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Sources of Methyl Ester Yield Reduction in Methanolysis of Recycled Vegetable Oil

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Abstract Recycled vegetable oil (RVO) is a relatively cheap raw material for biodiesel production, but biodiesel grade methyl ester yields from RVO were found to be considerably lower than those from pure plant oil. The present paper investigates sources of yield loss during methanolysis of RVOs with free fatty acids (FFA) contents of 0.4–3.3%, and makes suggestions for the improvement of methyl ester yields. Data presented here indicated that yield losses of methyl esters during methanolysis were due to triglyceride and methyl ester hydrolysis and to the dissolution of methyl esters in the glycerol phase. Hydrolysis of triglycerides and methyl esters seemed to be the only side reaction causing yield losses, and the amount of fatty acids from hydrolysis increased with concentration of the potassium hydroxide catalyst. Dissolution of methyl esters in the glycerol phase was probably caused by the detergent effect of potassium salts of fatty acids originating from FFA in the RVO and from triglyceride hydrolysis, and the amount of dissolved methyl esters increased with FFA content of the RVO. The FFA content of the RVO had no effect on hydrolysis, and the amount of triglycerides and methyl esters hydrolysed during methanolysis remained constant with increasing FFA content of the RVO.

Keywords Recycled vegetable oil · Methanolysis · Yield reduction · Hydrolysis · Methyl esters in the glycerol phase

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Introduction

Biodiesel grade methyl esters have been routinely used in diesel engines for over a decade, and current European production is over 3 million tons p.a. (per annum). Present triglyceride feedstock for biodiesel production in Europe is mainly rapeseed oil, but smaller amounts of palm and soya oils are also being used. On the other hand soya oil is the main feedstock for biodiesel production in the US. However both rapeseed and soya oils are relatively expensive, and a cheaper alternative feedstock is desirable. The cost of RVO (recycled vegetable oil) in Ireland at present is about half of that of degummed rapeseed oil and it is estimated that about 12,000 tons p.a. is available for biodiesel production. Considering that recycled vegetable oil can no longer be used in animal feeds in Europe, conversion to biodiesel is a cost effective alternative use.

It has been shown that it is possible to produce biodiesel which meets EU specifications EN 14214 from RVO [1, 2] by the base catalysed methanolysis used for rapeseed oil, but the RVO has to be cleaned, and several processing steps need to be modified. Biodiesel yields from RVO are, however, considerably lower than from rapeseed oil and vary from batch to batch [2–5]. Yields in the range of 63–87% have been reported. Low yields were attributed to the relatively high FFA content of the RVO which normally varies between 0.5 and 5.0% [1, 2], but FFA content as high as 10% has been reported [4]. Removal of FFA from RVO was found to increase yields to about 98%, which was only slightly lower than that obtained from pure rapeseed oil [2].While a considerable amount of work has been carried out to show that FFA in RVO reduces yields of methyl esters [1, 3, 4], there is very little reported work on where yield losses occur. The objective of the present work is to identify sources of methyl ester yield loss, to quantify the material not recovered as product, and to determine the yield limit from high FFA RVO with one stage base catalysed methanolysis.

Materials and Methods

Materials

RVO with high FFA levels were obtained from Bolton Oil, Castledermot, Co. Kildare, Ireland and refined rapeseed oil was purchased from Tesco Stores, Carlow, Ireland. The RVO used in the present work was filtered and steam treated by the supplier to remove suspended solids and water soluble impurities and it was dried before use by vigorous stirring at 110–120 °C until constant weight. The final water content of the dried RVO was determined according to ISO 12937 [6]. Fatty acid-free RVO was prepared for laboratory use by the addition of sufficient potassium hydroxide in 700 g/l aqueous solution at 30–35 °C to neutralise the free fatty acids [2]. The precipitated solids were allowed to settle overnight and the clear oil was decanted and centrifuged at 8,000 rpm for 30 min. RVOs with FFA contents ranging from 0.4 to 3.3%, which is representative of the material available in Ireland, were obtained by blending appropriate amounts of fatty acid-free and high FFA RVOs. The FFA content of the blended RVO samples was determined according to ISO 660 [7].

Preparation of the Methyl Esters

Methanolysis ratios of RVO, methanol and potassium hydroxide were obtained from the literature [8, 9], and reaction conditions and purification of the methyl esters were worked out in our laboratory. The following methods were found to give methyl esters from RVO and vegetable oils of acceptable quality [2, 10]. Either 1.8 g potassium hydroxide (5.4% w/v, low catalyst concentration) dissolved in 33.5 ml methanol [8] or 2.5 g potassium hydroxide (10.4% w/v, high catalyst concentration) dissolved in 24 ml methanol [9] was added to 120 g of RVO or rapeseed oil at 35–40 °C, vigorously stirred with a magnetic stirrer on a hot plate in a 250-ml conical flask. The temperature was controlled with the hot plate. Stirring was continued for 1 h at the same temperature, the mixture was then transferred to a separating funnel, and the glycerol layer was allowed to separate for a minimum of 3 h. After removal of the glycerol layer, the methyl ester was transferred into a clean separating funnel. It was washed gently with one volume of water, and after the layers separated completely (ca. 1 h) residual water and methanol were removed from the methyl ester by heating at 110–120 °C until constant weight. Methanolysis with sodium methoxide was carried out according to the method reported by Freedman [8], and the methyl ester was purified according to the above method. Four methanolyses were carried out with each RVO and rapeseed oil, using both high and low catalyst concentrations, and an additional set of four was carried out with rapeseed oil using sodium methoxide catalyst.

Analysis of the Methyl Esters

The properties of the methyl esters produced from the RVOs were determined by methods listed in EN 14214:2003. Monoglyceride, diglyceride, triglyceride and free glycerol contents were determined by EN 14105 [11], methanol by EN 14110 [12] and FFA and water contents content according to ISO 660 [7] and ISO 12937 [6] respectively.

Analysis of the Glycerol Phase

To determine the methyl ester and fatty acid content of the glycerol phase, glycerol from each methanolysis (20 g) was acidified (pH $\leq$ 2.0) with sulphuric acid (3.0 M) after adding water (40 ml), and the precipitated organic phase was removed by washing with hexane (3 × 40 ml). The hexane extract was washed with water (2 × 40 ml) which in turn was washed with dichloromethane (2 × 20 ml), the combined solvent layers were evaporated to dryness on a steam bath, and the residue was dissolved in ethanol (50 ml). One half of the solution (25 ml) was used to determine the FFA content (mmol) of the glycerol phase by titration with aqueous potassium hydroxide (1.0 M or 0.1 M) [7], and the amount of FFA formed during methanolysis (mmol) was calculated by subtracting the FFA content of the RVO from that of the glycerol phase. The remaining half of the extracted material was saponified according to AOAC method no. 28.027 [13] after the evaporation of ethanol, and the total saponified material (mmol) in the glycerol phase was determined from the difference between the blank and the saponification titre. The methyl ester content (mmol) of the glycerol phase was calculated by subtracting the FFA content of the same from the determined total saponified material. The glycerol bonded fatty acid content (mmol) of the RVO and methyl ester content of the product (mmol) were also determined by saponification, and the product and both the FFA and methyl ester contents of the glycerol phase were expressed as mol% of glycerol bonded fatty acids in the RVO. Qualitative analysis glycerol phase was carried out by thin layer chromatography, using 20 × 20 cm, 0.25 mm silica gel plates (Silica gel 60, no. 5721 Merck KGaA, Darmstadt, Germany), hexane/diethyl ether/acetic acid 90:10:1 as developing solvent [14] and iodine vapour for visualisation. The ethanolic glycerol extract used for saponification (10 μl) was spotted on the TLC plate.

Results and Discussion

Methanolysis of the RVOs

The RVO used in the present work was filtered and steam treated by the supplier to remove suspended solids and water soluble impurities, and it was dried before use by heating at 110–120 °C until constant weight. The fatty acid profile of the RVO indicated that rapeseed oil was the predominant component.

The water content of the dried RVO was 0.09%, considerably less than the water formed in the methanolic potassium hydroxide solutions used here, which is about 0.5% of the weight of the oil, when determined from the equilibrium of the methanol/hydroxide/water/methoxide system. Considering that the pKa values of the dissociation of water and methanol are about the same in aqueous solution [15], it was assumed that they were also the same in methanol, and accordingly an equilibrium constant of one was used to calculate the water content of methanolic potassium hydroxide solution.

Conditions of methanolysis used here were adapted from an earlier method [8] which reported high yields (>96%) of methyl ester from soya oil with 1% sodium hydroxide w/w (equivalent to 1.4% potassium hydroxide) at 32°, 45° and 60 °C. The particular method was used successfully before for pilot scale methanolysis of RVOs [2], and was very suitable for the present study because the same methanolysis conditions could be used for RVOs with FFA contents from 0.1 to 3.0%. On account of the relatively high FFA content of the RVOs catalyst concentrations (potassium hydroxide) had to be 50% higher, 1.5 vs. 1% of the starting material, than reported for soya [16] and sunflower oils [17], to ensure complete methanolysis of the triglycerides. The use of sodium methoxide as catalyst was not investigated, because it is not recommended for vegetable oils with FFA contents above 1% [18], probably due to the high cost of the additional reagent required to neutralise the FFAs.

Methanolysis related impurities of methyl esters obtained in the present study, such as glycerides and FFA, were within ASTM specifications for biodiesel grade methyl esters and also within EN specifications up to 1.5 and 2.5% (w/w) FFA in RVO with the high and low catalyst methods respectively (Table 1). At higher FFA levels both di- and triglycerides increased above the specified EN levels, but total glycerol levels remained below the specified maximum of 0.25%. In our pilot plant work we used additional potassium hydroxide for RVO with FFA content above 3% to ensure that glyceride levels remained within EN specifications [2]. Other methanolysis related impurities such as methanol and glycerol contents were well within EN and ASTM specifications, but the water content was 0.03–0.05% higher in each methyl ester than the specified value (Table 1). It was not possible to reduce the water content of the methyl esters to 0.05% by the method of drying used in the present work, and further reduction by

Table 1 Methanolysis related properties of methyl esters obtained from RVO with different FFA contents

FFA in RVO	Glycerol	Mono-glyceride	Di-glyceride	Tri-glyceride	Total glycerol	Acid value[a]	Water	Methanol
Low catalyst concentration								
0.43	0.003	0.253	0.090	ND	0.081	0.135	0.088	
0.84	0.003	0.303	0.164	0.092	0.113	0.202	0.090	
1.59	0.003	0.316	0.128	0.040	0.107	0.230	0.094	
2.45	0.003	0.263	0.111	0.012	0.087	0.191	0.094	
3.27	0.003	0.385	0.361	0.510	0.207	0.269	0.103	
Average	0.003	0.304	0.171	0.131	0.119	0.205	0.094	0.005
High catalyst concentration								
0.06	0.005	0.214	0.204	0.178	0.108	0.202	0.094	
1.48	0.004	0.222	0.153	0.158	0.099	0.202	0.092	
2.11	0.094	0.273	0.330	0.536	0.177	0.213	0.093	
2.80	0.002	0.261	0.318	0.611	0.179	0.146	0.083	
Average	0.004	0.240	0.251	0.370	0.141	0.191	0.090	0.004
EN14214	0.02	0.8	0.2	0.2	0.25	0.5	0.05	0.2
ASTM6725	0.02				0.24	0.5	0.05	0.2

All impurities in %w/w except acid values

[a] Acid value in mg KOH/g RVO

an alternative method was beyond the scope of the present work. Raw material related properties, such as iodine number, density, kinematic viscosity, cold filter plug point and Conradson carbon residue of methyl esters obtained from Irish RVOs have been reported before [2, 19].

Material Balance of RVO Methanolysis

Biodiesel grade methyl ester yields from methanolysis of RVO are generally lower than those obtained from methanolysis of vegetable oils [2–5]. Although RVO with FFA removed was reported to give methanolysis yields of 97–98%, methyl ester yields from the same RVO before the removal of FFA were found to be considerably lower [2]. Data from the present work also indicates that obtained methyl ester yields from RVO were considerably lower than the maximum possible yield of methanolysis (all glycerol bonded fatty acids are converted to methyl esters), and the difference increased with FFA content of the RVO (Table 2). Hence some glycerol bonded fatty acids in the RVO must not end up in the methyl ester obtained as product. Considering that yield losses arising from phase separation, washing and drying are only about 0.5%, and impurities in the product are minimal [2, 10], glycerol bonded fatty acids not recovered as product must be present in the glycerol phase. Qualitative analysis of the organic (hexane soluble) fraction of the glycerol phase by thin layer chromatography indicated only the presence of methyl esters and FFA, and of traces of glycerides.

FFA and methyl ester content (mmol) of the glycerol phase was quantified by titration [7] and saponification [13] of the extracted organic fraction, and similarly saponification was used to determine glycerol bonded fatty acids (mmol) in the RVO and methyl esters (mmol) in the product. Yields and yield losses were expressed as molar percent of glycerol bonded fatty acids in the starting material. Saponification and titration were probably the most suitable methods for the accurate determination of molarities of mixtures of methyl esters, triglycerides and fatty acids, because for each group of compounds the molarity of the common functional group, the carboxyl group, was determined. The two methods were standard methods for the determination of molecular weights of organic carboxylic acids and the corresponding esters [20] before the more widespread use of mass spectrometry.

Material balances of methanolysis of RVOs with different FFA contents were determined by adding the amounts of FFA formed during methanolysis, methyl esters in the glycerol phase, and methyl esters in the product, each expressed as molar percent of glycerol bonded fatty acids in the RVO. Four methanolyses were carried out for each RVO, each tabulated value represents an average of four determinations, and the CVs (coefficients of variation) of the calculated material balances were below 0.5%. The good repeatability was due to the high precision of methyl ester yield determinations (CV 0.15–0.26), but it was not possible to determine methyl ester (CV 2.1–8.3) and FFA (CV 5.1–10.3) contents of the glycerol phase with the same degree of precision. Material balances of methanolyses of five RVOs with FFA contents ranging from 0.4 to 3.3% indicated that about 98% of the starting material was accounted for by the product, the FFA formed during methanolysis, and the methyl esters remaining in the glycerol phase (Table 3). The amount of material accounted for did not vary significantly with the FFA content of the RVO. Material losses incurred by phase separation and purification of the product contribute an additional 0.5% to the material balance, and the remaining 1.5% could not be accounted for.

Table 2 Obtained and expected yields of methyl ester from methanolysis of RVO

Maximum possible yields[a]	Obtained ME yields[b]	Conventional yields[c]	FFA content[d]
99.9	96.0	95.6	0.42
99.5	95.3	94.5	0.81
98.8	95.1	93.6	1.55
97.9	93.2	90.9	2.38
97.2	91.8	88.8	3.18

[a] (RVO − FFA)/RVO %w/w

[b] ME/(RVO − FFA) %w/w ME methyl ester

[c] ME/RVO %w/w

[d] FFA/RVO %w/w

Sources of Yield Loss

Material balances of methanolysis of RVOs with FFA contents from 0.4 to 3.3% showed that yield losses in each case were due to FFA formed during methanolysis (hydrolysis of triglycerides and methyl esters) and dissolution of methyl esters in the glycerol phase irrespective of the FFA content of the RVO (Table 3). The amount of triglycerides and methyl esters hydrolysed during methanolysis, was not affected by the FFA content of the RVO, and FFA from hydrolysis in the glycerol phase remained more or less constant. On the other hand methyl ester content of the glycerol phase was not constant, but it increased with increasing FFA content of the RVO and methyl ester yields were reduced accordingly. There were linear correlations between the methyl esters dissolved in the glycerol phase and the FFA content of both the glycerol phase ($r^2 = 0.89$) and the RVO ($r^2 = 0.94$). While methyl ester yields were reduced by dissolution of the product in the glycerol phase, total yields, that is the methyl esters obtained plus the methyl esters in the glycerol phase, were

Table 3 Yield losses during methanolysis of RVO, low catalyst concentration

Yield of ME	FFA in RVO[a]	Loss from hydrolysis	Loss from ME in glycerol	Total yield loss	Total ME yield	Material accounted for
96.0 (95.6)[a]	0.43	1.65	0.40	2.05	96.4	98.1
95.3 (94.5)	0.84	2.50	0.56	3.06	95.9	98.1
94.8 (93.6)	1.59	2.00	1.10	3.26	95.9	98.1
93.1 (90.0)	2.45	2.28	2.77	5.05	95.9	98.2
91.8 (88.8)	3.27	2.15	4.43	6.58	96.2	98.4

Yields and yield losses in mol% of glycerol bonded fatty acids in the RVO. Yields and yield losses are averages of four determinations

[a] FFA in RVO and yields in parenthesis in %w/w

Table 4 Yield losses during methanolysis of RVO, high catalyst concentration

Yield of ME	FFA in RVO[a]	Loss from hydrolysis	Loss from ME in glycerol	Total yield loss	Total ME yield	Material accounted for
91.8 (91.8)[a]	0.06	4.93	0.70	5.63	92.5	97.8
90.9 (88.6)	1.48	5.47	2.58	8.05	93.5	99.0
88.2 (86.3)	2.11	5.22	4.72	9.94	92.9	98.4
86.6 (84.1)	2.80	5.03	6.75	11.8	93.4	98.1

Yields and yield losses in mol% of glycerol bonded fatty acids in the RVO. Yields and yield losses are averages of four determinations

[a] FFA in RVO and yields in parenthesis in %w/w

not affected by FFA content of RVO and remained more or less constant in the five methanolyses (Table 3).

Changing reaction conditions by increasing catalyst concentration did not alter the role of FFA in methanolysis (Table 4). As with low catalyst concentration (Table 3) material balance indicated that methyl ester yield losses were due to dissolution of same in the glycerol phase and to hydrolysis of triglycerides and methyl esters. The former increased with FFA content in the RVO, whereas the latter remained constant. Similarly total methyl ester yield also remained constant. However both obtained and total methyl ester yields were considerably lower than with low catalyst concentration (Tables 3 and 4), mainly because more triglycerides and methyl esters were hydrolysed, and both FFA and methyl ester contents of the glycerol phase were considerably higher for each FFA content of the RVO (Table 4).

Hydrolysis of triglycerides and methyl esters can be explained in terms of the composition of the methanolic potassium hydroxide solution. Calculations based on the equilibrium of the methanol/hydroxide/water/methoxide system show that about 93 and 96% of the dissolved potassium hydroxide in the high and low catalyst solutions respectively is in the form of water and potassium methoxide. The methoxide ion displaces the glycerol from the triglycerides to form methyl esters, and simultaneously there will be hydrolysis of the triglyceride and probably also of methyl esters by residual potassium hydroxide or water. Methanolysis must stop as soon as the glycerol layer begins to separate, mainly because the catalyst moves into the glycerol phase [21, 22], but hydrolysis could continue in the glycerol phase if there is methyl ester dissolved in it. Data obtained in the present work however suggest that under conditions used here hydrolysis in the glycerol phase is minimal, and most of the hydrolysis occurs during methanolysis. Methyl ester content of the glycerol phase increased ten fold as FFA contents of the RVO increased from 0.4 to 3.3% (w/w) but the amounts of triglyceride and methyl ester hydrolysed remained constant at all FFA levels in both sets of methanolyses (Tables 3 and 4).

Control of Yield Loss

The results indicate that one of the main sources of yield loss during methanolysis is the dissolution of methyl esters in the glycerol phase. Considering that the methyl ester content of the glycerol phase increases linearly with the FFA content of the same, dissolution of methyl esters must be caused by the detergent effect of the potassium salts (soaps) of the fatty acids dissolved in the glycerol phase. The pH of the glycerol phase (50% aqueous solution) obtained by the methanolysis used here was above 13, hence dissolved fatty acids must be in the form of potassium salts. Dissolution of methyl esters in the glycerol phase during methanolysis has been reported before [17, 21].

Table 5 Yield losses during esterification of refined rapeseed oil

Method of esterification	Yield of methyl esters	Loss from hydrolysis	Total yield loss	Material accounted for
Low catalyst	98.5	0.84	0.84	99.4
High catalyst	92.6	3.90	>3.90	96.5
Na methoxide	99.6	0.22	0.22	99.8

Yields and yield losses in mol% of glycerol bonded fatty acids in the rapeseed oil. Yields and yield losses are averages of four determinations

The other source of yield loss was the hydrolysis of triglycerides and methyl esters by the potassium hydroxide catalyst. Hydrolysis must be the only significant side reaction competing with methanolysis because the sum of the methyl esters obtained, the methyl esters dissolved in the glycerol phase, the FFA from hydrolysis and yield losses from purification and phase separation, account for almost 99% of the glycerol bonded fatty acids in the RVO (Tables 3 and 4) in each methanolysis. Considering that more triglycerides and methyl esters are hydrolysed when the concentration of the catalyst is increased, the rate of hydrolysis must increase with the concentration of potassium hydroxide catalyst faster than the rate of methanolysis. Increased hydrolysis with increased concentration of potassium hydroxide catalyst is not restricted to RVO, but also occurs with rapeseed oil, although the amounts of triglycerides and methyl esters hydrolysed are somewhat less than with RVO (Table 5). When a non-hydroxylic catalyst such as sodium methoxide was used, which generates no water or hydroxide ions when dissolved in methanol, the amount of hydrolysis was negligible, and yields were almost quantitative (Table 5).

Considering that methyl ester yield losses during RVO methanolysis were due to hydrolysis of triglycerides and dissolution of the product in the glycerol phase, it should be possible to obtain optimum yields by controlling these two variables. Hydrolysis of triglycerides and methyl esters and the resulting FFA in the glycerol phase can be reduced by minimising the amount of hydroxide-based catalyst used, such as the low catalyst methanolyses of RVO and rapeseed oil in the present work (Tables 3 and 5), or almost eliminated by using sodium methoxide catalyst (Table 3). Sodium methoxide is however expensive and it is not recommended for vegetable oils with an FFA content above 1% [18].

While yield losses caused by hydrolysis of triglycerides and methyl esters can be minimised or even eliminated, most RVOs contain varying amounts of FFA and it is not possible to esterify these by base catalysed methanolysis. Neither does it seem to be possible to prevent dissolution of methyl esters in the glycerol phase by optimising methanolysis conditions, as it is caused by the detergent effect of FFA salts originating from the RVO. Hence in order to ensure optimum methyl ester yields from RVO, acid catalysed esterification of FFA either before or after alkali catalysed methanolysis has been proposed by some authors [4, 23].

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