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The Conversion of Low Grade Tallow into Biodiesel-Grade Methyl Ester

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Abstract The conversion of low grade tallow with free fatty acid contents of 11.0–26.0% into biodiesel-grade methyl ester was investigated on a laboratory scale. Methanolysis of low grade tallow could not be carried out by the standard base-catalysed process, because the high free fatty acid content of low grade tallow caused incomplete methanolysis and prevented phase separation. The problem was able to be partly overcome by adding more potassium hydroxide to neutralise the free fatty acids, 50–100% more methanol and some water to promote phase separation. However, even with the modified method only about 55% of the starting material could be recovered as methyl ester and this fell to 35 and 14% when the free fatty acid content of tallow increased to 20 and 26%, respectively. It was shown that yield losses were caused mainly by the dissolution of methyl ester in the glycerol phase, and to a lesser extent to hydrolysis of the triglycerides. In order to prevent yield losses caused by the dissolution of methyl ester in the glycerol phase the possibility of esterifying free fatty acids either before or after base catalysed methanolysis was investigated. Both methods involving methanolysis and esterification gave good conversions of low grade tallow to methyl ester, and in each case yields above 90% were obtained by relatively simple processes.

Keywords Biodiesel · Esterification · Fatty acid methyl esters · Low grade tallow · Methanolysis

Introduction

A total of 78,200 tonnes of tallow was produced in Ireland in 2003 by the rendering industry [1]. Of this total, 34,500 tonnes was classified as risk material, and precluded from use in animal feed by regulations to control the spread of bovine spongiform encephalopathy (BSE). A further 21,900 tonnes of low-risk material was classified as low-grade, i.e. with free fatty acids (FFA) content >8%. So a total of 56,400 tonnes of tallow should be available for biofuel production in, at a price well below that of rapeseed oil, the main European biodiesel feedstock. Considering the availability and relatively low cost of low-grade tallow, conversion to biodiesel-grade methyl ester is a cost-effective alternative use of this raw material.

Biodiesel-grade methyl ester has been prepared from food grade tallow [2–4], and reported properties with a few exceptions such as cold filter plug point (CFPP) were within EN specifications [2–4]. On account of the high CFPP, 14 °C, tallow methyl ester cannot be used directly in diesel engines, but it can be safely used in Ireland in blends of up to 10% with mineral diesel [4]. Food grade tallow is costly, and considering the high CFPP of the methyl ester they are unlikely to compete with rapeseed oil as a source of biodiesel. On the other hand low grade tallow is relatively inexpensive, but its high FFA content makes it unsuitable for the one step base catalysed methanolysis currently in use in most biodiesel plants in Europe. Very little work has been done to date on the conversion of low grade tallow to methyl ester, but there are numerous reports on methanolysis and esterification of recycled vegetable oil (RVO) with FFA contents of 2–12%.

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Acid-catalysed methanolysis of high FFA material, made up by adding 5–33% of palmitic acid to soybean oil, was investigated, but it was much slower (96 h) than the base-catalysed process, and conversion rate fell rapidly as FFA content increased [5]. A one-step enzyme catalysed methanolysis of high FFA RVO showed that lipase enzyme converted both FFA and triglycerides to methyl ester in good yields in RVO with 2.1% FFA, but no conversion occurred when FFA content was increased to 9% [6]. Later work indicated that immobilised lipases converted RVO with 6.9% FFA to methyl esters with 88% yield, and higher yields could be obtained with butyl and isobutyl alcohols [7]. Methanolysis of rapeseed oil with up to 5% FFA in supercritical methanol at 320 °C, gave almost quantitative yields of methyl ester, but RVO with higher FFA content was not evaluated [8]. Another approach used single phase esterification followed by methanolysis to convert the low grade fats to methyl esters [9]. A cosolvent was added to the methanol to dissolve the high FFA triglyceride and the catalysts, and yields around 99% were reported from RVO with 14% FFA using high methanol to triglyceride molar ratio and tetrahydrofuran [10]. A two phase conversion of RVO with 12% FFA into methyl esters by acid catalysed esterification of FFA followed by base-catalysed methanolysis was also investigated [11], but yields of methyl ester were only 80% and the purity of the product was not determined.

Immobilised enzymes with supercritical methanol gave high yields of methyl ester from RVO, but enzymes and high temperature processes are expensive, and the cost of recovering large amounts of cosolvent, and of ensuring safe operation with cosolvents such as tetrahydrofuran or methyl *t*-butyl ether could outweigh the obvious technical advantages of the process. Furthermore, it was not evaluated if the methyl esters produced by the above methods meet either EN or ASTM specifications. However, limited work on the esterification of low grade tallow indicated, that it was possible to obtain biodiesel grade methyl ester from tallow with 20.4% FFA using base catalysed methanolysis, albeit the yield was only 33%. A recently reported study on base-catalysed methanolysis of RVO with different amounts of FFA showed that 98% of the triglyceride in the starting material could be accounted for by the obtained methyl ester, the FFA formed by hydrolysis of triglycerides and the methyl ester dissolved in the glycerol phase [12], the latter caused by the detergent effect of the potassium salts of the FFA originating from both the RVO and from hydrolysis. Furthermore, removal of FFA from RVO increased methyl ester yields from 83 to above 97%, thus indicating that dissolution of methyl ester in the glycerol phase by FFA from the raw material was the main cause of yield loss in high FFA RVO [13, 14]. Hence it should be possible to obtain methyl esters in almost quantitative yields from high FFA material by esterification of the FFA at some stage during the conversion process.

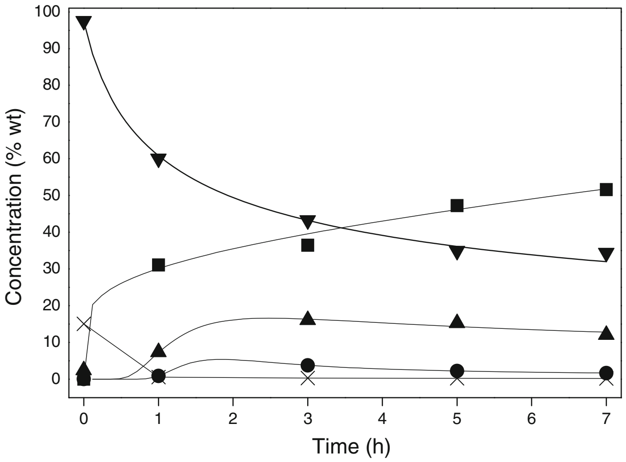

Fig. 1 Esterification and partial methanolysis with sulphuric acid, $T = 65$–70 °C, *filled squares* methyl ester, *filled circles* monoglyceride, *filled triangles* diglyceride, *filled inverted triangles* triglyceride, × FFA

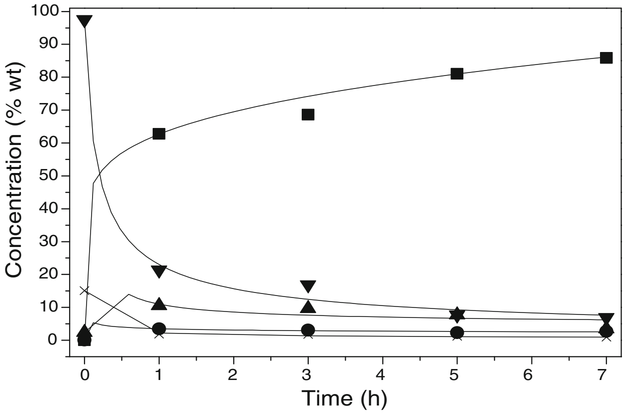

Fig. 2 Esterification of FFA and partial methanolysis with hydrochloric acid, $T = 65$–70 °C, *filled squares* methyl ester, *filled circles* monoglyceride, *filled triangles* diglyceride, *filled inverted triangles* triglyceride, × FFA

A preliminary study indicated that in order to obtain high yields from low grade tallow, FFA in the raw material needs to be esterified in a separate reaction step [15]. The objective of the present work was to evaluate possible methods for the conversion of all lipid material in high-FFA tallow to methyl esters, and to determine the limitations of base-catalysed methanolysis with the same material.

Materials and Methods

Materials

Low-grade tallows were supplied Dublin Products, Dunlavin, Co. Kildare, and 3 M hydrochloric acid in methanol, 14% boron trifluoride in methanol, diethyl-adipate and mono-, di-, and tri-glycerides, ACS grade methanol and hexane were obtained from Sigma–Aldrich (Ireland) Ltd. Analytical reagent grade potassium hydroxide, sulphuric acid and diethyl ether were obtained from Riedel de Hahn AG, Seelze, Germany, Merck AG, Darmstadt, Germany and Lab-Scan Ltd., Dublin Ireland, respectively.

Base-Catalysed Methanolysis

Tallow (120 g) was stirred vigorously with a magnetic stirrer in a closed conical flask with potassium hydroxide (1.8 g + the amount required to neutralise FFA) in methanol [33.5 ml (6:1 methanol to tallow molar ratio)] at 50–55 °C for 1 h [12]. The methyl ester was allowed to separate from the glycerol phase for minimum 3 h and after the removal of the glycerol phase it was washed gently with water (2 × 50 ml) and dried to constant weight at 120 °C [12]. Tallow with FFA content above 15% required 20 ml water and 50% more methanol (50 ml), and above 19% FFA 100% more methanol (77 ml), both added at the end of esterification to promote phase separation.

Methanolysis Followed by Esterification

FFA and methyl ester were precipitated from the reaction mixture obtained by the above base-catalysed methanolysis of tallow with 15.8% FFA, by the addition of water (40 ml) and sufficient 3 M sulphuric acid to lower the pH to $\leq$2.0. The mixture was heated to 80 °C, the water layer was removed and the organic phase was washed with warm water ($\geq$60 °C) (2 × 40 ml) and dried at 120 °C to constant weight. The dried organic phase (20 g,) was esterified by stirring with 3 M hydrochloric acid [40 ml (70:1 methanol to FFA molar ratio)] or 16% w/v boron trifluoride [40 ml (72:1 methanol to FFA molar ratio)] or 20 or 40% w/w sulphuric acid [10 ml (15:1 methanol to FFA molar ratio)] at 60–65 °C for 30 min, 30 min and 2 h respectively in a closed conical flask. The excess methanol was evaporated and the methyl ester was washed with water until neutral, and dried at 120 °C until constant weight.

Methanolysis with Methanol/Acid Pre-Treatment

Tallow (120 g) with 15.1% FFA was esterified by stirring vigorously with 1% methanolic sulphuric acid [165 ml (63:1 methanol to FFA molar ratio] or 3 M methanolic hydrochloric acid [180 ml (65:1 methanol to FFA molar ratio)] in a closed conical flask at 60–65 °C for 1 and 3 h, respectively. The obtained low FFA tallow was washed with warm (50–60 °C) water (2 × 20 ml) and FFA content and glyceride composition was determined at this stage by gas chromatography as described under "Analysis of Esterified Tallow". Considering that only about 70 and 25% of the sulphuric and hydrochloric acid esterified tallows, respectively were glycerides, the amounts of basic catalysts used for methanolysis had to be calculated accordingly. Methanolysis of sulphuric acid esterified tallow obtained from 120 g starting material was carried out with potassium hydroxide (1.1 g) in methanol (24 ml) and of hydrochloric acid esterified tallow with sodium methoxide (0.25 g) [12] in methanol (11.5 ml) by vigorous stirring at 50–60 °C for 1 h in a closed conical flask. The reaction mixture was allowed to separate for 3 h, and after the removal of the glycerol phase the methyl ester was washed gently with water (2 × 50 ml), and dried to constant weight 120 °C.

Analysis of the Glycerol Phase

Methyl ester and fatty content of the glycerol phase from base-catalysed methanolysis of low grade tallow was determined according to the method reported for RVO [12] except the water layer used to wash the hexane extract of the acidified glycerol phase was washed with diethyl ether instead of dichloromethane. FFA was separated from the glycerol phase (20 g) obtained from the methanolysis of tallow esterified with sulphuric acid, by the addition of water (40 ml) and sufficient sulphuric acid (3.0 M) to lower the pH to 2. The aqueous layer was removed and the FFA was washed several times with water (3 × 40 ml) at 80–90 °C and dried at 120 °C until constant weight.

Analysis of Methyl Ester

The properties of the methyl esters obtained from low-grade tallow with potassium hydroxide and potassium hydroxide sulphuric acid were determined by methods listed in EN 14214:2003. Monoglyceride, diglyceride, triglyceride and free glycerol contents were determined by EN 14105 [16], and methanol, FFA and water contents content according to EN 14110 [17], EN 14104 [18] and EN 12397 [19], respectively. Glyceride contents of tallows esterified with hydrochloric acid were determined by the direct method as described under "Analysis of Esterified Tallow".

Analysis of Esterified Tallow

Glyceride composition of tallow after esterification of FFA was determined without derivatisation using a gas chromatograph, equipped with flame ionisation detector, split–splitless injector and an HP-5MS capillary column 12 m × 0.31 mm with a film thickness of 0.71 μm [20, 21]. Helium was the carrier gas, injector and detector temperatures were 325 °C, and 1 μl of 0.5% esterified tallow and 0.1% diethyl adipate internal standard in heptane was injected with split ratio of 50:1. The carrier gas flow rate was 1 ml/min, the initial column temperature was 80 °C for 0.5 min, which was increased to 160 °C at 5 °C/min, followed by a 30 °C/min increase to 320 °C, and held at this temperature for 15 min. Groups of glyceride peaks were identified from mixtures of linoleoyl, oleoyl, palmitoyl and stearoyl mono-, di-, and tri-glycerides with the same fatty acids. The groups of peaks were well separated, the separation time between the methyl ester and each of the mono-, di-, and tri-glyceride groups of peaks was about 4 min.

Table 1 Base catalysed esterifications of tallows with high FFA content

FFA content[a]	11.2	15.8	15.8	20.0	26.0
Yield of FAME[a]	53.5	41.6	55.6[b]	34.5	14.2
Methanol/triglyceride[c]	6	6	9	12	12
Water added[a]	None	None	16.5	16.5	16.5

[a] % w/w

[b] Average of five determinations, SD ± 0.21

[c] Molar ratio, methanol above molar ratio of 6 was added after methanolysis

Results and Discussion

One Step Conversion, Base Catalysed Methanolysis

Methanolysis of low-grade tallows with FFA contents of 11–26% were carried out by the base-catalysed method, we found to be suitable for both laboratory and pilot plant scale methanolysis of RVO [14], and of high FFA camelina oil [22]. Methyl ester could be obtained from tallow with 11% FFA as long as the FFA were neutralised by additional potassium hydroxide. However, the method had to be modified for tallow with 15.8, 20 and 26% FFA, and additional methanol and water had to be added at the end of methanolysis to promote phase separation. If water and extra methanol were not added, yields of methyl ester were reduced considerably (Table 1). Methyl ester yields from high FFA tallow with simple base-catalysed methanolysis were low, and they decreased rapidly with increasing FFA content (Table 1). While it was possible to obtain yields above 50% of good quality methyl ester from tallow with 11 and 15% FFA, these were reduced to 34.5 and 14.2% when the tallow contained 20 and 26% FFA, respectively. Considering that the FFA content of the tallow was 15.8%, a yield around 84% would be expected if all triglyceride were converted to methyl ester and the latter were recovered.

Sources of yield loss in base-catalysed methanolysis were established by material balance carried out according to the method reported for RVOs [12]. Thin layer chromatography showed that the organic fraction isolated from the glycerol phase after methanolysis contained only methyl ester, FFA and traces of glycerides. Hence in spite of the low yields all triglycerides must have reacted, and significant yield losses were probably caused by the hydrolysis of triglycerides to FFA and the dissolution of methyl ester in the glycerol phase. Quantification of the methyl ester and the FFA in the glycerol phase indicated that about 98% of the initial triglyceride fatty acids were accounted for by the methyl ester obtained, the FFA formed by hydrolysis, and the methyl ester in the glycerol phase (Table 2). The amount of triglyceride hydrolysed during methanolysis, about 2.5%, contributed little to yield reduction, and similar amount of hydrolysis was reported during methanolysis of RVO with the same method [5]. Most of the yield loss (over 85%) was caused by the dissolution of methyl ester in the glycerol phase, attributed previously to the detergent effect of FFA potassium salts [5], which originated mainly from the starting material. Therefore, esterification of FFA either before or after base-catalysed methanolysis, could increase yields of methyl ester from low grade tallow above 56% obtained in the present work.

Two-Step Conversion, Methanolysis Followed by Esterification

A two step conversion starting with the base-catalysed methanolysis described in the previous section, followed by esterification of FFA in the separated organic fraction was evaluated first. Separation of the organic fraction involved acidification of the reaction mixture after methanolysis, followed by separation of the organic phase at 70–80 °C to prevent gelling of FFA with high melting points. There was good phase separation, and almost 99% of the starting tallow could be recovered as organic phase (Table 3). Thin layer chromatography showed only the presence of methyl ester, FFA and traces of glycerides in the recovered material.

Conversion of FFA to methyl ester in the recovered organic fraction was evaluated with three acid catalysts dissolved in methanol, namely boron trifluoride, hydrochloric and sulphuric acids. Methanolic sulphuric acid (2.5 ml) at 10, 20 and 40% w/w and methanolic boron trifluoride (14% w/v) and hydrochloric acid (11% w/v) at the rate of 1, 5, 10, 20, and 40 ml were used per gram of FFA, and FFA contents were monitored periodically. Each methanolic acid catalyst reduced FFA content to below 1%, and FFA levels decreased with increasing catalyst concentration. Lowest FFA levels (highest conversion rate) were obtained with: 10 ml boron trifluoride, 10 ml hydrochloric acid for 30 min, and 40% sulphuric acid (2.5 ml) for 2 h, higher concentrations and/or longer esterification times did not reduce FFA levels any further. Esterification conditions giving the lowest FFA levels were used for

Table 2 Material balance of base catalysed esterifications of low grade tallow

Yield of ME[a]	FFA in tallow[b]	Loss from hydrolysis	Loss from ME[a] in glycerol	Total yield loss	Total ME[a] yield[c]	Material accounted for
67.4 (55.6)[a]	15.8	2.9	26.1	29.0	93.6	96.4
68.4 (55.8)	15.8	2.8	26.8	29.6	95.2	98.0
67.6 (55.8)	15.8	3.4	27.2	30.6	95.0	98.2
67.9 (55.3)	15.8	3.2	27.5	30.7	95.4	98.6

Yields and yield losses in mol% of glycerol bonded fatty acids in the tallow

[a] ME methyl ester

[b] FFA in tallow and yields in parenthesis in % w/w

[c] SD ± 0.81

Table 3 Two step conversion (methanolysis + esterification) of high FFA tallow to methyl ester

Starting material	FFA content		
	15.8	15.8	15.8
Base catalysed methanolysis + recovery of the organic fraction			
Triglycerides	n.d.	n.d.	n.d.
Yield of organic fraction	98.9	98.9	98.9
Catalyst	Sulphuric acid	Boron trifluoride	Hydrochloric acid
Esterification of FFA in organic fraction			
Yield of methyl ester after esterification[a]	95.3	97.0	98.3
FFA content of methyl ester	0.73	0.24	0.33
Acid value of methyl ester (mg KOH/g)	1.45	0.48	0.66
Final yield of methyl ester	94.3	95.9	97.2

All values in % w/w except acid values

n.d. Not detected

[a] Average of two esterifications, yield differences 0.2% (H_2SO_4), 0.6% (BF_3) and 1.1% (HCl)

determination of methyl ester yields from methanolysis followed by esterification.

A yield of 94.2% methyl ester (based on tallow) was obtained with methanolic sulphuric acid, but the acid value of the final product, 1.45 mg KOH/g (0.73%), was almost three times as high as the EN limit of 0.5 mg KOH/g specified by EN 14214 (Table 3). Yields were higher with boron trifluoride (96.8%) and hydrochloric acid (97.8%), but very large amounts of methanolic catalysts (four times more than methanolic sulphuric acid) were required in both cases. However, in spite of the large amounts of catalysts used, the FFA content of the obtained methyl ester was still not significantly below the EN limit.

Some methyl ester was lost during phase separation after esterification, the loss was only about 0.5% with hydrochloric acid but it increased to 3.5% with sulphuric acid. The yield loss could be almost eliminated by using 20% instead of 40% methanolic sulphuric acid catalyst, but FFA content of the final product was 0.85% (1.69 mg KOH/g). In order to reduce FFA content to below the EN limit a second esterification was carried out with 20% methanolic sulphuric acid. Yield losses were minimal, but FFA content was reduced by only about 30%, and acid value of the methyl ester was still above the EN limit. However, FFA could be removed from the methyl ester almost quantitatively by the addition of sufficient concentrated aqueous potassium hydroxide, but the process was not investigated in detail.

Two-Step Conversion, Esterification of Tallow Followed by Base Catalysed Methanolysis

To reduce the FFA content of the obtained methyl ester, and the amount of potassium hydroxide and sulphuric acid used for neutralisation of the tallow and acidification of the methanolysis reaction mixture, a two-step conversion involving esterification of FFA in the starting tallow, followed by base-catalysed methanolysis of the low FFA tallow was also investigated. A similar two step conversion of RVO with 12% FFA, using different conditions of esterification and methanolysis has been investigated before [11]. Esterification of FFA in tallow was investigated with both sulphuric acid (1 and 2% w/v) and hydrochloric acid (1.5 and 3 M) using esterification times of 1, 3, 5, and 7 h with each catalyst at 65–70 °C. Most suitable catalyst concentrations were 1% sulphuric acid and 3 M hydrochloric acid, higher sulphuric acid concentration did not reduce FFA content any further, and lower hydrochloric acid concentration resulted in higher FFA levels. FFA contents were reduced to about 0.9 (Table 4) and 2.6% (Table 5) with sulphuric acid and hydrochloric acid catalysts in 1 and 3 h respectively, and there was only small reduction of FFA content after those times.

Yields of esterified tallow were about 2% higher with hydrochloric acid, probably because of better phase separation (Tables 4, 5). However, yields of esterified tallow less FFA, that is material which can be converted to methyl ester by methanolysis, were not significantly higher with hydrochloric acid. Along with esterification of FFA there was also acid-catalysed methanolysis, and triglycerides were converted to methyl ester, and mono- and di-glycerides (Tables 4, 5), and the amount of catalyst used in the subsequent methanolysis had to be adjusted accordingly. However, full conversion of triglycerides into methyl ester was not possible even after 7 h (Figs. 1, 2), and subsequent alkali catalysed methanolysis was necessary. Usually long reaction times (2–4 days) and a high methanol to triglyceride molar ratio (30:1) were required to obtain above 95% conversion of triglycerides to methyl ester with acid catalysts [5, 23].

Base-catalysed methanolysis of esterified tallow was evaluated with different concentrations of potassium hydroxide and sodium methoxide, and the amounts required were determined from the glyceride content of esterified tallow. The most suitable concentration of potassium hydroxide for the methanolysis tallow esterified with sulphuric acid, was the concentration used in this laboratory for the methanolysis of RVO [12], namely 1.5% based on tallow (Table 4). Higher concentrations of potassium hydroxide gave lower yields of methyl ester (83.5 and 86.0%), and the methanolysis did not go to completion with lower concentrations (Table 4). Sodium methoxide was evaluated because it does not hydrolyse triglycerides, and it was reported to give higher yields of methyl ester than potassium hydroxide [12]. Methoxide was used only with hydrochloric acid esterified tallow, because the acid catalyst could be removed more effectively than from tallow esterified with sulphuric acid. However, relatively large amounts of methoxide (2.0%), four times the amount used for rapeseed oil [12, 23], were required for methanolysis (Table 5), probably because the catalyst was neutralised by FFA, residual water and residual hydrochloric acid.

Yields of methyl ester from base-catalysed esterification of esterified tallow were 93% with potassium hydroxide and 1.3% higher with sodium methoxide and combined average yields of the two step conversions were 90.2 and 92.9% with sulphuric acid/potassium hydroxide and

Table 4 Two step conversion (esterification + methanolysis) of high FFA tallow to methyl ester

Starting material	FFA content			
	15.1	15.1	15.1	15.1
Esterification with sulphuric acid				
Yield of organic fraction[a]	96.7	97.0	96.9	96.2
FFA content of organic fraction	0.96	0.96	0.78	0.70
Acid value (mg KOH/g)	1.91	1.91	1.55	1.39
Triglycerides	62.1	60.1	61.1	61.2
Diglycerides	8.30	7.90	8.10	8.10
Monoglycerides	0.91	0.93	0.85	0.99
Total glycerol	7.95	7.69	7.80	7.85
Methanolysis with potassium hydroxide				
Catalyst concentration (% of triglycerides)	2	1.75	1.5	1.4
Yield of FAME	86.3	88.7	93.1	95.0
FFA content	0.06	0.05	0.06	0.06
Acid value (mg KOH/g)	0.12	0.10	0.12	0.12
Triglyceride content	n.d.	n.d.	n.d.	0.89
Diglyceride content	0.43	0.47	0.38	0.35
Monoglyceride content	0.40	0.41	0.38	0.26
Total bonded glycerol	0.17	0.18	0.15	0.21
Final yield	83.5	86.0	90.2[b]	91.4

All values in % w/w unless indicated otherwise

[a] SD ± 0.21

[b] Average of two esterifications, yield difference 0.5%

Table 5 Two step conversion (esterification + methanolysis) of high FFA tallow to methyl ester

Starting material	FFA content		
	15.1	15.1	15.1
Esterification with hydrochloric acid			
Yield of organic fraction	98.9	98.6	98.4
FFA content of organic fraction	2.6	2.6	2.6
Acid value (mg KOH/g)	5.2	5.2	5.2
Triglycerides	13.1	14.6	14.9
Diglycerides	7.11	5.57	6.07
Monoglycerides	3.51	2.96	2.11
Total glycerol	3.33	3.11	3.00
Methanolysis with sodium methoxide			
Catalyst concentration (% of triglycerides)	1.4	2.0	2.0
Yield of FAME	93.1	94.5	94.1
FFA content	0.36	0.05	0.06
Acid value (mg KOH/g)	0.72	0.10	0.12
Triglyceride content	10.1	n.d.	n.d.
Diglyceride content	6.77	n.d	n.d
Monoglyceride content	1.33	0.11	0.12
Total bonded glycerol	2.41	0.02	0.03
Final yield	92.1	93.2	92.6

All values in % w/w unless indicated otherwise

[a] SD ± 0.25

hydrochloric acid/sodium methoxide catalysts, respectively. However, methanolysis yields were about 5% lower with each catalyst than obtained from pure plant oils under the same conditions [12, 22], hence hydrolysis must occur and FFA and some methyl ester remains dissolved in the glycerol phase. Acidification of the glycerol phase from potassium hydroxide-catalysed methanolysis yielded an organic layer of fatty acids, which if esterified, could increase methyl ester yield by about 5%.

Quality of Methyl Esters

Process related impurities, that is impurities which arise during methanolysis of the tallow and washing of the TME, were determined in the methyl esters obtained by one step base catalysed methanolysis and by two-step conversions involving esterification and methanolysis, using methods specified by EN 14214 or similar methods. Impurities formed during methanolysis namely glycerides, and FFA were well within EN and ASTM specifications (Table 6), except FFA content of the methyl esters obtained by the methanolysis first two-step conversion. Glyceride levels were lowest in methyl ester from methanolysis followed by esterification, probably because residual glycerides from the initial base-catalysed methanolysis (Table 6) were converted to methyl ester during the subsequent acid-catalysed esterification.

Other process related impurities such as methanol and glycerol contents were also within EN and ASTM specifications, but water content was 0.05–0.12% higher in each methyl ester than the specified value (Table 6). The water content of the methyl ester could not be reduced to the EN and ASTM limit of 0.05% by the method of drying used here [12, 14], and further reduction by 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 tallow have been reported before [4].

Evaluation of Methods

Yields of methyl ester obtained from high FFA tallow with the two step conversions ranged from 90 to 97%, much higher than obtained with the one-step base-catalysed methanolysis from the same starting material, indicating that most of the FFA in the tallow were converted to methyl ester. Under optimum laboratory conditions, potassium hydroxide-catalysed methanolysis followed by esterification of FFA with hydrochloric acid, gave almost theoretical yields, 98.9 and 98.3% was obtained (Table 7). Hence it is possible to convert nearly all triglyceride and FFA in low grade tallow to methyl ester. Similarly high yields could be obtained with methanolysis followed by esterification with 20% sulphuric acid, but the methyl ester contained 1.5% FFA. Methyl ester yields were lower when tallow was esterified first, mainly because the esterification mixture of glycerides and methyl ester and FFA, gave lower yields than methanolysis of triglycerides. We were unable to find published work on methanolysis of high FFA tallow, but a yield of 80% has been reported from RVO with 12% FFA [11], which is considerably lower than obtained in the present work. Higher yield, 88% were obtained from RVO with 6.8% FFA using immobilised lipase [7], but the enzyme is considerably more costly than the acid and alkali catalysts used here.

While somewhat higher yields of low FFA tallow and methyl ester were obtained with hydrochloric acid or boron trifluoride than with sulphuric acid (Table 7), it is more convenient to use the latter for large scale esterification of

Table 6 Methanolysis and esterification related quality parameters of tallow methyl esters

Impurity	Methanolysis	Esterification + methanolysis		Methanolysis + esterification		EN 14214	ASTM 6725
	KOH only	HCl + MeONa	H_2SO_4 + KOH	KOH + HCl[a]	KOH + H_2SO_4		
Monoglycerides	0.180	0.120	0.440	n.d	0.050	0.8	
Diglycerides	0.044	n.d.	0.044	n.d	0.080	0.2	
Triglycerides	0.013	n.d.	0.013	n.d	0.014	0.2	
Free glycerol	0.002	–	0.006	–	n.d.	0.02	
Total glycerol	0.056	0.030	0.126	–	0.026	0.25	0.24
Acid value	0.220	0.120	0.120	0.660	1.46	0.5	0.5
Methanol	0.003	–	0.009	–	0.008	0.2	0.2
Water	0.174	–	0.138	–	0.096	0.05	0.05

All values in % w/w, except acid value in mg KOH/g

n.d. Not detected

[a] Glycerides were determined only by thin layer chromatography

Table 7 Summary of tallow to methyl ester conversion yields

Conversion method	1st stage yield	2nd stage yield	Total yield
Methanolyis (KOH) only	55.6	–	55.6
Methanolysis (KOH)–esterification (H_2SO_4)	98.9	95.3	94.3
Methanolysis (KOH)–esterification (HCl)	98.9	98.3	97.2
Methanolysis (KOH)–esterification (BF_3)	98.9	97.0	95.9
Esterification (H_2SO_4)–methanolysis (KOH)	96.9	93.1	90.2
Esterification (HCl)–methanolysis (NaOMe)	98.5	94.3	92.9

All values in % w/w

FFA in both two-stage processes. Sulphuric acid dissolved in methanol in situ is considerably cheaper and easier to handle than methanolic hydrochloric acid, and the neutralisation product, potassium sulphate, can be readily used as fertiliser. Furthermore esterification of the methanolysis mixture with hydrochloric acid requires five times as much methanol as esterification with sulphuric acid. Similarly potassium hydroxide is probably more suitable for methanolysis of the esterified tallow than sodium methoxide, because the latter would be far more expensive for the amount, 2% w/w with respect to tallow, required for methanolysis of esterified tallow. Sodium methoxide is not recommended for methanolysis of triglycerides with an FFA content above 1% [24], and apart from FFA there must be residual acid and water in the tallow esterification mixture, which will also neutralise the catalyst.

The method based on initial methanolysis followed by esterification with 40% sulphuric acid gives about 3% higher methyl ester yield than the method based on initial esterification with the same acid (Table 7). However, the yield difference is not significant considering that it should be possible to obtain yields above 95% by both conversions, either by recycling the FFA recovered from the glycerol phase [25], or by using 20% sulphuric acid for esterification of the methanolysis mixture and precipitating excess FFA from the methyl ester. However, if methanolysis is carried out first, the FFA in the tallow and in the methanolysis reaction mixture will need to be neutralised with an equivalent amounts of potassium hydroxide and sulphuric acid, respectively. Hence about three times as much potassium hydroxide and four times as much sulphuric acid will be required for the same amount of tallow, and correspondingly larger amounts of the potassium sulphate by-product is produced, than in the case of initial esterification.

Considering the relatively large amounts of reagents required for neutralisation when methanolysis is carried out first, initial esterification of the FFA in the tallow is probably a more convenient process for large scale conversion of high FFA tallow to methyl ester. Yields around 90% were obtained in the present work (Table 4), which could be increased further by recycling the FFA recovered from the glycerol phase [25]. On the other hand, the method based on initial methanolysis apart from being a useful laboratory procedure, has also potential for large scale production, which has not been explored here. It must be difficult to esterify fats with a high FFA content (>20%) hence the reported development of high temperature [10] and cosolvent based processes [8, 9]. However, the present work indicated that tallow with FFA levels as high as 26% can be converted to methyl ester, albeit most of it remains dissolved in the glycerol phase (Table 1). The organic phase, methyl ester and FFA, can be recovered from the methanolysis mixture in almost quantitative yields (Table 3), and it should be possible to esterify solutions of 20–30% FFA in methyl ester in good yields.

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