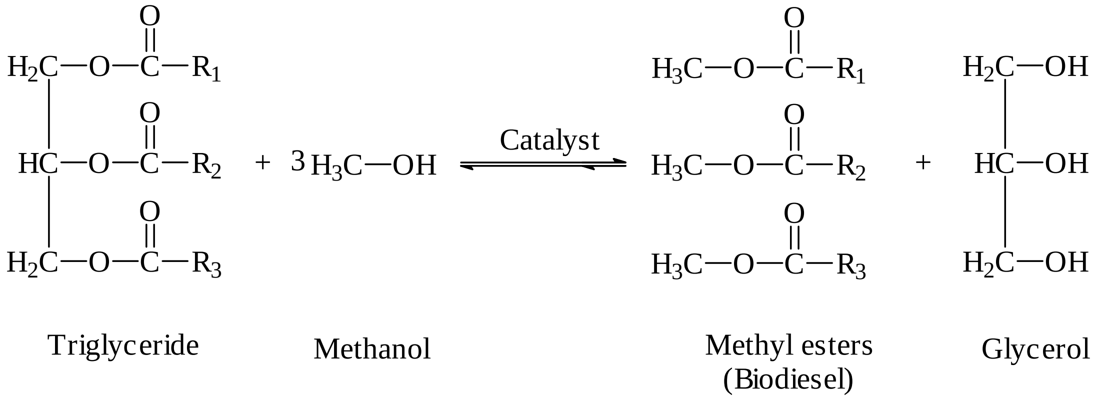
Table 1 - Fatty acid composition of rapeseed oil (% by weight), (Ma and Hanna, 1999).

16:0 (Palmitic)	18:0 (Stearic)	18:1 (Oleic)	18:2 (Linoleic)	18:3 (Linolenic)
3.49	0.85	64.40	22.30	8.23

Table 2 - Properties of rapeseed oil (Ma and Hanna, 1999).

Kinematic viscosity, 38 ºC (cSt)	Cetane no.	Heating value (MJ/kg)	Cloud point (ºC)	Pour point (ºC)	Flash Point (ºC)	Density (kg/l)
37.0	37.6	39.7	-3.9	-31.7	246	0.91

Biodiesel is produced using a process known as transesterification, as shown in the equation below,



Transesterification of triglycerides produces fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In the presence of alcohol excess, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali (Meher, Vidya Sagar et al., 2006).

Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts. The most commonly used alkali catalysts are NaOH, CH_3ONa, and KOH. The reaction mechanism for alkali-catalyzed transesterification was formulated in three steps. Alkali-catalyzed transesterification of vegetable oils proceeds faster than acid-catalyzed reaction. The problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the free fatty acids (FFA), expensive separation of the homogeneous catalyst from the reaction mixture and generation of large amount of wastewater during separation and cleaning of the catalyst and the products (Vyas, Verma et al., 2010).

As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil (Meher, Vidya Sagar et al., 2006).

Since the oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significant factor that affects the reaction rate.

Although, the miscibility of the two phases can be enhanced by increasing the temperature, this is an energy-consumptive process.

Several authors have suggested that methanolysis occurs only in the methanol phase. They suggested that addition of a cosolvent could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system (Boocock, Konar et al., 1996; Guan, Kusakabe et al., 2009; Guan, Sakurai et al., 2009; Peña, Romero et al., 2009).

Boocock et al (1996), presented a study showing that the methoxide base-catalyzed methanolysis of soybean oil at 40°C (6:1 methanol:oil molar ratio) to form methyl esters proceeds approximately 15 times more slowly than butanolysis at 30°C. This is interpreted to be the result of a two-phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in the methanol causes an initiation period. Intermediate mono- and diglycerides preferentially remain in the methanol and react further, thus explaining the deviation from second-order kinetics. The same explanations apply for hydroxide ion catalyzed methanolysis.

At the 6:1 methanol:oil molar ratio the addition of a cosolvent, such as 1.25 volumes of tetrahydrofuran (THF) per volume of methanol, produces an oil-dominant one-phase system in which methanolysis speeds up dramatically and occurs as fast as butanolysis. The critical separation of the glycerol-rich phase still occurs and does so faster than in the cosolvent-free system. For THF, recycle of solvent is simplified because of the similar boiling points of THF (67°C) and methanol (65°C).

Possible explanations for the abnormal slowing of the methanolysis reactions are presented in terms of (1) lower rate constants for mono- and diglyceride reactions due to the formation of cyclic intermediates, (2) a fall in the polarity of the reaction mixture due to either methanol depletion or mixing of the oil, methanol and cosolvent, and (3) depletion of hydroxide ion when this is present (Boocock, Konar et al., 1996).

With these considerations, and as a continuation of previous works (Encinar et al, 1999, 2002, 2005 and 2007), we carried out a study on the transesterification process of rape oil utilizing different co-solvent. The variables affecting the methyl ester yield during transesterification reaction, such as amount and type al catalyst, reaction temperature, methanol:oil molar ratio, agitation rate and co-solvent:methanol molar ratio were investigated.

2. EXPERIMENTAL PROCEDERES AND METHODS

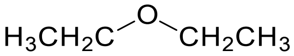
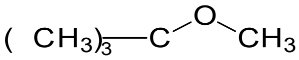
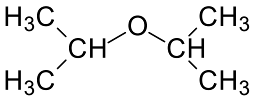
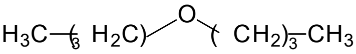
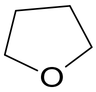
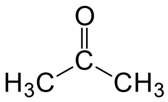
2.1. Materials

Rapeseed was provided by Research Center "The Order", Section of Non-Food Crops. Potassium hydroxide, 85% (KOH) was supplied by Merck (pellets GR for analysis), Lithium Hydroxide 1-hidrate, 99% ($LiOH \cdot H_2O$) and Barium hydroxide 8-hydrate, 97% ($Ba(OH)_2 \cdot 8H_2O$) were purchased from Panreac. Aluminium chloride anhydrous, 98% ($AlCl_3$), Zinc Chloride, 97% ($ZnCl_2$) and Boron trifluoride, 14% in methanol (CH_4BF_3O) were purchased from Panreac. p-Toluenesulfonic acid monohydrate, 98.5% was supplied by Sigma-Aldrich. Methanol (96%) and all co-solvents used were also purchased from Panreac. All other chemicals were obtained commercially and of analytical grade. The rapeseed oil studied was characterized, as Table 3. Table 4 presents the co-solvents properties.

Table 3 - Characterization of the Rapeseed oil studied.

Density 15ºC (kg/m^3)	Viscosity 40ºC (cSt)	Iodine value (g_{I2}/100g)	Acid value (mg_{KOH}/g)
906.8	32.0	112.2	2.29

Table 4 - Co-solvents properties used in this study.

Co-solvent	Chemical formula	Molecular weight (g/mol)	Booling point (ºC)
Diethyl ether, stabilized with ~6 ppm of BHT QP	 $H_3CH_2C-O-CH_2CH_3$	74.12	34-35
tert- Butylmethyl ether, 99.5%	 $(CH_3)_3-C-O-CH_3$	88.15	55-56
Di-isopropyl ether, 99%, stabilized with ~50 ppm of BHT PS		102.18	68-69
Di-n-butly ether, 99%	 $H_3C-(H_2C)_3-O-(CH_2)_3-CH_3$	130.23	142-143
Tetrahydrofuran, stabilized with ~300 ppm of BHT PRS		72.11	65-67
Acetone, 99.5%, PS		58.08	56

2.2. Reaction procedure

Reaction of transesterification was carried out in a 1000 mL spherical reactor, provided with a thermostat, mechanical stirring, sampling outlet, and condensation systems. This installation was consistent with that described in the literature (Ma and Hanna, 1999), and with that utilized in previous works (Encinar et al, 2002, 2005). Two hundred fifty grams of vegetable oil was weighed and placed in the continuously stirred reactor. The reactor was initially charged with only rapeseed oil and heated up to the reaction temperature. The desired amount of catalyst was dissolved in the desired amount of methanol. To this solution was added the desired amount of co-solvent, and the resulting solution was added to the agitated reactor. The reaction was carried out until it reached the desired reaction time.

After reaction time, the mixture was placed in the separatory funnel and allowed to stand overnight to ensure that the separation of methyl esters and glycerol phase occurred completely. Glycerol phase (bottom phase) was removed and left in a separate container. Methyl esters (biodiesel) were heated to remove methanol and co-solvent.

Remaining catalyst was extracted by successive rinses with hot and soured distilled water. Finally, water present was eliminated by heating at 383K.

2.3 Methods of analysis

Methyl ester content was assayed by gas chromatography in a VARIAN 3900 chromatograph, provided with a FID, employing a silica capillary column of 30 m length, 0.32 mm ID, and 0.25

µm film thickness. Heptane was used as solvent, and the carrier gas was helium at a flow rate of 0.7 mL/min. The injector temperature was kept at 270 ºC, and the detector temperature, 300 ºC. Temperature ramp starts with 200 ºC, then 20 ºC/min up to 220 ºC. The calibration curve of peak area and quantity of biodiesel was linear. Samples were taken out from the reaction mixture, heated to remove methanol and co-solvent, centrifuged 5 minutes at 6000 rpm, and then analysed by gas chromatography.

The characteristics of the biodiesel, such us density, viscosity, water content, iodine and saponification values, acidity and cetane indexes, filter plugging point (CFPP), and flash and combustion points were determined according to the European Standard UNE-EN 14214.

Density is one of the most important properties of fuels, since injection systems, pumps and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion (Dzida and Prusakiewicz, 2008).

The effects of viscosity can be seen in the quality of atomization and combustion as well as engine wears. The higher viscosity of biodiesel fuel compared to diesel makes it an excellent lubricity additive. On the other hand, the high viscosities of biodiesel fuels are reportedly responsible for premature injector fouling leading to poorer atomization (Tate et al., 2006). Kinematic viscosity was measured with a Canon-Fenske routine viscosimeter immersed in a constant temperature bath.

Water content is a more critical variable in the transesterification process. The presence of water in biodiesel fuels can cause engine corrosion (Peña et al., 2009). Water content was measured with a Karl Fisher (701 KF Titrino-Metrohm).

Iodine number is a measure of the degree of fuel unsaturation and it is only dependent on the origin of the vegetable oil. In consequence, biodiesel obtained from the same oil should have similar iodine values. Unsaturation can lead to deposit formation and storage stability problems with biodiesel (Prakash, 1998). Iodine number was measured according the Hanus method.

Acid value or neutralization number is a measure of the fatty acid level in biodiesel. It is expressed in mg of KOH required to neutralize 1 gram of sample. Acid value was determined by volumetric method.

Flash point is a measure of the flammability of fuels and thus an important parameter for assessing hazards during fuel transport and storage. Flash point is the lowest temperature at which an applied ignition source will cause the vapors of a sample to ignite (van Gerpen, 2004).

On of the most important measure of ignition characteristics of diesel and/or biodiesel fuels is cetane number, since it directly pertains to ignition within compression ignition engines. Cetane number is a dimensionless descriptor for the ignition delay time of a diesel fuel upon injection into the combustion chamber. Higher cetane numbers were correlated with reduced nitrogen oxides (NOx) exhaust emissions, although this may not always resulted for all types of engine technologies (Knothe et al., 2003; van Gerpen, 2004). Cetane index is a calculated quantity that is intended to approximate cetane number.

The cold filter plugging point (CFPP) reflects the cold weather performance of a fuel. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Similar to CFPP is the cloud point and pour point respectively. Both parameters are often used to specify cold temperature usability of fuel oils. These parameters follow a parallel evolution with CFPP. However, CFPP defines the fuel limit of filterability, having a better correlation than cloud point for biodiesel, as well as petroleum diesel (Enweremadu and Mbarawa, 2009).

3. RESULTS AND DISCUSSION

The employed operation variables were methanol/oil molar ratio, catalyst type and concentration, co-solvent type and concentration, temperature, and agitation rate. Reaction time (120 min), oil type (rapeseed) and alcohol type (methanol) were fixed as common parameters in all experiments. Table 5 shows the conditions of the experiments in this work.

3.1. Influence of methanol:oil molar ratio on biodiesel yield

Many researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. Yield of biodiesel is increased when alcohol triglyceride ratio is raised beyond 3 and reaches a maximum. Furthermore increasing alcohol amount beyond the optimal ratio will not increase the yield, but will increase cost for alcohol recovery. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of the glycerol, thus adding more cost to the process. In addition, the molar ratio is associated with the type of catalyst used. For alkaline catalysis the molar ratio of alcohol to triglycerides in less than the necessary amount for acid-catalyzed transesterification. (Ma and Hanna, 1999; Leung et al. 2010).

In this study it was performed three experiments (0, 1 and 2 run from Table 5) varying the molar ratio of methanol to oil, and it was obtained a methyl ester conversion of 93.7%, for a 9:1 methanol:oil molar ratio (see Table 6). As a consequence of these results, all other experiments were performed with a molar ratio 9:1.

3.2. Influence of catalyst amount on biodiesel yield

Amount of potassium hydroxide is vital for the reaction. First the cost of production depends on the raw materials, and then more catalyst will increase the complexity of separation of product. So the experiment about the effect of catalyst in co-solvent method was carried out (run 2, 4 and 6 from Table 5). As shown in Figure 1, the highest yield of 97.6% was obtained with the amount of KOH 0.7 wt%. Compared with conventional alkali method, the dosage of KOH decreased. This fact seems to be related to the free acidity of the oil. When there is a large free fatty acid content, the addition of more alkaline catalyst compensates this acidity and avoids catalyst deactivation. However, addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels. The result of these two opposing effects is an optimal catalyst concentration that, in this case, is 0.7 % KOH. Obviously, as it can be observed in Table 5, all the other experiments were carried out with 0.7 % catalyst concentration.

Table 5 - Conditions of the experiments in this work.

Run	MeOH:oil molar ratio	Catalyst type and wt.%	Co-solvent type and MeOH:Co-solvent molar ratio	T, K	Agitation rate, rpm
0	12:1	KOH, 1.0	DEE, 1:1	303	700
1	6:1	KOH, 1.0	DEE, 1:1	303	700
2	9:1	KOH, 1.0	DEE, 1:1	303	700
3	9:1	KOH, 1.0	DEE, 1:0.5	303	700
4	9:1	KOH, 0.5	DEE, 1:1	303	700
5	9:1	KOH, 0.7	DEE, 1:0.5	303	700
6	9:1	KOH, 0.7	DEE, 1:1	303	700
7	9:1	KOH, 0.7	DEE, 1:1.5	303	700
8	9:1	KOH, 0.7	DEE, 1:2	303	700
9	9:1	KOH, 0.7	DEE, 1:1	303	500
10	9:1	KOH, 0.7	DEE, 1:1	303	900
11	9:1	KOH, 0.7	DEE, 1:1	303	1100
12	9:1	KOH, 0.7	DEE, 1:1	313	700
13	9:1	KOH, 0.7	DEE, 1:1	308	700
14	9:1	KOH, 0.7	DEE, 1:1	300	700
15	9:1	KOH, 0.7	DEE, 1:1	293	700
16	9:1	$Ba(OH)_2$, 0.7	DEE, 1:1	303	700
17	9:1	LiOH, 0.7	DEE, 1:1	303	700
18	9:1	p-TSA, 0.7	DEE, 1:1	303	700
19	9:1	$ZnCl_2$, 0.7	DEE, 1:1	303	700
20	9:1	$AlCl_3$, 0.7	DEE, 1:1	303	700
21	9:1	BF_3, 0.7	DEE, 1:1	303	700
22	9:1	KOH, 0.7	tBME, 1:1	303	700
23	9:1	KOH, 0.7	diIPE, 1:1	303	700
24	9:1	KOH, 0.7	diBE, 1:1	303	700
25	9:1	KOH, 0.7	THF, 1:1	303	700
26	9:1	KOH, 0.7	Acetone, 1:1	303	700
27	9:1	KOH, 0.7	None	303	700

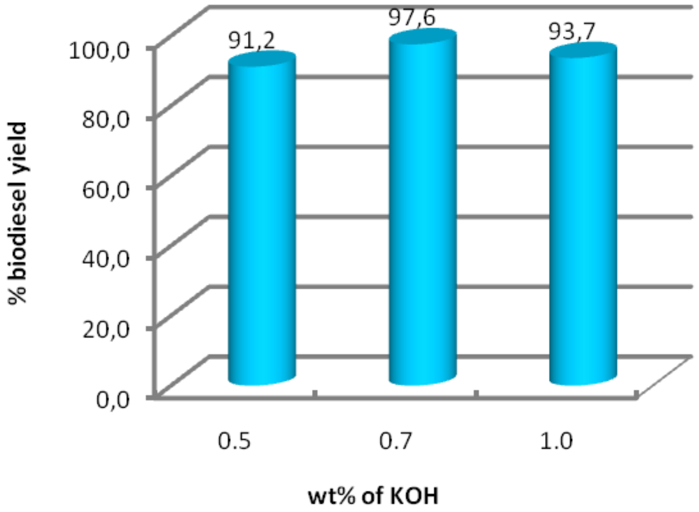


Figure 1. Influence amount of KOH (catalyst) on biodiesel yield (MeOH:oil: 9:1, MeOH:DEE: 1:1, T: 303K, Agitation rate: 700 rpm).

3.3. Influence of MeOH:Co-solvent molar ratio

Since oil and alcohol phases in a transesterification system are immiscible, mass transfer between the two phases becomes a significant factor that affects the reaction rate. In this work several experiments (5-8 from Table 5) were conducted to study the influence of MeOH:DEE molar ratio on biodiesel yield. Figure 2 shows that, when the methanol: co-solvent molar ratio was lower than the minimum ratio, the oil conversion decreased because of the immiscibility of oil and methanol, but excessive addition of co-solvent into the reaction system decreased the transesterification rate, due to a dilution effect on the reagents. In any case the differences amount the experiments are not very significant.

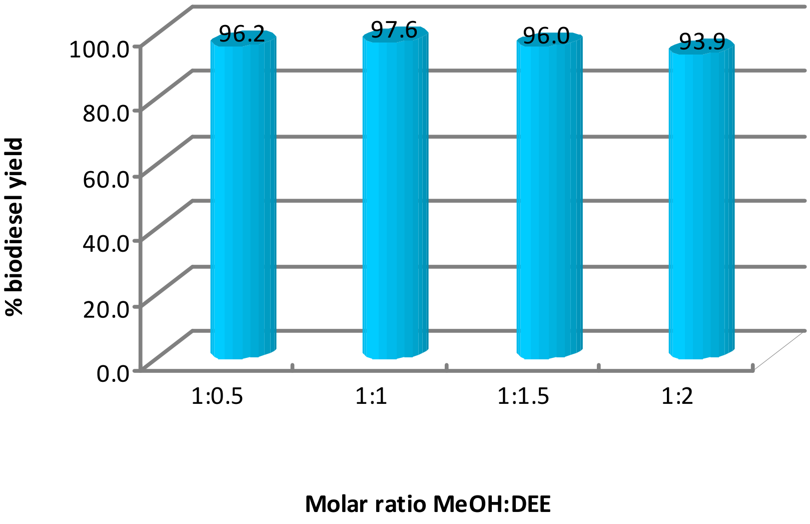


Figure 2. Influence of molar ratio of co-solvent to MeOH on biodiesel yield ([KOH]: 0.7wt.%, MeOH:Oil: 9:1, T: 303K, Agitation rate: 700 rpm).

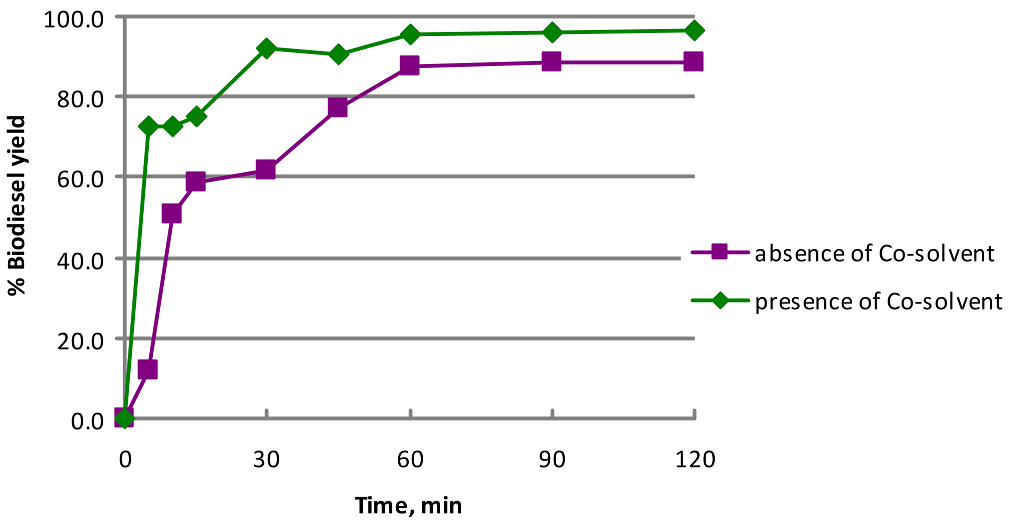


Figure 3. Evolution of transesterification reaction, over time, in the presence and absence of co-solvent ([KOH]: 0.7 wt.%, MeOH:Oil: 9:1, T: 303K, Agitation rate: 700 rpm).

Figure 3 shows the evolution of transesterification reaction, over time, in the presence and absence of co-solvent. As it can be observed, the use of co-solvent allows higher conversion values. Both curves show an initial growing section, ending with an asymptotic trend in which the percentage of methyl esters rarely varies. In the initial stage of growth (30 min) there is a clear positive influence by using DEE as co-solvent.

3.4 Influence of agitation rate on biodiesel yield

Mixing is very important in transesterification reaction, because oils are immiscible with potassium hydroxide-methanol solution. To study the influence of these variable several tests were conducted (experiments 6, 9-11, from Table 5). As it can be seen in Figure 4, the influence of agitation rate was not very significant. This is probably due to the effect that the use of co-solvent has on the solubility between methanol and oil. Effectively, in transesterification reaction, the reactants initially form a two-phase liquid system. In these conditions, the reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. In our case, the presence of co-solvent contributes to that the region of slow rate not be significant. In consequence, the influence of agitation rate is not important.

3.5 Influence of reaction temperature on biodiesel yield

To study the influence of reaction temperature several tests were carried out (experiments 6, 12-15 from Table 5). Temperature is one of the factors that influence the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and results in an increased reaction rate, and a shortened reaction time. However, high reaction temperature can decrease biodiesel yield because a higher reaction temperature accelerates the saponification reaction of triglycerides. Reaction temperature must be lower than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization.

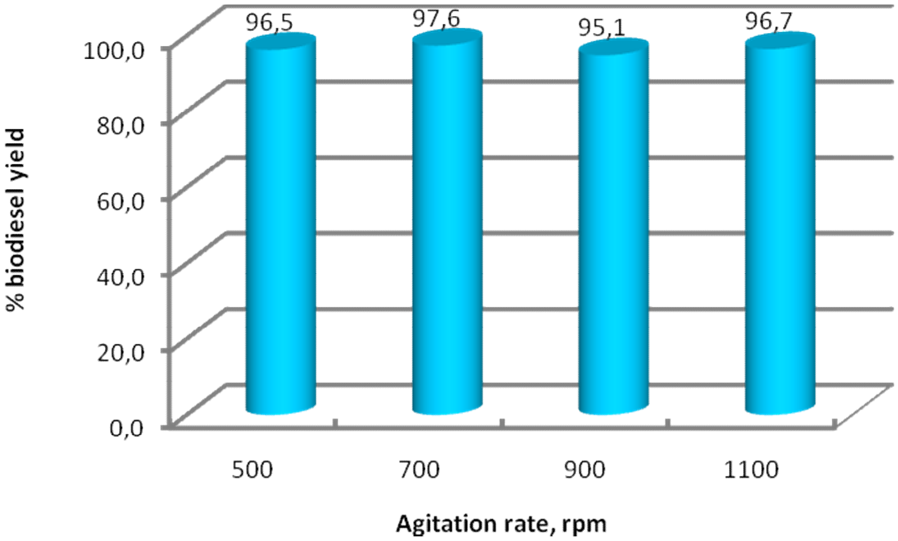


Figure 4. Influence of agitation rate on biodiesel yield ([KOH]: 0.7wt.%, MeOH:Oil: 9:1, MeOH:DEE: 1:1, T: 303K).

As it can be seen in Figure 5, high biodiesel conversions were obtained at temperatures far below the boiling point of methanol (64.7 ºC or 337.9 K). For example, in the experiment carried out to room temperature (T_{room} = 293 K) a biodiesel yield of 96.3% is obtained. These circumstances, from the economical point of view, allow the reduction of process costs. In addition, for the studied temperature range, there were no large differences in biodiesel yield.

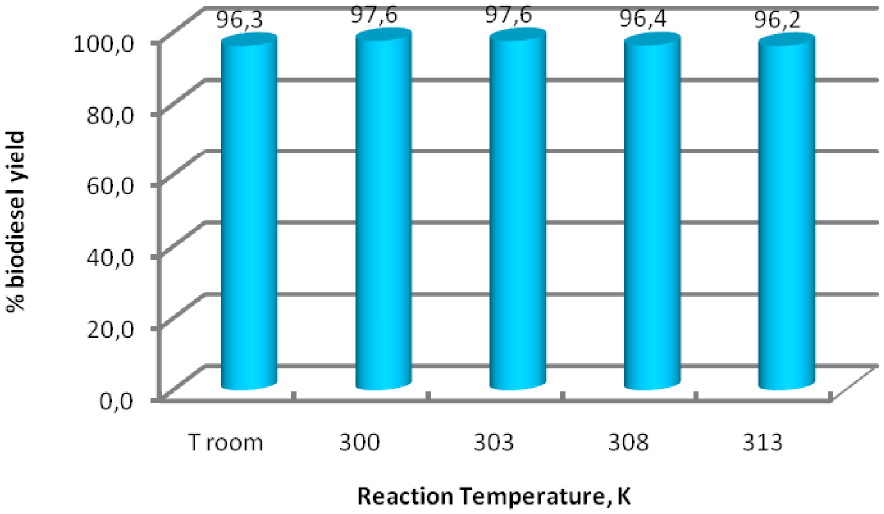


Figure 5. Influence of reaction temperature on biodiesel yield ([KOH]: 0.7 wt %, MeOH:Oil: 9:1, MeOH:DEE: 1:1, Agitation rate: 700 rpm).

3.6 Transesterification reaction with other catalysts

As complement to the carried out experiments, in this work it was already studied the use of other catalysts. As alkaline catalysts, in addition to the KOH, have been used $Ba(OH)_2 \cdot 8H_2O$ and $LiOH \cdot H_2O$. As acid catalysts have been used $AlCl_3$, $ZnCl_2$, 14% in methanol BF_3 and p-toluenesulfonic acid monohydrate (experiments 16-21, from Table 5). At reaction conditions, 0.7 wt% catalyst, 9:1 MeOH:Oil, 1:1 MeOH:DEE, 303K, 700 rpm and 120 min of reaction, there was no biodiesel conversion, in any of the reactions with acid catalyst. For alkaline catalysts, high conversions were obtained, 96.8% with lithium hydroxide and 76.9% with barium hydroxide. However the process of biodiesel purification was slow and difficult. In consequence, the utilization of these catalysts in the presence of co-solvent does not seem to improve the results obtained with KOH.

3.7 Influence of co-solvent type on biodiesel yield

For a more complete study, other compounds as co-solvents were tested (Table 4), some of which are referenced in the literature. Figure 6 shows the results, as it can be observed, almost all the studied compounds allowed conversions above 90%, with the exception of di-n-butyl ether.

After purification steps, some of biodiesel (experiments 22, 23 and 24) have a strong smell of co-solvent used in the test. Furthermore, as shown in Table 4, the boiling point of the compounds studied is within a very large temperature range. *tert*-Butylmethyl ether, di-isopropyl ether, tetrahydrofuran and acetone have boiling point values relatively close to the methanol boiling point, which allows to eliminate them at same time, but not allow their reuse. Di-n-butyl ether has a high boiling point, which hampers its elimination, making the process more expensive. Diethyl ether has a low boiling point, allowing on the one hand its rapid elimination and on the other hand it can allow its reuse, since it is much lower than the methanol.

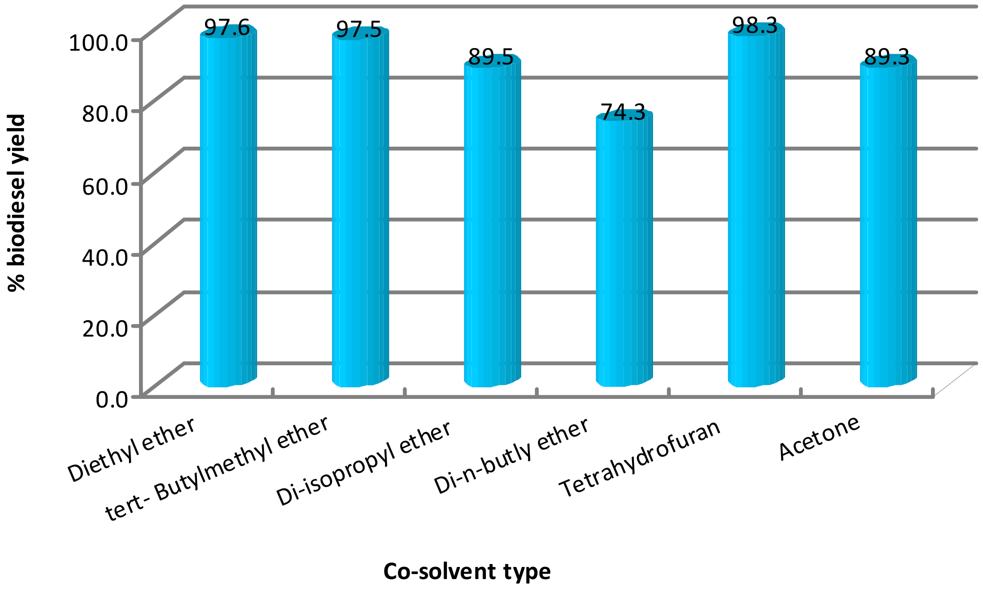


Figure 6. Influence of co-solvent type on biodiesel yield ([KOH]: 0.7wt.%, MeOH:Oil: 9:1, MeOH:Co-solvent: 1:1, T: 303K, Agitation rate: 700 rpm).

3.8. Fuel specifications

Table 6 shows, methyl ester yield, density$_{15\ °C}$ and viscosity$_{40°C}$ obtained in each experiment, Table 7 shows the influence of operating variables on other parameters of biodiesel characterization obtained in some of the experiments performed in this study. These parameters are very important since the quality of final product (biodiesel) is strongly conditioned by them. The fuel properties of the biodiesel were determined with the help of standard tests, and it was found that the biodiesel properties were very close to diesel fuel specifications, according to EN-590, and biodiesel European Standard draft. For comparison, in Tables 6 and 7, standard EN-14214 values have been enclosed.

Density presents values mainly between 862.3 and 879.4 kg.m^{-3}, which are within the values recommended by EN-14214. As it can be seen in Table 6, density remains practically constant because the methanol, oil and esters have very similar density.

Viscosity is a very important property concerning the biodiesel utilization in direct injection diesel engines. High values of viscosity lead to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Therefore, the biodiesel viscosity must be low. The value required by EN-14214, at a temperature of 40 °C, must range between 3.5 and 5.0 cSt. As it can be observed, in Table 6, for experiment 16 the viscosity value obtained is above the maximum allowed. The variables studied showed a similar behaviour; that is, as methyl esters yield increased, viscosity decreased. In consequence, viscosity, as the other properties, is related with the grade of conversion achieved, depending on the final yield.

The experiment 24 (di-n-butly ether as co-solvent) has a lower density and viscosity than the limits given by the standard, which can be explained by low yield obtained, but also by some reaction with the co-solvent.

Experiment 24 also presents different values for the parameters analyzed and so it was not considered in the following text.

In most experiments water content (%) is above the value indicated by the standard.

As it can be observed saponification values ranged from 167.5 to 183.8 mg of KOH per gram of sample. Saponification value is related to the average molecular weight of the sample, but the acids that are present in glycerides or in methyl esters are the same. Only the change of glycerol by methanol is produced. In consequence, the average molecular weight does not change significantly and so it may not be observed changes in the saponification value.

The number of double bonds of fatty acids is related to iodine value. This parameter describes the content of unsaturated fatty acids and it is only dependent on the origin of the vegetable oil. In consequence, biodiesel obtained from the same oil should have similar iodine values. In our case the iodine values ranged between 106.8 and 119.0. This dispersion can be attributed to the heterogeneity of the samples and to the dilution of these with ethanol but, in all cases, the iodine values were inferior to the maximum iodine given by standard EN-14214, which is 120.

A limitation of unsaturated fatty acids may be necessary because the high heating of unsaturated fatty acids results in polymerisation of glycerides. This can lead to the formation of deposits or to the deterioration of the lubricating oil. This effect increases with the number of double bonds in the fatty acid chain.

Acidity index, expressed as mg KOH/g of sample, is in accordance with the maximum required limits given in the EN-14214 biodiesel standard norm (0.5 mg KOH/g), except for biodiesel 16 and 24. In these experiments the value was above the limit, which is explained by the low yield achieved.

In EN-14214 the CFPP value is not specified, since it is different at each country. However, the value obtained in the sample of biodiesel 23, 25 and 26 is a little high.

Table 6 - Methyl ester yield, density$_{15\ °C}$ and viscosity$_{40°C}$ obtained in each experiment.

Run	Methyl ester yield, %	Density $_{15\ °C}$, kg.m^{-3}	Viscosity $_{40\ °C}$, cSt
EN-14214	96.5	860-900	3.5-5.0
0	91.5	874.3	4.8
1	87.6	873.2	5.0
2	93.7	875.1	4.6
3	94.5	870.5	4.6
4	91.2	874.7	5.0
5	96.2	868.6	4.6
6	97.6	868.6	4.5
7	96.0	872.9	4.8
8	93.9	867.8	4.9
9	96.5	869.3	4.6
10	95.1	877.0	4.6
11	96.7	874.7	4.6
12	96.2	876.4	4.6
13	96.4	867.6	4.6
14	97.6	871.0	4.9
15	96.2	870.7	4.8
16	76.8	879.4	6.7
17	96.8	870.8	4.7
18	Without biodiesel conversion		
19	Without biodiesel conversion		
20	Without biodiesel conversion		
21	Without biodiesel conversion		
22	97.5	869.0	4.6
23	89.5	871.8	5.0
24	74.3	844.6	3.0
25	98.3	862.3	4.6
26	89.3	870.3	4.8
27	89.8	873.6	5.1

A higher flash point indicates a higher degree of safety for storage, transportation, and usage of liquid fuel. Flash point of biodiesel is higher than the diesel oil, which is safe for transport. Flash point for all samples of biodiesel was between 167.8 and 162 °C, well above the minimum amount stated on the EN-14214.

In general, as it can be observed in Table 7, the values of cetane index are very similar and ranged from 38.1 to 45.8. The standards EN-14214 and EN-590 specify that cetane number must have a minimal value of 51. A quantitative relation between cetane index and cetane number does not exist. Hence, according to the EN- 590, we can only state that biodiesel shown in Table 7 has, in general, a correct cetane index.

Table 7 - Other parameters of biodiesel characterization.

Parameter	Run									EN-14214
	6	16	17	22	23	24	25	26	27	
	DEE	Ba(OH)$_2$	LiOH	tBME	diIPE	diBE	THF	Acet.	none	
Water content, %	0.07	0.13	0.09	0.04	0.05	0.08	0.07	0.06	0.07	< 0.05
Saponification value, mg/g	174.4	180.7	183.8	168.0	168.4	127.7	167.5	175.0	170.3	-
Iodine value, %	111.9	106.8	112.3	114.6	111.6	91.8	115.3	118.4	119.0	≤ 120
Acidity index, mg KOH/g	0.23	0.75	0.20	0.21	0.19	0.69	0.34	0.27	0.13	≤ 0.5
CFPP,ºC	-2	-1		-1	7	3	6	10	-4	
Flash point, ºC	178.0	183.8		183.0	192.0	--	167.8	182.0	187.0	≥ 120
Combustion point,ºC	191.5	194.0		193.1	178.0	65.0	185.0	191.0	195.0	
Cetane index	41.3			38.1	44.4		45.8		44.0	

4. CONCLUSIONS

In general the presence co-solvent facilitates the reaction of transesterification. The utilization of these co-solvents produces high biodiesel yields in small times of reaction.

The main factors affecting the methyl ester yield during transesterification reaction were the catalyst type and content, co-solvent type and molar ratio of alcohol to co-solvent, molar ratio of oil to alcohol. High methyl ester yield and fast reaction rate could be obtained even if reaction temperature was relatively low, which is quite favorable to the production of biodiesel in industry.

In this sense it is possible to affirm that the KOH has comported as the best catalyst. Small concentrations of this catalyst (0.7 %) are enough for getting out high yield in small times of reaction.

Between the co-solvents used, DEE can consider the most effective. THF allows obtaining similar conversions, but its recuperation is more difficult. In general a molar ratio 1:1 between methanol and the co-solvent is enough for assuring a good conversion.

It was obtained a biodiesel yield of 97.6 % when using 0.7% of KOH as catalyst, a molar ratio of methanol to oil 9:1, a molar ratio of methanol to DEE 1:1, a reaction temperature of 303K, 700 rpm and 120 minutes of reaction.

Fuel properties of biodiesel were determined with the help of standard tests, and it was found that biodiesel properties were very close to diesel fuel specifications, according to EN-590 and EN-14214.

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