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Comparison of purification methods for biodiesel

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ABSTRACT

In order to meet the very high purity requirements laid down on the European Standard for biodiesel fuel (EN 14214), a significant amount of post transesterification purification is needed. Until recently the preferred method was water washing but considerable interest is now being shown in purification by ion exchange resins and the use of magnesium silicate as a solid adsorbent. The three methods have been tested under several reaction conditions (temperature, concentration, agitation rate, etc.) in order to compare which gives better results. It has been found that it is necessary a previous methanol removal to avoid the saturation of the adsorbents. Glycerol and soap content have been removed in all the processes. Not many differences have been found on the other tested parameters.

1. Introduction

The world energy demands, the price of the petroleum and the environmental concerns about pollution coming from the car gases continue to increase. The most feasible way to solve these problems is by using alternative fuels. Among 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 derived from vegetable oils or animal fats [2].

1.1. Basic chemistry

The most common way to produce biodiesel is by transesterification. In this reaction, triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid mono-alkyl esters and glycerol. Methanol is the most common alcohol because of its low price compared to other alcohols. In this case, the reaction is referred to as methanolysis. The stoichiometry of methanolysis reaction requires 3 mol of methanol and 1 mol of triglyceride to give 3 mol of fatty acid methyl ester and 1 mol of glycerol. This reaction, in turn, consists of three consecutive reversible reactions with intermediate formation of diglycerides and monoglycerides. After the reaction, the glycerol is separated by settling or centrifuging and the layer obtained is purified to be used in its traditional applications (the pharmaceutical, cosmetics and food industries) or in its recently developed applications (animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants). The biodiesel phase is also purified before being used as diesel fuel in order to fulfil the EN 14214 Standard [2].

One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat (refine, crude or frying oils and fats) making it biodegradable and nontoxic [3]. There are different types of catalyst: basic, acid, ion exchange resin, enzymes and supercritical fluids. However, the basic catalysts are the most commonly used in industry, because the process proves faster and the reaction conditions are moderated [4,5]. The reaction can be carried out in two ways: discontinuous (batch) and continuous.

There are several advantages in the use of biodiesel: renewable; biodegradable; lower greenhouse emissions; contains little or no sulphur; mixes in all proportions with petrodiesel; no engine modifications are required; low hydrocarbons, CO and particle emissions; acts as lubricant; agricultural and environmental benefits.

There are some disadvantages too: high freezing point (between 0 and −5 °C); filter obstruction (due to solvent power); lower energy capacity than petrodiesel and storage problems (due to it is biodegradable).

The glycerol is largely removed by gravity separation or centrifugation and the methanol may in some cases be removed the

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Table 1
Effects of impurities on biodiesel and engines

Impurity	Effect
Free fatty acids (FFA)	Corrosion Low oxidation stability
Water	Hydrolysis (FFA formation) Corrosion Bacteriological growth (filter blockage)
Methanol	Low values of density and viscosity Low flash point (transport, storage and use problems) Corrosion of Al and Zn pieces
Glycerides	High viscosity Deposits in the injectors (carbon residue) Crystallization
Metals (soap, catalyst)	Deposits in the injectors (carbon residue) Filter blockage (sulphated ashes) Engine weakening
Glycerol	Settling problems Increase aldehydes and acrolein emissions

flash evaporation. Neither process is 100% efficient hence a final purification stage is needed in order to meet the requirements of EN 14214 Standard.

1.2. *Purification processes*

The methyl esters cannot be classified as biodiesel until the EN 14214 Standard specifications are fulfilled. Therefore, the purification stage is essential. The untreated biodiesel contains several impurities: free glycerol, soap, metals, methanol, free fatty acids (FFA), catalyst, water and glycerides. The engine life can be reduced by high levels of impurities. Table 1 shows the effect of each impurity.

There are two generally accepted methods to purify biodiesel: wet and dry washing. The more traditional wet washing method is widely used to remove excess contaminants and leftover production chemical from biodiesel. However, the inclusion of additional water to the process offers many disadvantages, including increased cost and production time. Dry washing replaces water with an ion exchange resin or a magnesium silicate powder to neutralize impurities. Both dry washing methods are being used in industrial plants [6].

Whilst it has been proved for some time that it is possible to meet the specifications by water washing, this process gives rise to some disadvantages. A highly polluting liquid effluent is generated as it is shown in Table 2. Significant product loss can be carried out for retention in the water phase. Furthermore, emulsions formation when processing used cooking oils or other feeds with high FFA content can happen due to the soap formation [7].

Table 2
Characterization of the effluent from water washing purification

Parameter	Results
Total COD[a] (mg/L)	18,362
pH	6.7
Conductivity (μS/cm)	1119
TSS[b] (mg/L)	8850
VSS[c] (mg/L)	8750
MSS[d] (mg/L)	100

[a] Chemical oxygen demand.
[b] Total suspended solids.
[c] Volatile suspended solids.
[d] Mineral suspended solids.

Two alternative commercial processes are now being promoted, one using ion exchange resin and the other using magnesium silicate (Magnesol®). Both processes have the advantage of being waterless thus eliminating many of the problems outlined above but, other than some fairly sketchy advertising material little is really known about their performance.

Since both glycerol and methanol are highly soluble in water, water washing is very effective in removing both contaminants and, until recently was the most common method of purification. It also has the advantage of removing any residual sodium salts and soaps, the latter being a by product of high FFA feeds, due to their water solubility. But as above mentioned the water washing has some disadvantages.

The use of ion exchange resin as a purification method is promoted by two resin manufactures, Rohm & Haas (BD10 Dry) and Purolite (PD206). Though sold as ion exchange materials neither supplier advocates regeneration in normal use and they are really acting as adsorbents. It has not been possible, for reasons of commercial confidentially, to obtain any information on the chemical composition of either of the resins.

The use of a very fine form of magnesium silicate (Magnesol®) is promoted in the UK by Hydrotechnik (UK) and in the US by the Dallas Corporation, again this is purely an adsorbent and the spent material has to be disposed of to landfill or other applications (compost, potential animal feed additive and potential fuel).

1.3. *Objectives*

The main objective has been to look at the efficiency of the removal of methanol and glycerol by all three methods under a variety of conditions though conditions have been kept as close to commercial operating practise as possible. Subsidiary objectives have included efficiency of soap removal and the effect of the processes on final FFA and oxidation stability. In the case of the ion exchange process an attempt has been made to look at resin capacity, vital to compare the relative economics of the processes at a possible industrial application.

2. Experimental

2.1. *Experimental materials*

Two feedstocks were used; one produced in house using the University of Cambridge Oscillatory Flow Mixing (OFM) biodiesel pilot plant [8] and the other supplied by Hydrotechnik (UK). The in house product, referred to hereafter as 'pilot plant' was made from refined cooking oil (Holland UK Ltd.) and the feed was taken immediately after the gravity settler, sodium methoxide was used as the catalyst. For the ion exchange capacity test it was necessary to make up a synthetic feed by re-mixing some of the ion exchange treated product with raw glycerol from the pilot plant and allowing it to settle. The Hydrotechnik (UK) feed hereafter known as 'parasol' was produced for them from used cooking oils in a batch process using potassium hydroxide as catalyst. About 100 L of this feed was available so back mixing did not prove necessary. Table 3 shows a comparison of the two feeds.

Although none of feed fulfils the methyl ester content on EN 14214 Standard (see Table 3), these biodiesel have been used in the purification process in order to study the removal of impurities.

Rohm & Hass (R&H) supplied a small sample of BD10 Dry (particle size diameter: 900 μm) and further amounts were obtained free issue from Hydrotechnik (UK). Purolite supplied samples of PD206 (particle size diameter: 600 μm) and further quantities were purchased from the Biodiesel Warehouse. Hydrotechnik (UK) supplied the magnesol free issue (particle size diameter:

Table 3
Feed compositions

	Biodiesel pilot plant	Biodiesel parasol	EN 14214 maximum
Methyl ester content (% (m/m))	95.3	90.1	96.5
Free glycerol content (% (m/m))	0.11	0.10	0.02
Monoglycerides content (% (m/m))	0.46	0.73	0.80
Diglycerides content (% (m/m))	0.21	1.21	0.20
Triglycerides content (% (m/m))	0.43	5.69	0.20
Methanol content (% (m/m))	1.40	1.32	0.20
Soap content (g soap/g sample)	0.000909	0.00124	–
Water content (mg/kg)	1050	1050	500
OSI (h)	1.8	3.3	6.0
Acid value (mg KOH/g sample)	0.18	0.24	0.50

60 μm). Chemical and standards for analysis were purchased from Sigma–Aldrich.

2.2. *Ion exchange experiments*

The ion exchange resins must be transferred dry and all air must be purge with free impurities biodiesel before running the tests. Temperature of the fixed bed experiment was set up at 22 °C (room temperature).

The ion exchange resins were investigated by passing the feed through a column of resin supported in a glass tube. As it was necessary to work in parallel two tubes were used one 3.5 cm diameter and the other 3.0 cm diameter. The flow was controlled by metering pumps and the outlets were restricted to ensure a head of liquid above the resin at all times. Initially the resin was supported on sintered glass discs but after the supports fractured on both tubes the resin was simply supported on a plug of glass wool. The initial loadings and flows for both types of resin were as recommended in the R&H trade literature. The initial resin sample size was 80 g and the flow rate based on the R&H recommendation of 3 L/h per kg of resin giving an actual flow of 0.25 L/h. In order to estimate final loadings the resin quantities in the last two experiments were reduced to 50 g and the flow rate doubled after the first day of operation.

Four experiments were conducted with the two feeds and the two resins. Samples were initially taken at 2 h intervals and analysed for free glycerol and methanol, once no more methanol was removed the sample interval was increased and continued until the free glycerol level exceeded that in EN 14214 Standard (0.02% (m/m)). The products from each experiment were bulked and the bulk samples analysed for acid value and soap. Mono-, di- and triglycerides contents and the OSI were also determined.

2.3. *Magnesol experiments*

The work was carried out in a batch reactor with sample size of 200 mL fitted with a variable speed agitator and immersed in a water batch. The standard washing time was 30 min but samples were also taken at 10 and 20 min. Separation of the final product was by vacuum filtration using a Büchner funnel and water ejector, the intermediate samples were centrifuged as it was not practicable to filter small samples.

Experiments were carried out at ambient temperature and 60 °C and four (w/w) concentrations of magnesol: 0.25, 0.50, 0.75 and 1.00% as suggested by the suppliers. All experiments were performed on both feed materials. Samples were analysed for methanol and free glycerol using standard GC methods, note that due to sample size it was not possible to determine methanol on the intermediate samples. Water content (Karl-Fischer method) was measured on a number of samples. Again the products of the various runs were bulked and the bulk samples analysed for acid value, soap, OSI and mono-, di- and triglycerides.

Since magnesol is hygroscopic once the bag was opened, care was taken to re-seal the bag as tightly as practicable. Material for immediate use was transferred to sealable plastic containers and for some experiments the magnesol was oven dried overnight at 100 °C for comparison with non-dried material. Due to the very fine nature of the magnesol powder a face mask was worn when handling it.

2.4. *Water washing experiments*

Water washing used three wash waters: deionised, town's water and acidified water (5% phosphoric acid). Table 4 shows the properties of the town's water. Washing was carried out at ambient temperature and 60 °C. Three water/oil ratios and two agitator speeds were investigated. Again all experiments were performed on both feed materials.

The work used the same batch reactor in the water bath as the magnesol work with sample size of 200 mL. The standard washing time was 30 min but samples will be taken at 10 and 20 min. Separation of the final product was by gravity settling for 30 min but it was necessary to centrifuge the intermediate sample.

The analysis was the same as for the magnesol work.

2.5. *Analytical methods*

An automatic 'cool on column' injection Gas Cromatograph (GC, Agilent Technologies, USA, 6890) was used for the determination of mono-, di- and triglycerides and free glycerol in accordance with British Standard EN 14105. A capillary GC column (Agilent Technologies, USA, DB-1HT) with 0.32 mm i.d. was used in the apparatus. The temperature of flame ionisation detector was 380 °C, and carrier gas pressure was 80 kPa. The analysis of biodiesel for each sample was carried out by sylating then dissolving 100 mg of biodiesel sample in 8 mL of heptane and injecting 1 μL of this solution in GC. Two internal standards are used, one for glycerol and one for the glycerides. The monoglycerides (MG), diglycerides (DG), triglycerides (TG) and free glycerol contents were expressed as weight percent (% (m/m)). The instrument was calibrated using glycerol, monoolein, diolein and triolein in *n*-heptane solutions in accordance with BS EN 14105.

Methanol was determined using an Agilent 6850 manual injection GC using the head space method in accordance with BS EN 14110, with 2-propanol as the internal standard. Water content was

Table 4
Properties of town's water (Cambridge, UK)

Parameter	Results
pH	6.9
Conductivity (μS/cm)	2513
Hardness (mg $CaCO_3$/L)	174
Turbidity (NTU)	1

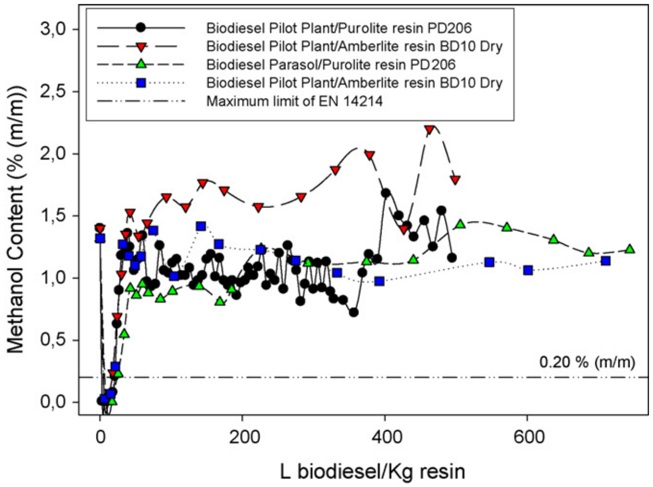

Fig. 1. Evolution of methanol content vs. L biodiesel/kg resin.

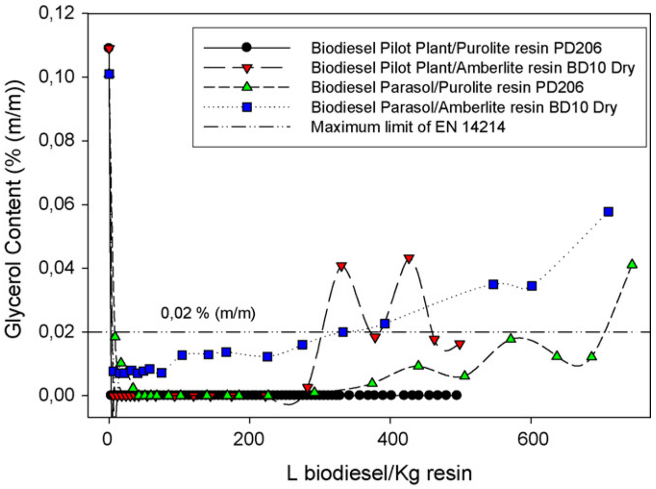

Fig. 2. Evolution of glycerol content vs. L biodiesel/kg resin.

determined by the Karl-Fischer method (ISO 12937) and acid value was determined by titration with alcoholic potassium hydroxide in accordance with BS EN 14104.

The oxidation stability index (OSI) was determined following the ‘rancimat’ method in accordance with BS EN 14112. Soap content was determined in accordance with a method from ‘Biodiesel Analytical Methods’ [9].

3. Results and discussion

3.1. Ion exchange work

The results show that the ion exchange resins have little effect on methanol after the first few hours of operation and they do not have any effect on the various glycerides. There may be some evidence of back washing of methanol towards the end of the cycle (Fig. 1). There is some indication of a slight increase in acid value as the products pass through the ion exchange column which could be explained by the fact that the resins are ‘acid’. Any effects on OSI are within the experimental limits of the method so cannot be considered significant. Soap content appears to be reduced by a factor of about 10 but as there is no limit set on soap in EN 14214 Standard the significance may not be great. Both feeds were low in soap and since only the bulk samples were analysed it is not possible to say if there is saturation level for soap. However, the fact that soap is absorbed may indicate a limitation for high soap containing feeds. Table 5 shows the characterization of bulked products from ion exchange work.

Thus the main advantage of the ion exchange resins is that they bring the free glycerol level down to an acceptable standard as shown in Fig. 2.

The two resins have similar capacity for the same feed, approximately 500 L biodiesel pilot plant treated/kg resin and 720 L biodiesel parasol treated/kg resin. These numbers are below that claimed by the manufacturers but do depend very heavily on the free glycerol content of the feed which was 10% higher for the pilot plant.

3.2. Magnesol work

Magnesol does not have any significant effect on the various glycerides or the OSI but, unlike the ion exchange does have some, though not large, effect on the methanol content. The higher methanol removal at 60 °C could well be due to evaporation losses rather than any other reason. It is interesting to observe the dried magnesol seemed to have a greater effect with the pilot plant feed than with the ‘parasol’ feed; no reason can be given for this at the moment. None of the experiments decrease the methanol content below the maximum limit of EN 14214 Standard, but the best results are reached with the maximum magnesol concentration at 60 °C.

There are no significant differences between the use of dried or non-dried magnesol in the removal of free glycerol and soap from the two feeds. With the exception of the experiments with 0.25% (w/w) magnesol concentration, all the experiments remove in satisfactory way the glycerol content in 10 min of reaction. The same happens in the soap removal. The reduction in soap values is less than that achieved by the ion exchange resins. There also

Table 5
Characterization of bulked products from ion exchange work

	Resin PD206		Resin BD10 dry		EN 14214 maximum
	Biodiesel pilot plant	Biodiesel parasol	Biodiesel pilot plant	Biodiesel parasol	
Free glycerol content (% (m/m))	0.04	0.03	0.04	0.03	0.02
Monoglycerides content (% (m/m))	0.36	0.71	0.39	0.70	0.80
Diglycerides content (% (m/m))	0.12	1.15	0.11	1.15	0.20
Triglycerides content (% (m/m))	0.34	5.63	0.35	5.64	0.20
Methanol content (% (m/m))	1.02	1.13	0.94	1.14	0.20
Soap content (g soap/g sample)	0.000097	0.000101	0.000108	0	–
Water content (mg/kg)	1050	1050	1050	1050	500
OSI (h)	1.5	3.3	1.5	3.3	6.0
Acid value (mg KOH/g sample)	0.21	0.27	0.20	0.24	0.50

Table 6
Characterization of bulked products from magnesol work

	Biodiesel pilot plant	Biodiesel parasol	EN 14214 maximum
Free glycerol content (% (m/m))	0.03	0.05	0.02
Monoglycerides content (% (m/m))	0.41	0.71	0.80
Diglycerides content (% (m/m))	0.21	1.19	0.20
Triglycerides content (% (m/m))	0.35	5.68	0.20
Methanol content (% (m/m))	0.51	0.80	0.20
Soap content (g soap/g sample)	0.00025	0.00034	–
Water content (mg/kg)	1050	1050	500
OSI (h)	1.7	3.3	6.0
Acid value (mg KOH/g sample)	0.11	0.20	0.50

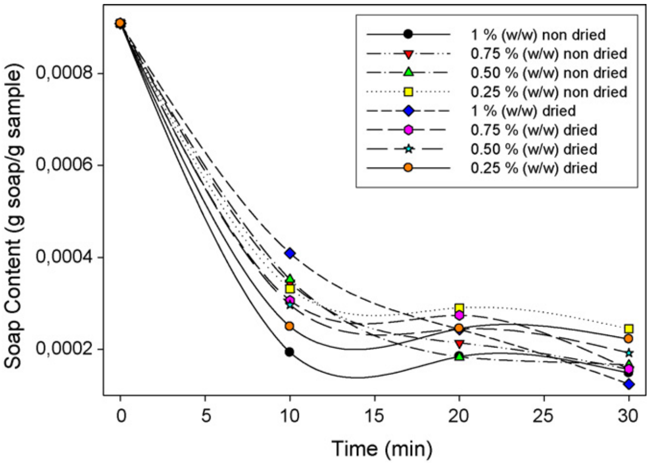

Fig. 3. Evolution of soap content vs. time in the purification of biodiesel pilot plant with magnesol at ambient temperature.

appears to be a small effect on acid value. These results can be observed in Table 6.

The results show that like the ion exchange resins, can bring the glycerol levels down to that required by EN 14214 Standard and can bring about large reductions in the soap content but are not successful in removing sufficient methanol to satisfy EN 14214 Standard. Figs. 3 and 4 show some examples about the evolution of soap and glycerol content in the magnesol work. At least 0.75% (w/w) is required with a contact time of 10 min but there seems to be little advantage to be gained by pre-drying the material or operating at above ambient temperature. The fact that the bulk sample shows slightly higher glycerol content is because it included material form test with less than 0.75% (w/w) magnesol.

3.3. *Water washing work*

Water washing is the only process that has reduced both methanol and free glycerol levels down to those required by EN 14214 Standard. Like the other processes it does not have any effect on the various glycerides. Table 7 shows the characterization of bulked products from water washing work.

Methanol removal is affected by temperature due almost certainly to the reduced solubility of methanol in water but it was possible to meet EN 14214 Standard with a 0.5/1 water to oil ratio at any temperature. There seemed to be no advantage in using deionised or acidified water and increasing agitation also had very little effect.

Soap removal was influenced to some extent by the degree of agitation and it was completely removed by acidified water. In general soap removal efficiency was on a par with ion exchange and significantly better than with magnesol.

In most cases, the glycerol removal by water washing is complete in 10 min in all the experiments with the exception of acidified water washing that needs 30 min for decreasing until the maximum limit of EN 14214 Standard. It can be observed in Figs. 5 and 6. The results show that the temperature does not have an important influence over the removal of glycerol by water washing. Something similar happens with the agitation speed and biodiesel/water ratio. Thus the best conditions overall for the water washing are the most economical conditions: ambient temperature, towns' water, 200 rpm and water/biodiesel ratio of 0.5/1.

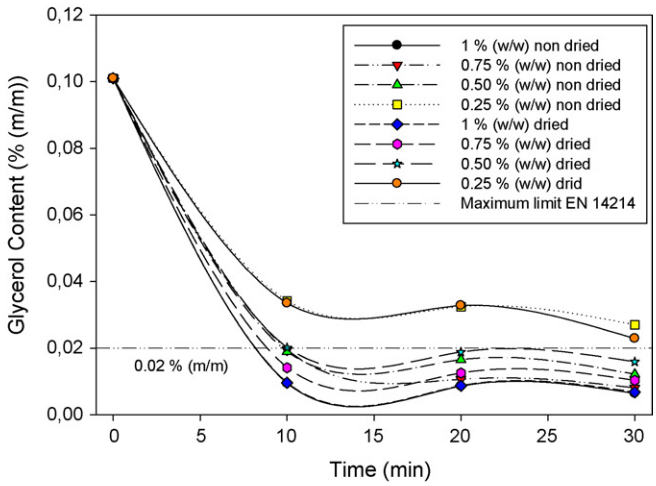

Fig. 4. Evolution of glycerol content vs. time in the purification of biodiesel parasol with magnesol at ambient temperature.

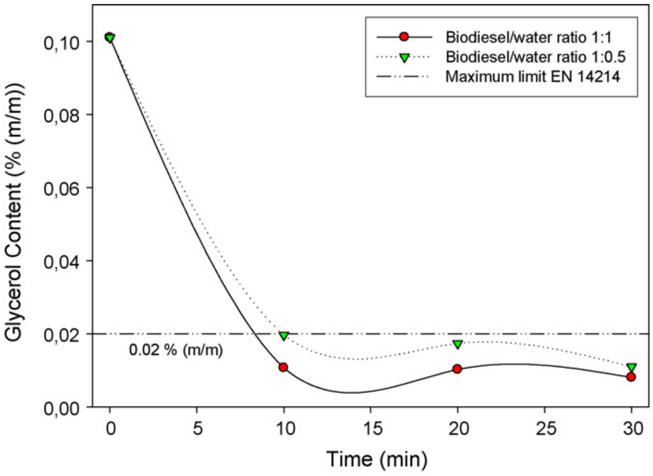

Fig. 5. Evolution of glycerol content vs. time in the purification of biodiesel parasol by towns' water washing at ambient temperature and 400 rpm.

Table 7
Characterization of bulked products from town's water washing work

	Biodiesel pilot plant	Biodiesel parasol	EN 14214 maximum
Free glycerol content (% (m/m))	0.01	0.01	0.02
Monoglycerides content (% (m/m))	0.44	0.72	0.80
Diglycerides content (% (m/m))	0.18	1.21	0.20
Triglycerides content (% (m/m))	0.33	5.69	0.20
Methanol content (% (m/m))	0.04	0.07	0.20
Soap content (g soap/g sample)	0.000115	0.000211	–
Water content (mg/kg)	1050	1050	500
OSI (h)	1.1	3.0	6.0
Acid value (mg KOH/g sample)	0.18	0.22	0.50

3.4. Comparison of processes

The work has demonstrated that all three methods of purification can remove glycerol and are reasonably successful in removing soaps, only water washing has any real effect on methanol and none have any significant effect on glycerides, AV or OSI. There may be some slight evidence of increase in AV with the ion exchange resin though the product is still within specification. Neither of the dry washing processes (magnesol and ion exchange purifications) had any effect on the dissolved water content. With respect to water washing, according to Oliveira et al. [10], the equilibrium water solubility in biodiesel at 20–22 °C is around 1500 mg/kg. This value is close to the constant water amount obtained for the untreated biodiesel in this study (1050 mg/kg). In this way, it is possible that the water content in the water-washed biodiesel remains constant due to the low contact time in the process and the proximity of the equilibrium concentration (jointed to the experimental error in the used Karl-Fischer method). The matter transfer is slowed down by these factors. In general little is to be gained by going to elevated temperatures or very energetic mixing though purification at temperatures in the order of 60 °C, i.e. direct from production, do not seem to have any significant disadvantage except perhaps with water washing. There were no measurable differences in the treatment efficiencies between feedstocks.

The magnesol and ion exchange resin manufacturers' recommendations re-loading, flow rates, etc. have resulted in glycerol levels to below EN 14214 Standard. It was found that somewhat less than the recommend concentrations of magnesol and mixing times were needed but it was not possible to achieve the ion exchange resins life suggested with either resin or either feed. This could have been due to a higher than average glycerol level, both feed having been separated by gravity rather than centrifuge though in the case of the parasol feed it had been allowed to settle for a very long period before treatment.

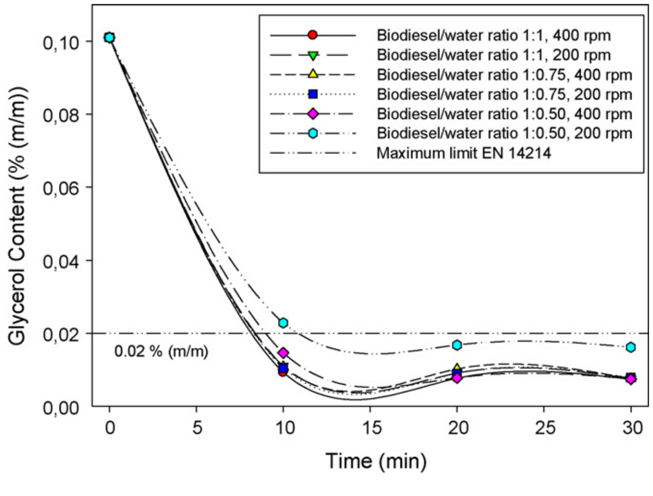

Fig. 6. Evolution of glycerol content vs. time in the purification of biodiesel parasol by de-ionised water washing at ambient temperature.

4. Conclusions

Although each biodiesel comes from different feedstock and catalyst, the purification processes have obtained similar results. In this way, these treatments can be tested in any process of biodiesel production.

The work has shown that it is vital to remove as much glycerol as possible in the primary separation stage (settling or centrifugation) and that methanol must be removed by flash separation or a similar process.

Only water washing has purified biodiesel, direct from glycerol separation, to the requirements of EN 14214 Standard. But it has some disadvantages: water supply and cost, emulsions, wastewater treatment and drying of final product.

The ion exchange process has brought the free glycerol level down to the specifications in EN 14214 Standard. The capacity of methanol removal for both resins was really low (around 20 L biodiesel/kg resin).

The magnesol process has had better effect on the methanol content than the resins but none of the experiments fulfil the limit in the EN 14214 Standard. At least 0.75% (w/w) is required with a contact time of 10 min in order to decrease the glycerol and soap content. Any improvement was observed when pre-drying the material or operating at high temperature was selected.

None of the processes had any significant effect on acid value, OSI, glycerides or water content.

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