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A Conparative Study of Biodiesel Purification with Magnesium Silicate and Water

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Abstract: *It is not justifiable to use excess of water to purify biodiesel only because it is the "most economical" method. Actually it is one of the problems in the biodiesel production industry an adequate purification method; the most commonly used one is the water washing. Currently, there is considerable interest in the biodiesel purification with other solid materials such as synthetic magnesium silicate, which is an effective absorbent to remove impurities. The two methods discussed here have been tested in similar conditions of temperature, time and concentration of reactants. It was found that it is very important to remove the remaining methanol to avoid saturation of the absorbent. The analysis concluded that residues of glycerol and soap content in the two processes are similar and efficient enough and did not find many differences. The purity requirements and analysis of biodiesel were based on the American standard ASTM D6751.*

Keywords: Biodiesel, magnesium silicate, water, transesterification

1. INTRODUCTION

The price per barrel of petroleum rises mainly due to the global demand for fuel. The issue is not entirely restricted to consumption and prices, but to increasing environmental concerns over pollution from the combustion of fuels. The most feasible way to resolve these problems is through the use of alternative fuels. Among the alternative fuels, biofuels are defined as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass [1]. Biodiesel is a biofuel, which is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids prepared from vegetable oils and / or animal fats, treated by a process called transesterification, which results in a significant reduction in its viscosity and has proved to be usable in any diesel engine and can be treated in the same way as the diesel fuel [2].

1.1. Biodiesel Production

The most reliable, economical and common process to produce biodiesel is transesterification. The transesterification process is currently used for the production of biodiesel; glycerol is removed from the triglycerides contained in the oil and replaced by radicals of alcohol used in the conversion process. With this process the viscosity of the oil is reduced, maintaining the cetane number and calorific value [2], further reducing the boiling point of the oil and its ignition temperature (flash point). Methanol is the most commonly used alcohol because of its low price compared to other alcohols, the physical and chemical advantages (polar compound, short chain alcohol etc.), but ethanol is also used.

In the case of methanol, the reaction is known as methanolysis. The methanolysis reaction stoichiometry requires 3 moles of methanol and 1 mole of triglyceride to produce 3 moles of fatty acid methyl ester and 1 mole of glycerol. This reaction, in turn, comprises three consecutive reactions reversible with intermediate formation of diglycerides and monoglycerides (Table 1). After the reaction, glycerol is separated by decantation or centrifugation, and the product obtained is purified and used in traditional applications (pharmaceutical, cosmetic 90% purity) or in their more recent applications (animals food, carbon materials in fermentations, polymers and lubricants). Biodiesel phase is also purified (containing small amounts of methanol, catalyst and water) before being used as diesel fuel in order to comply with the standard ASTM D6751 [2].

Of the advantages of bio-fuels, one is that the raw materials used for production are natural and renewable. All types of oils derived from vegetable or animal fat (refined oil, crudes, cooking oils and recycled fats of chips) are non-toxic and biodegradable. Biodiesel

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degrades about four times faster than diesel oil; in 28 days biodiesel contained in water degrades from 85-88% [3]. There are different types of catalysts: basic, acidic, ion exchange resin, enzymes and supercritical fluids. However, basic catalysts (NaOH, KOH) are most commonly used in industry since the process is faster and the reaction conditions are moderate [4,5]. The reaction can be performed in two ways: continuous and discontinuous (batch) in different capacities. There are several advantages in the biodiesel usage: they are renewable, biodegradable, reduce greenhouse gas emissions, contain little or no sulfur. It is mixed in any proportion with petroleum diesel, no engine modifications necessary, low CO and suspended particulates and has environmental benefits. It has some disadvantages too: high freezing point (between 0 and -4 ° C), filter clogging (due to solvent power), lower power capacity than diesel oil and has storage problems (because it is biodegradable). Glycerol is largely removed by gravity separation or centrifugation and the methanol in some cases can be recovered by flash evaporation. The process is not 100% efficient so the final stage "purification" is necessary to meet the requirements of the standard ASTM D6751.

1.2. Purification Methods

The fuel cannot be called biodiesel until it meets the standard specifications of ASTM D 6751. Therefore, the purification step is essential. Untreated biodiesel contains impurities such as free glycerin, soaps, metals, methanol, free fatty acids, catalyst, water and glycerides. The high impurities level can reduce engine life. Table 2 shows each impurity effect.

There are generally two accepted methods for purifying biodiesel: wet and dry. The most traditional method is the wet cleaning and is widely used to remove contaminants and the excess of leftover chemicals in the biodiesel production. However, the addition of additional water to the process offers many disadvantages, including increased cost and production time. Dry cleaning replaces water with ion exchange resin, bentonite, silica gel or magnesium silicate powder (as in this case) to neutralize the impurities. These dry cleaning methods are used in industrial plants [6].

It has been known for some time that it is possible to meet the specification only by washing with hot water, but this technique results in some disadvantages. Heavy contamination of liquid effluent is generated as shown in table 3. Significant loss of product may be held for retention in the aqueous phase. Moreover, the formation of emulsions in the cooking oil treatment or other oils with high free fatty acid content may occur due to the formation of soap [7].

There are three alternative commercial processes that are being studied, bentonite clay, ion exchange resin and magnesium silicate. These processes have the advantage of not using water, which eliminates many of the problems outlined above. But, except for some rather sketchy advertising materials little is really known about their performance, in our case the comparison is made using synthetic magnesium silicate.

Since both the glycerin and methanol are very soluble in water, washing with water is very effective in removing pollutants. Until recently, it was the most common method of purification. Also, it has the advantage of eliminating the residual sodium salts and

Table 1. Reaction mechanisms in the production of biodiesel.

Process	Reaction	Description
Esterification	$\underset{\text{FFA}}{RCOOH} + \underset{\text{Methanol}}{CH_3OH} \xrightarrow{H_2SO_4} \underset{\text{Methyl-esters}}{RCOOCH_3} + \underset{\text{water}}{H_2O}$	Convert free fatty acids (FFA) into useful esters
Reaction of methanol and sodium hydroxide	$NaOH + \underset{\text{Methanol}}{CH_3OH} \leftrightarrow \underset{\text{Catalyst}}{CH_3ONa} + \underset{\text{water}}{H_2O}$	Catalyst reaction
Transesterification	$C_3H_5(OOCR)_3 + 3CH_3OH \xrightarrow{NaOH} 3RCOOCH_3 + C_3H_5(OH)_3$	Overall transesterification reaction
	$\text{Diglyceride} + \text{Methanol} \leftrightarrow \text{Monoglyceride} + R'COOR_2$ $\text{Monoglyceride} + \text{Methanol} \leftrightarrow \text{Glycerin} + R'COOR_3$	Intermediate steps of the reaction
Hydrolysis	$C_3H_5(OOCR)3 + 3H_20 \rightarrow 3RCOOH + C_3H_5(OH)_3$	Reacts undesirable water and free fatty acids
Saponification	$RCOOH + CH_3ONa \rightarrow RCOONa + CH_3OH$	Unwanted soaps, consumes more catalyst.
Neutralization	$H_2SO_4 + 2NaOH \rightarrow NaSO_4 + 2H_2O$	Neutralize excess catalyst.

Table 2. Effects of impurities on biodiesel and engines

Impurity	Effect
Water	Oxidation, corrosion and bacteriological growth (filter blockage)
Glycerol	Deposits in the injectors (carbon residue), high viscosity, crystallization, settling problems
Methanol	Low values of density and viscosity, low flash point (transport, storage and usage problems), corrosion of Al and Zn
Soap	Deposits in the injectors (carbon residue), filter blockage (sulphated ashes), engine weakening

Table 3. Characterization of the effluent from water washing purification

Parameter	Results
pH	6.5
TSSA (mg / L)	7550
MSSB (mg / L)	80
Total CODC (mg / L)	18,800
Conductivity (mS / cm)	1200

a Total suspended solids; b Suspended mineral solids; c Chemical oxygen demand.

soaps, due to its solubility in water. But, as previously mentioned the water washing has disadvantages.

Employment of refined magnesium silicate powder (magnesol) has been promoted in the U.S. and Mexico by The Dallas Group of America, Inc. This material has a purely adsorbent unwanted biodiesel waste and material used has been used in other applications (fertilizer, fuel and as an additive in animal food).

The main objective of this study is to analyze the effectiveness of methanol removal, water, glycerol, and sulfates, from the two methods studied (biodiesel purification with water and synthetic magnesium silicate) in a variety of conditions and combinations. Secondary objectives include soap removal efficiency, the effect of the final process of FFA and oxidation stability. The attempts in the case of the purification process with synthetic magnesium silicate was to see the absorptive capacity, which is vital to compare the relative costs in the two processes for a possible industrial applications.

2. EXPERIMENTAL DETAILS

In this paper we analyzed the performance of synthetic magnesium silicate (dry cleaning) against water (wet purification) to find out the optimal fuel purification. Five experiments with 27 samples of 5 ml each were performed. In total, 135 samples were prepared of which 45 were chosen randomly (9 of each type). We used a single type of oil as raw material (recycled cooking oil) but from two different sources. The characteristics and conditions for converting to biodiesel have already been tested earlier in the Renewable Energy Institute (IER-UNAM), experiments were performed to determine the optimal conditions for the conversion process, using a combination of the three variables from a previous experiment (temperature, alcohol percentage and time) and two more for water purification (number of washes) and magnesium silicate (proportion of synthetic magnesium silicate). Samples were taken immediately after decanting the glycerin cone gravity; sodium methoxide was used as catalyst. Table 4 shows a comparison of the parameters with respect to the standard fuel obtained in the Biodiesel pilot plant of the IER-UNAM. Although none of the samples fully complies with the content of methyl ester in the standard, this biodiesel have been used in the purification process in order to study the removal of impurities. We used tap water and deionized water, also a particle size of 80μm for synthetic magnesium silicate. Chemicals and standards for analysis were purchased from Sigma-Aldrich.

Table 4. Feed compositions

Test description	Biodiesel oil 1 pilot plant	Biodiesel oil 2 pilot plant	ASTM D6751 Max. biodiesel
Methanol content (% (m / m))	1.3	1.25	0.2
Water content (mg / kg)	1010	1000	500
Methyl ester content (% (m / m))	95	93	96.5
Free glycerol content (% (m / m))	0.10	0.11	0.02
Monoglyceride content (% (m / m))	0.55	0.65	0.8
Diglyceride content (% (m / m))	0.3	0.6	0.2
Triglyceride content (% (m / m))	0.5	2.1	0.2
Acid value (mg KOH / g sample)	0.24	0.25	0.5
Soap content (g soap / g sample)	0.00124	0.0029	-
OSI (h)	2.2	2.7	15

2.1. Magnesium Silicate Experiments

The work was carried out in test tubes with 5 ml sample fitted with a variable speed agitator; two samples were immersed in a water bath. Purification standard time was 10 minutes, but samples were taken at 5 and 7 minutes. The final product separation was by centrifugation; it is not advisable to filter very small samples.

Experiments were conducted at room temperature and at the following concentrations (w / w) of magnesol: 0.5, 1, 2, 3 and 1% combined with washing, as suggested by the supplier. All experiments were performed in both raw materials [8]. Only nine samples from each experiment were analyzed. Samples were analyzed for methanol and free glycerol by GC (gas chromatography) techniques, taking into account that due to the size of the sample these are the recommended techniques. The water content was measured by the Karl-Fischer method in each sample as well as the acidity, the content of soap, and mono, di- triglycerides.

Considering that magnesol is hygroscopic once the package is opened, care was taken to re-seal as tightly as possible. The material for immediate use was placed in sealable plastic containers and for some experiments was dried in the oven at a temperature of about 100 ° C to maximize its effectiveness.

2.2. Water Experiments

The water washing water was used in two ways: deionized water and tap water from the city. Table 5 shows the properties of tap water from Temixco, Mexico. Washing was carried out at 65 ° C.

Table 5. Properties of tap water (Temixco, Mex.) [9].

Parameter	Results
pH	6.9
Hardness (mg of $CaCO_3$ / L)	450
Turbidity (NTU)	0.23
Dissolved solids (mg/L)	680

Table 6. Experiments with magnesol

Expt.	Sample	t (hr)	T (° C)	% of alcohol	% of magnesium silicate	Water washed	Characterized samples
1	27	1	65	100	3	-	9
2	27	1	65	100	2	-	9
3	27	1	65	100	1	-	9
4	27	1	65	100	0.5	-	9
5	27	1	65	100	1	2	9

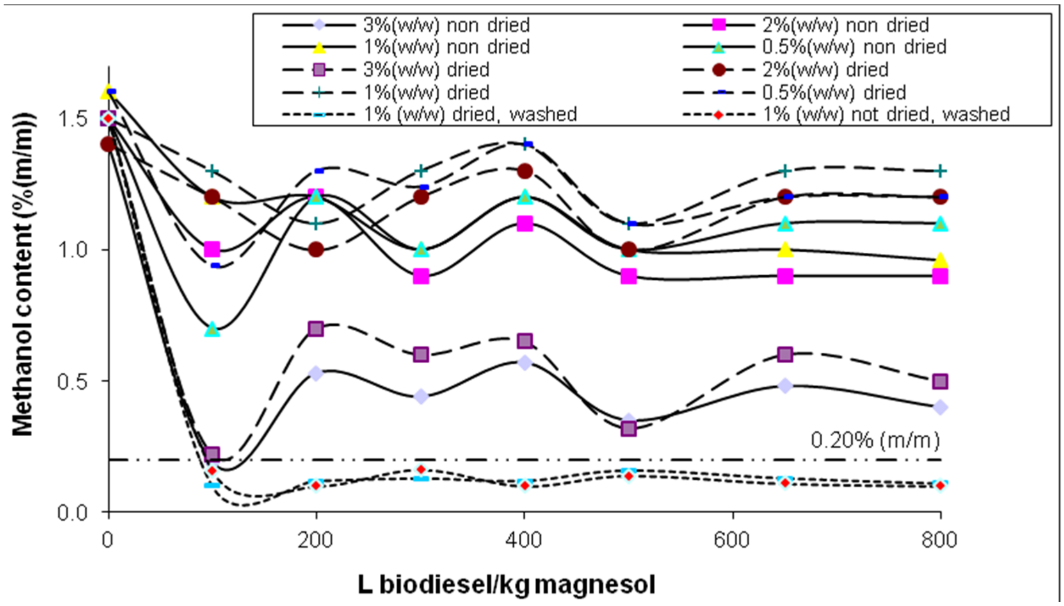

Figure 1. Evolution of methanol content vs. biodiesel / kg of magnesol

Three water relations (number of washes) and two agitation speeds were adopted. Once again the experiments were performed with both raw materials.

The process with magnesol used the same procedure as in the case of water washing used with the sample size of 5 ml. The standard washing time was 10 minutes, but the samples were taken at 5 and 7 minutes. The separation of the final product was by gravity from the solution for 30 minutes, but it was necessary to centrifuge the sample [8]. The analysis was the same as in the previous case, nine tests for each experiment (table 6).

2.3. Analysis Methods

An automatic injection system "cool on-column" in a gas chromatograph (Trace GC Ultra brand Thermo Finnigan Corporation) was used for the determination of mono-, di-, triglycerides and free glycerol, according to the American Standard ASTM D6584. GC capillary column (30 m x 0.25 mm x 0.25 microns) was coupled to a mass spectrometer detector at 250 ° C and helium as carrier gas at 1 ml / min. Biodiesel analysis for each sample was conducted by slating, dissolved in 100 µl of biodiesel sample in 0.8 ml heptane and 1µl of this solution was injected in GC. Two internal standards were used, one for glycerol and other for glycerides. Monoglycerides (MG), diglycerides (DG), triglycerides (TG) and free glycerol content were expressed as percent by weight (% (m/m)). The instrument was calibrated using glycerol, mono-olein, di-olein and tri-olein in solutions of n-heptane, in accordance with standard D6584.

Methanol was also determined using the Thermo Finnigan Trace GC Ultra using the manual injection method in accordance with ASTM D6751, with 2-propanol as internal standard. The water content was determined by the Karl Fischer method (ISO 12937) and the acid was determined by titration with potassium hydroxide [10], in accordance with ASTM D664. The rate of oxidation stability (OSI) was determined using the method of "Rancimat" in accordance with ASTM D2274 standard. The soap content was determined according to the method of "Biodiesel Analytical Methods" [11].

3. RESULTS AND DISCUSSION

3.1. Magnesol

Magnesol does not have a significant effect on the glycerides and the OSI, unlike other dry methods such as bentonite clay or ion exchange; the effect of the methanol content is less relevant. The methanol elimination could be due to evaporation losses at temperatures above 65 °C and not due to magnesol. Interestingly, the dry Magnesol has a slightly better effect than the one that has not been

Table 7. Magnesol fuel characterization ASTM D6751

Test description	Biodiesel oil 1 pilot plant	Biodiesel oil 2 pilot plant	ASTM D6751 Max. biodiesel
Methanol content (% (m / m))	0.9	1.1	0.2
Water content (mg / kg)	950	920	500
Free glycerol content (% (m / m))	0.09	0.09	0.02
Monoglyceride content (% (m / m))	0.51	0.5	0.8
Diglyceride content (% (m / m))	0.2	0.21	0.2
Triglyceride content (% (m / m))	0.37	0.2	0.2
Acid value (mg KOH / g sample)	0.19	0.23	0.5
Soap content (g soap / g sample)	0.00032	0.00029	-
OSI (h)	2	2.5	15

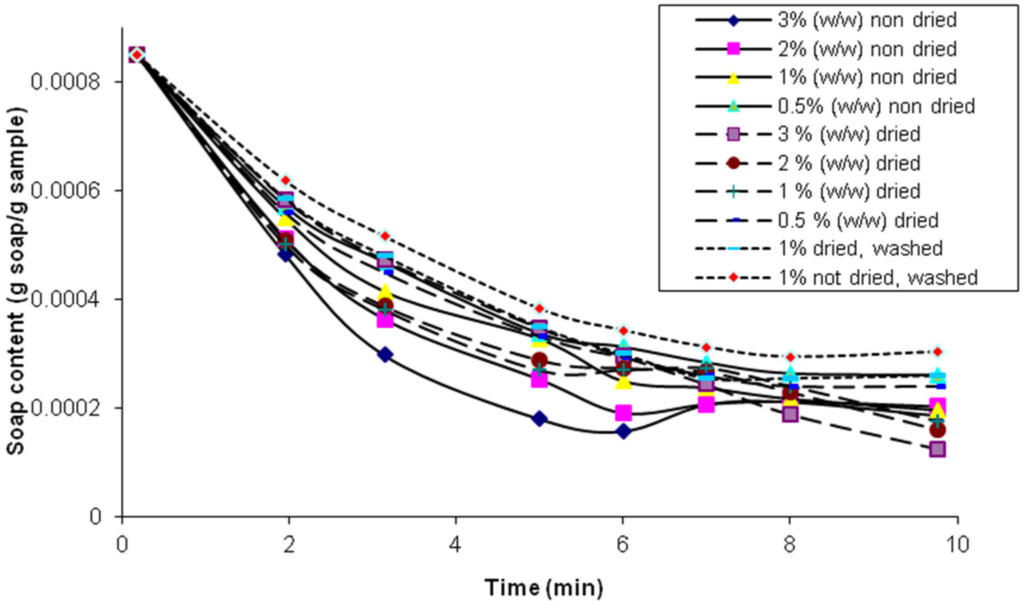

Figure 2. Evolution of soap content vs. time for the purification of biodiesel with magnesol at room temperature

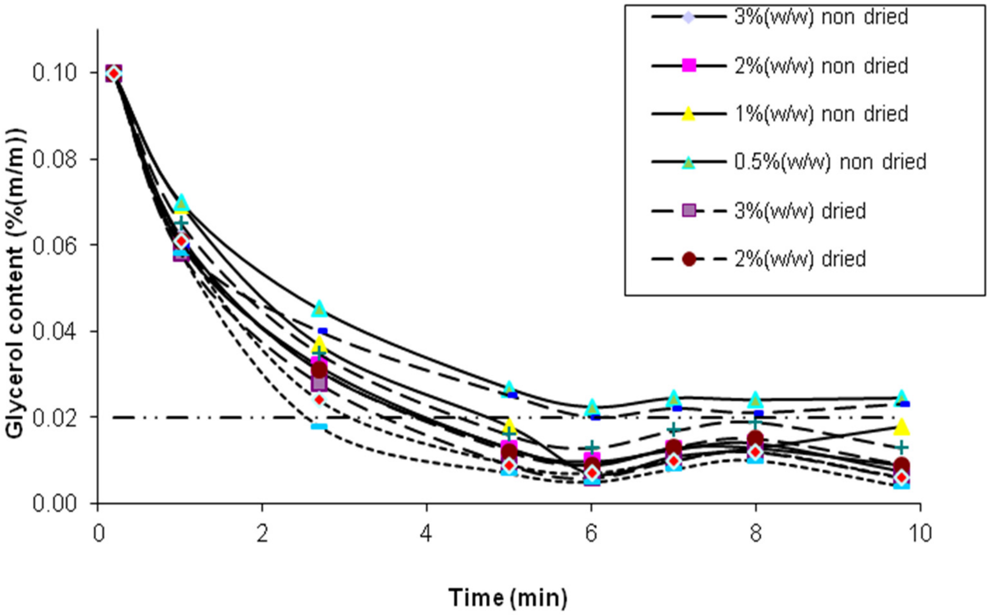

Figure 3. Evolution of glycerol content vs. time for the purification of biodiesel with magnesol at room temperature

dried for removal of methanol excess; the reason is that it is more absorbing. None of the experiments decreased the methanol content below the limit of the standard ASTM D6751, but best results were achieved with the maximum magnesol concentration and the combinations with washes at 65 ° C, as shown in Figure 1.

There are no significant differences between the use of dry or humid magnesol in removing free glycerol and soap from the two types of biodiesel. With the exception of experiments with 0.5% (w/w) of magnesol concentration, all experiments satisfactorily eliminated glycerol content in 10 minutes of reaction. The same applies to the soap removal. Reduction in the soap values is less than that achieved by other means of dried purification (ion exchange resins, bentonite and silica gel). Also, it seems to have little effect on the acid value. These results are shown in table 7.

The results shown in the above table, it can be seen that glycerol levels reach below the standard required by ASTM D6751 and can produce large reductions in the soap content. But, it is not successful in removing methanol sufficient to satisfy the standard.

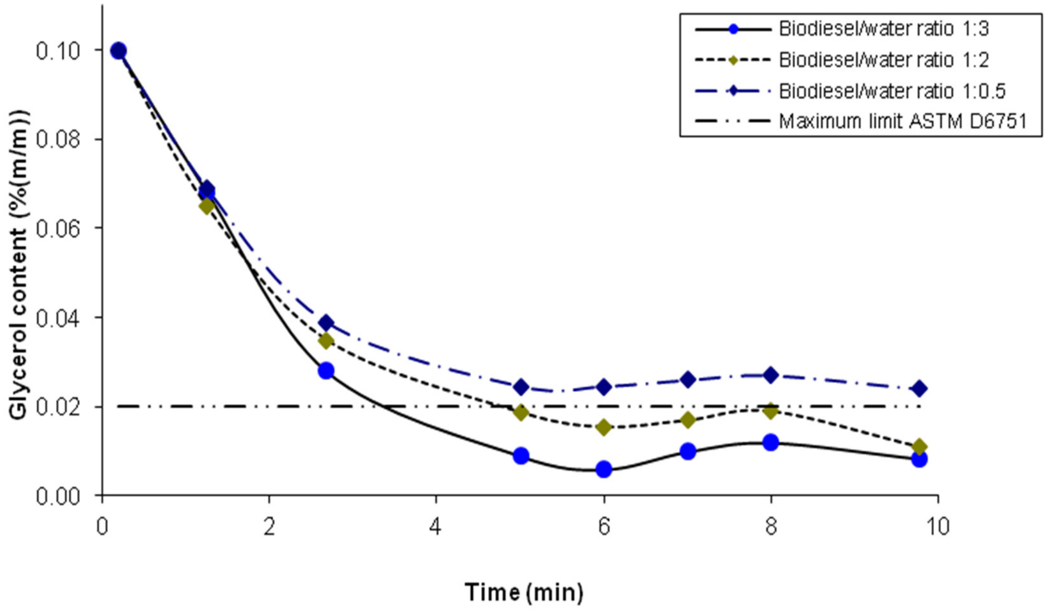

Figure 4. Evolution of glycerol content vs. time for the purification of biodiesel by tap water washing at room temperature and at 500 rpm

Figures 2 and 3 show the behavior of the soap evolution and glycerol content respectively from the magnesol processing. At least 1% (w / w) is required with a contact time of 10 minutes, but there seems to be little advantage in pre-drying the material or operation over room temperature. The content is slightly higher in some glycerol samples because the tests included less than 0.5% (w / w) of magnesol.

Table. 8. Characterization of samples from tap water washing process

Test description	Biodiesel oil 1 pilot plant	Biodiesel oil 2 pilot plant	ASTM D6751 Max. biodiesel
Methanol content (% (m / m))	0.05	0.08	0.2
Water content (mg / kg)	1000	1000	500
Free glycerol content (% (m / m))	0.01	0.01	0.02
Monoglycerides content (% (m / m))	0.45	0.65	0.8
Diglycerides content (% (m / m))	0.17	0.2	0.2
Triglycerides content (% (m / m))	0.3	0.5	0.2
Acid value (mg KOH / g sample)	0.2	0.25	0.5
Soap content (g soap / g sample)	0.00012	0.0003	-
OSI (h)	1.2	2.5	15

3.2. Water Wash

Washing with water is the only process that has reduced levels of methanol and free glycerol to those required by the norm ASTM D6751. As with magnesol, it has a similar effect on the various glycerides. Table 8 shows the characterization of the fuel after water washing.

Methanol removal is affected by temperature, probably due to the reduced solubility of methanol in water, but is enough to meet the standard ASTM D6751. There is no great benefit in deionized water usage and increasing agitation also had little effect. Soap removal was influenced to some extent by the degree of agitation. Overall efficiency of soap removal was significantly better with magnesol. In most cases, the removal of glycerol by washing with water is completed in 10 minutes in all experiments except water at a ratio of 1:0.5 or taking more time to achieve the maximum limit of the ASTM D6751. The results can be seen in fig. 4 and fig. 5 respectively. These results show that the temperature has an important influence on the elimination of glycerol in water washing. Something similar occurs with the stirring speed and biodiesel / water ratio. Thus, the best conditions for the water wash are the most economical conditions: room temperature, tap water, 300 rpm and the biodiesel / water ratio of 1:2.

3.3. Comparison of the Processes

In this paper, we showed that the two methods of purification could remove glycerol and have reasonable success in eliminating soaps. Only washing with water has a real effect on the methanol and none of the processes has any significant effect on glycerides, AV or OSI. The dry cleaning process with magnesol has no effect on the content of dissolved water. With respect to washing with water, according to Oliveira et al. [8,12] the equilibrium water solubility in the biodiesel at 20-22° C is about 1,500 mg / kg. This value is nearly close to the amount of water obtained for biodiesel

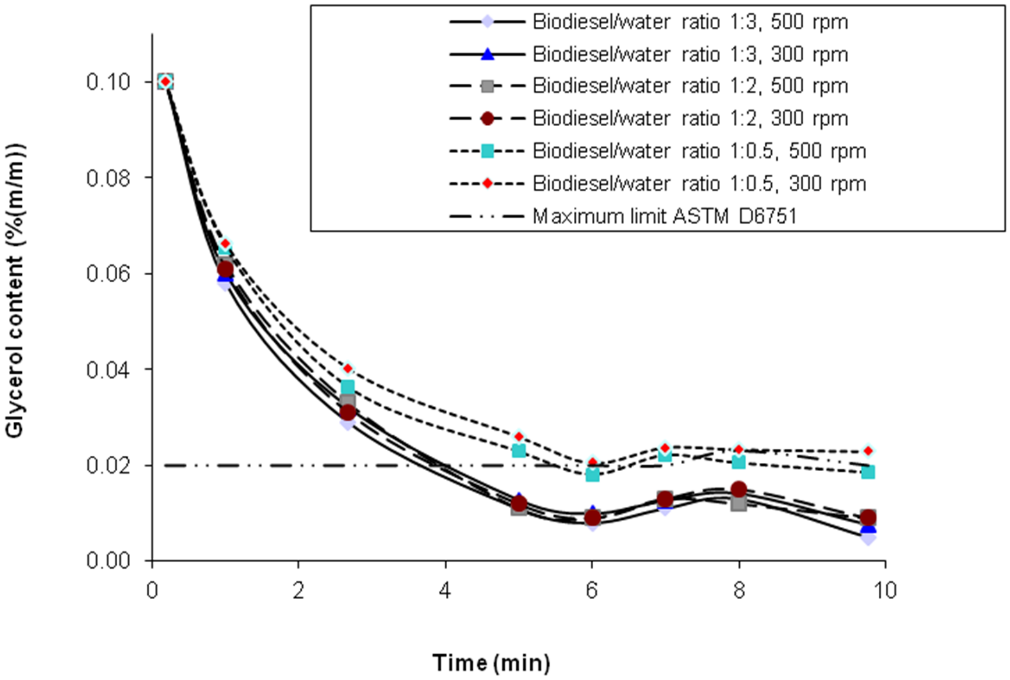

Figure 5. Evolution of glycerol content vs. time for the purification of biodiesel by de-ionized water washing at room temperature.

not addressed in this study (1000 mg / kg). Thus, it is possible that the water content in the water washing biodiesel remains constant due to the contact time in the process and the proximity of the equilibrium concentration (related to experimental error in the Karl-Fischer method used). Mass transfer is delayed by these factors. In general, the gain does not increase at elevated temperatures or by a powerful agitation in purification at a temperature of 65 °C.

4. CONCLUSIONS

Regardless of the two types of raw materials, which gave us two slightly different fuels, purification processes have similar results. Thus, these treatments can be tested at any biodiesel production processes. This study showed that it is vital to remove as much of glycerol in the primary separation stage (sedimentation or centrifugation) and flash evaporation or a similar process must remove methanol. Only water washing of biodiesel can purify directly glycerol meeting the requirements of ASTM D6751. But water washing has some disadvantages such as: supply, cost, emulsions, wastewater treatment and drying of the final product. Magnesol process has a good effect on the methanol content, but none of the experiments complied with the ASTM D6751 limit. At least 2% (w / w) is required with a time of 10 minutes contact to decrease the content of glycerol and soap. Improvement was observed when the pre-dry or magnesol was applied at a temperature of above 65 ° C. It failed only to meet the standard when combining the two processes (washing with water and magnesol). Neither process has a significant effect on the acid, OSI, glycerides or water content.

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