Scale-up of Biodiesel Synthesis in Chemical Interesterification Reaction of Rapeseed Oil with Methyl Formate and Methyl Acetate

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Abstract - Production and use of biofuels is important to minimize carbon dioxide emissions in the world. One of biofuels – biodiesel – is obtained from vegetable oils in form of fatty acid methyl esters (FAME). Industrially production of biodiesel proceeds by transesterification with methanol and production of by-product glycerol. In order to exclude the glycerol production, we have researched biodiesel synthesis in potassium *tert*-butoxide catalyzed chemical interesterification reaction with methyl formate and methyl acetate. In order to ensure the scale-up of 50-times the synthesis has been made using flasks from 100 mL volume to 4 L batch reactor. Scale-up process of biofuel synthesis shows that it proceeds without considerable differences in synthesis procedure and composition of products, but the excess reagent evaporation step is more efficient for smaller volumes. Reactions with methyl acetate allow to make full conversion of oil to biofuel, however the FAME content is only 72%, following conditions were used: temperature 55 ºC, 60 minutes, methyl acetate to oil molar ratio 30, catalyst 1M *t*BuOK in THF, and catalyst to oil molar ratio 0.10. Reactions with methyl formate allow to obtain biofuel with lower yield but containing 93% of FAME, following conditions were used: temperature 30 ºC, 45 minutes, methyl formate to oil molar ratio 36, catalyst 1M *t*BuOK in *t*BuOH, and catalyst to oil molar ratio 0.15. Fuel properties were tested for both biofuels obtained in 4 L reactor. Biofuel obtained in reaction with methyl formate showed better properties, although both fuels could be used as diesel fuel additives. The area of using the methyl formate biofuel would be wider, therefore we propose that methyl formate is more promising reagent for synthesis of biodiesel. Obtained different glycerol formates could be a valuable by-product.

Keywords: FAME, biodiesel, triacetin, triformin, scale-up

1. Introduction

European Union aims to reduce emissions of carbon dioxide and other greenhouse gases and promote use of renewable energy and fuel such as sustainable and advanced biofuels [1]. Biological processes use carbon dioxide as source for generation of all organic compounds including fatty acid triglycerides, therefore the net emissions of carbon dioxide from burning of fatty acid methyl esters (FAME), the main constituent of biodiesel, are less than from burning of petrol diesel [2]–[5].

Biodiesel industrially is manufactured by transesterification process and up to 10% by weight of crude glycerol is also obtained [6], [7]. Chemical interesterification of vegetable oils with low-molecular weight esters is advantageous, because this process does not lead to over-production of crude glycerol. Glycerol esters with short-chain acids are produced instead, which could be incorporated in biofuel composition [8]–[10]. Mostly researched is chemical interesterification of vegetable oils with methyl acetate resulting in mixture of FAME and triacetin [7], [9]–[14]. We have investigated also chemical interesterification of rapeseed oil with methyl formate resulting in separate products, FAME containing biofuel and mixture of glycerol and its formates [15]–[17].

To apply for industrial process, scale-up from laboratory synthesis is needed either in synthetic process itself or instrumentation, e. g. reactor type and design [18]–[20], recently scale-up process is investigated for enzymatic transesterification [21]–[23], but not for chemical interesterification process. We present here laboratory scale-up results from 100 mL flask to 4 L glass reactor synthesis of biodiesel in base catalyzed chemical interesterification reaction of rapeseed oil with methyl formate and methyl acetate.

2. Experimental Procedures and Methods

2.1. Reagents

The refined rapeseed oil was purchased from a local producer Iecavnieks & Co Ltd (for characteristics see Table 1) and methyl formate (97%) was obtained from Acros Organics, both were dried over 4Å molecular sieves from ROTH. tBuOH was obtained from ROTH, tetrahydrofuran (THF), phosphoric acid (85%), and potassium $tert$-butoxide (tBuOK) were obtained from Sigma-Aldrich, methyl acetate (99%) was obtained from Alfa Aesar.

Catalyst solutions were made in inert atmosphere using glove box shortly before use, we prepared 1M tBuOK in tBuOH and 1M tBuOK in THF.

Table 1: The main characteristics of refined rapeseed oil.

Property	Measured value
Average molecular weight (g/mol)	886
Saponification value (mg KOH/g)	190
Acid value (mg KOH/g)	0.044
Water content (wt%)	0.032
Density at 20 °C (kg/m^3)	921
Viscosity (mm^2/s)	34.9
Triglyceride (wt%)	97.7
Diglicerides (wt%)	0.7
Monoglicerides (wt%)	0.3
Fatty acid profile (wt%)	
Palmitic acid (C16:0)	4.1
Stearic acid (C18:0)	1.4
Oleic acid (C18:1)	62.5
Linoleic acid (C18:2)	21.7
Linolenic acid (C18:3)	8.7
Others	1.6

2.2. Interesterification reaction

Reactions were performed using four different reagent quantities, e.g., 15.00, 25.00, 250.0, and 750.0 g of rapeseed oil with appropriate amount of methyl ester. IKA yellow line MSC basic C magnetic stirrer with ceramic hotplate and IKA TC 2 electronic contact thermometer were used for heating round bottom flasks in silicone oil bath. Two-necked round bottom flasks of volume 100, 250, and 2000 mL were used for conducing reactions of 15.00, 25.00, and 250.0 g of rapeseed oil, respectively. Reactions using 750 g of rapeseed oil were performed in 4 L glass reactor equipped with stainless steel mechanical mixer (swing out dual blade impeller) and single external heating jacket. Sigma 4K15 sartorius centrifuge was used for separation of particulates. J.P.Selecta Vaciotem-T vacuum drying oven was used for drying of fuel samples at 60 °C for 6–24 h.

Rapeseed oil (15.00 g, 16.7 mmol) and methyl formate (36.18 g, 0.603 mol) were warmed to 30 °C in a two-necked round bottom flask with thermometer and reflux condenser. Then catalyst 1M tBuOK in tBuOH (2.5 mL, 2.5 mmol) was added. Reaction mixture was vigorously stirred at 30 °C for 45 min, thereafter H_3PO_4 (84 μL, 1.25 mmol) was added and stirring was continued for 10 min, then mixture was let to cool for 30 min. Clear solution was filtered from precipitates and evaporated, resulting emulsion was refrigerated for 10–16 h to allow completely set the resulting two layers. The two layers were carefully separated and weighted in individual containers.

Rapeseed oil (15.00 g, 16.7 mmol) and methyl acetate (37.07 g, 0.501 mol) were warmed to 55 °C in a two-necked round bottom flask with thermometer and reflux condenser. Then catalyst 1M tBuOK in THF (1.7 mL, 1.7 mmol) was added. Reaction mixture was vigorously stirred at 55 °C for 60 min, thereafter H_3PO_4 (57 μL, 0.85 mmol) was added and

stirring was continued for 10 min, then mixture was let to cool for 30 min. Clear solution was filtered from precipitates and evaporated.

Stoichiometric calculations at full triglyceride conversion indicate that theoretically predicted FAME and triacetylglycerol (TAG) content is 80.9 and 19.1 wt%, respectively, in reaction with methyl acetate; and FAME and triformylglycerol (TFG) content is 83.6 and 16.4 wt%, respectively, in reaction with methyl formate. The yield of fuel or both product layers was calculated as the product to oil mass ratio

$$Yield_P = \frac{m_P}{m_O} \cdot 100 \tag{1}$$

where $Yield_P$ is yield of fuel or both product layers (%), m_P is mass of fuel or both product layers (g), m_O is mass of substrate oil (g).

2.3. Analysis of product composition

GC analysis of samples was carried out on Analytical Controls biodiesel analyzer based on Agilent Technologies gas chromatograph 7890A using DB5-HT column (15 m, 0.32 mm ID, 0.10 μm). Internal standards, 1,2,4-butanetriol (Alfa Aesar, 96%) and tricaprin (TCI Europe, 98%) were used. In sample preparation *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (Alfa Aesar, 97%), pyridine (Lach-Ner, 99.5%), and CH_2Cl_2 (Chempur, 99%) were used. Oven temperature was set to 50 °C for 5 min and then temperature was first increased to 180 °C at the rate of 15 °C/min, then to 230 °C at the rate of 7 °C/min and finally to 370 °C at the rate of 10 °C/min. Helium was used as carrier gas and detector temperature was set to 390 °C. FAME, monoglycerides (MG), monoformylmonoacylglycerols (MFMG), monoformyldiacylglycerols (MFDG), diformylmonoacylglycerols (DFMG), monoformylglycerol (MFG), diformylglycerol (DFG), TFG, monoacetylmonoacylglycerols (MAMG), monoacetyldiacylglycerols (MADG), diacetylmonoacylglycerols (DAMG), diacetylglycerol (DAG), TAG, and glycerol were quantified as in our previous reports [15], [24]. Each measurement was carried out twice and the average value was calculated. Linear regression was used for sample composition results of standard solution measurements. Standard deviation for all analyzed compounds was not higher than 0.5 wt%, but for FAME it was 1.9 wt.%.

HPLC analysis was performed using Waters Alliance 2695 HPLC equipped with XTerra® MS C18 5 μm 2.1×100 mm column (0.2 mL/min flow), Waters 2996 PDA detector (209.2 nm). Isocratic eluent was used consisting of 0.1% $HCOONH_4$ in deionized water and MeOH (9:1). DFG and TFG were quantified as previously reported [15]. Each measurement was carried out twice and the average value was calculated. Linear regression was used for sample composition results of standard solution measurements. Standard deviation for DFG was not higher than 2.0 wt%, but for TFG it was 0.4 wt.%.

GC-MS analysis was carried out using Shimadzu GCMS-QP2020 NX with Rtx-5MS capillary column (30 m, 0.25 mm ID, 0.10 μm). Helium was used as carrier gas (1.47 mL/min). Split injection of 0.5 μL sample, split ratio 100, injector temperature 250 °C. Oven temperature was set to 30 °C for 5 min and then temperature was increased to 120 °C at the rate of 20 °C/min, and held for 3 min. Interface temperature was 250 °C. Mass spectrometer (EI source) was working at 200 °C in scan mode 20–200 Da.

2.4. Analysis of fuel properties

The water content was determined using METTLER TOLEDO DL39 Karl Fischer coulometer according to the standard method ISO 12937. The saponification value was determined according to the ISO 3657 standard method. The acid value was determined according to the EN 14104 standard method. Density (15 °C) was determined with Anton Paar DMA 4500 density meter according to the standard method EN ISO 12185. Kinematic viscosity (40 °C) was determined using Anton Paar SVM 3000 viscosity meter according to the standard method EN ISO 3104. The measurements of cold filter plugging point (CFPP) were performed on the basis of DIN EN 116 standard method with the use of ISL FPP 5Gs equipment. Cloud point (CP) and pour point (PP) were measured with ISL (by PAC) CPP 5Gs automated CP and PP analyzer, values of CP and PP were determined according to the standard methods ISO 3015 and ISO 3016, respectively. Carbon residue (from 100% sample) was determined using Alcor MCRT-160 tester according to the standard method ASTM D 4530. Flash point was determined using Stanhope-Seta 30000-0 flash point

tester according to the standard method EN ISO 3679. Each measurement was repeated twice and the average value was calculated and used.

3. Results and Discussion

We have explored how the volume of reaction mixture or mass of substrate oil influence interesterification reaction procedure and product composition. We researched interesterification reaction using two methyl esters as reagents, methyl formate and methyl acetate. Interesterification reaction of rapeseed oil with methyl formate was carried out using following conditions: temperature 30 ℃, reaction time 45 minutes, methyl formate to oil molar ratio 36, catalyst 1M *t*BuOK in *t*BuOH, and catalyst to oil molar ratio (COMR) 0.15, which were the highest FAME content yielding conditions from our patent [16]. Reaction conditions for interesterification reaction of rapeseed oil with methyl acetate were carried out using following conditions: temperature 55 ℃, reaction time 60 minutes, methyl acetate to oil molar ratio 30, catalyst 1M *t*BuOK in THF, and COMR 0.10, these conditions follow from our research [11], [25].

Reactions were carried out using 4 different rapeseed oil weights (15, 25, 250, and 750 g) ensuring 50-fold scale-up. For both reagents reaction in all quantities was performing visually similar, but differences arise from changes in volume of reaction mixture, e.g. filtration and evaporation took more time for large volume. Reaction with methyl formate and reaction with methyl acetate perform differently (see Table 2).

Reaction mixture and resulting fuel product is yellow like rapeseed oil color for reaction with methyl formate. Off-yellow wax is forming in the course of reaction with methyl formate and sticking to reaction vessel or tip of thermometer, this wax is mostly soaps, which are apparently insoluble in methyl formate. White crystals form, when the catalyst is neutralized, which in 10–20 minutes settle in the bottom of reaction vessel and filtration proceeds fast. Upper biofuel and lower formine layers both are very similar in color to substrate oil after evaporation of excess methyl formate.

Reaction mixture with methyl acetate is brown, catalyst neutralization leads to formation of precipitate, which is very fine and difficult to filter off. Neutralized solution of reaction with methyl acetate settles slowly, reaction mixtures from 15 and 25 g of oil are filtering for 4–6 h by gravity. Neutralized reaction mixtures from 250 or 750 g oil were cooled overnight and the precipitate settled during that time, decanted solution filtered fast by gravity, but the last fraction was centrifuged; dark brown and white layers of precipitate was forming in centrifugation vessel.

Filtered precipitate is the only waste material of this biofuel production process. Finding exact composition of precipitate was not the scope of this research, but various potassium phosphates are produced theoretically from potassium base and H_3PO_4.

Table 2: Comparison of interesterification reactions with methyl formate and methyl acetate.

Reagent	MeOOCH	MeOAc
Color of reaction	yellow	brown
Transparency	slightly turbid	non-transparent
Filtration after neutralisation	fast	slow
Precipitate	white crystals, off-yellow wax	dark brown and white fine particles
Product color	yellow	brown

Reaction with methyl formate yields two layers after evaporation of reagent excess and each layer is analyzed separately, also results are expressed separately in each layer. Contents of all products in upper (fuel) layer were determined using GC method (Table 3), but lower layer was analyzed using two methods: glycerol and MFG were analyzed with GC, but DFG and TFG with HPLC. Sensitivity towards TFG in GC analysis is considerably lower than in HPLC analysis, the peak is not symmetrical and sometimes the peak is even not detected. Contents of reaction products using all reaction volumes are equal in margins of error.

Upper layer contains mostly FAME, but DFMG is also found in considerable amounts. TFG, the other expected main product, is not found in upper layer by GC method, but the upper layer contains small amounts of side products MFMG, MFG and DFG. Trigliscerides have fully reacted, glycerol and diacylglycerols are not detected. FAME content is 92.6–93.0%, fuel yield is 97.5–103%. Initially mass of products obtained from reaction with 250 and 750 g of rapeseed oil was 1–3% higher, but vacuum drying oven was used for additional drying.

Table 3: Contents of products in upper layers of chemical interesterification reaction with methyl formate in wt%.

Entry	Oil mass, g	FAME	MG	MFMG	DFMG	MFDG	MFG	DFG	Yield$_P$, %
1	15.00	92.9	0.5	0.9	3.2	0	1.0	0.7	97.9
2	25.00	92.9	0.4	0.8	3.1	0.1	1.1	0.7	97.5
3	250.0	93.0	0.4	1.1	3.3	0.1	0.9	0.3	103
4	750.0	92.6	0.5	0.9	3.3	0	1.0	0.8	103

Lower layer contains only 4 components in detectable levels, most part of it is composed from MFG and DFG (see Table 4). The main expected product TFG is formed only partially or decomposes in reaction medium of strong alkoxide base (*t*BuOK) to glycerolate ion and carbon monoxide [26] producing DFG, MFG, and glycerol at the end of reaction. Second possibility is methyl formate reaction with *t*BuOK and formation of methoxide base, which could form MeOH at the end of reaction, but MeOH is not detected in GC-MS analysis of evaporated solvent. Mass fraction of lower layer is about 7.8% of total product mass (see Table 4). Mixture of glycerol formates could be perspective co-product to use in well-bore industry [27], for wood treatment [28], as feed acidifier for domestic animals [29], and as insecticide [30].

Table 4: Contents of products in lower layers of chemical interesterification reaction with methyl formate in wt%.

Entry	Oil mass, g	Glycerol	MFG	DFG	TFG	Fraction, %
1	15.00	8.4	44.0	41.8	4.8	7.8
2	25.00	7.9	44.4	42.2	4.5	7.8
3	250.0	8.0	43.8	42.6	4.6	7.9
4	750.0	9.5	44.8	40.4	4.3	7.8

Overall product distribution of chemical interesterification reaction of rapeseed oil with methyl formate is shown in Table 5. The contents of each product are given considering its amount in upper, lower, or both layers recalculated to total product mass. As the lower layer is just about 7.8% of total product mass it appears that TFG is produced totally just 0.4–0.5%. FAME is produced 85.4–85.7% from all products, but it is advantageous, that lower layer is separated and FAME content in fuel layer is increased. Total product yield of both layers is 106–113%. Theoretically predicted mass of ideal reaction where only FAME and TFG are formed is 120% of used rapeseed oil mass.

Table 5: Distribution of total products in chemical interesterification reaction with methyl formate in wt%.

Entry	Oil mass, g	FAME	MG	MFMG	DFMG	MFDG	Glycerol	MFG	DFG	TFG	Yield$_P$, %
1	15.00	85.7	0.5	0.8	3.0	0.0	0.7	4.4	3.9	0.4	106
2	25.00	85.7	0.4	0.7	2.9	0.1	0.6	4.5	3.9	0.4	106
3	250.0	85.7	0.4	1.0	3.0	0.1	0.6	4.3	3.6	0.4	113
4	750.0	85.4	0.5	0.8	3.0	0.0	0.7	4.4	3.9	0.3	112

Reaction of rapeseed oil with methyl acetate yields only one liquid product, which main constituents are FAME and TAG (see Table 6). Contents of all products were determined using GC method. Triglycerides are fully converted, intermediates and side products like diacylglycerols, glycerol, monoacetylglycerol are not detected. Reaction product contents in all reaction volumes are equal in margins of error. First after evaporation from syntheses with 250 and 750 g of rapeseed oil, the content of FAME was about few percent less than smaller batches, and the sum of all components was likewise decreased. Additional drying in vacuum drying oven was performed decreasing sample mass for 3.5%, and GC analysis was repeated, which led to FAME contents in Table 6. FAME content is 71.9–72.8% and TAG content is 14.0–14.5%. Mass of obtained fuel is higher than mass of used oil, fuel yield is 115–118%. The maximal possible fuel yield is 125%.

Reagent methyl ester is used in 10 to 12 times higher quantity than stoichiometric needed. The excess reagent is usable in next reaction after evaporation. We tested the purity of removed reagent using GC-MS. Methyl acetate contained *t*BuOH (0.19%) and THF (3.6%) from catalyst and *t*BuOAc (3.2%), which was formed in side-reaction of catalyst and acetate ester. Methyl formate very similarly contained *t*BuOH (3.3%) and HCOO*t*Bu (1.5%). Solvents/reagents could be used in next reaction after corrections of needed mass considering methyl formate or methyl acetate fraction in reusable solvent.

Table 6: Contents of products in chemical interesterification reaction with methyl acetate in wt%.

Entry	Oil mass, g	FAME	MG	MAMG	DAMG	MADG	DAG	TAG	Yield$_P$, %
1	15.00	71.9	0.8	1.0	5.6	0.9	2.3	14.1	115
2	25.00	72.7	0.8	0.8	5.9	0.6	1.8	14.5	117
3	250.0	72.8	0.8	0.9	5.7	0.7	2.1	14.0	117
4	750.0	72.1	0. 8	0.9	5.6	0.6	2.2	14.4	118

Main physical fuel properties were tested only for samples obtained from 750 g oil, the samples were designated F-biofuel and A-biofuel, obtained from methyl formate and methyl acetate, respectively. The properties are compared to distilled FAME, which is also obtained from rapeseed oil, and FAME-TAG composition, which is obtained by mixing pure FAME with pure TAG (see Table 7).

Table 7: Fuel properties of interesterification products.

Sample	Flash point, ºC	Density, kg/m^3	Viscosity, mm^2/s	Carbon residue, %	CP, ºC	CFPP, ºC	PP, ºC
Requirements[a]	>101	860–900	3.50–5.00	<0.05[b]			
FAME [10]	>200	882	4.09	< 0.01	–12	–10	–13
FAME-TAG[c] [10]	150	923	4.12	< 0.01	–11	–11	–14
F-biofuel	130	893	4.10	0.18	–5	–7	–15
A-biofuel	>200	923	4.89	0.28	–5	–8	–13

[a] EN 14214 limits
[b] ASTM D6751 limits
[c] Artificial mixture of FAME from rapeseed oil (80.6 wt%) and TAG (19.4 wt%)

F-biofuel conforms to the standard EN 14214 limits in density and viscosity values, and the values are close to values of pure FAME as the non-FAME constituents are in low amounts and do not affect the physical properties much. Acid value of F-biofuel is 0.49 mg KOH/g, that is just below allowed 0.5 mg KOH/g. FAME content does not correspond to standard and is lower than 96.5%, but the properties of the F-biofuel are good because free hydroxyl group count of glycerol derivatives in this fuel composition are less than in conventionally synthesized biodiesel in transesterification reaction.

A-biofuel has higher density and carbon residue than prescribed in standard EN 14214. Density of A-biofuel and FAME-TAG samples are almost equal, but considerably higher than pure FAME and standard requirements, which is explained with TAG presence and its density of 1155 kg/m^3. Acid value of A-biofuel is 1.2 mg KOH/g, which is more than twice higher than in standard allowed.

CP and CFPP temperatures are identical for both F-biofuel and A-biofuel and higher than pure FAME or FAME-TAG mixture, this could be explained with glycerol fragment containing intermediates of interesterification reaction. CFPP temperature is corresponding to summer diesel fuel properties of both F-biofuel and A-biofuel. The high carbon residue of both F-biofuel and A-biofuel most likely is caused by dissolved inorganic or organic potassium salts.

Peculiarities of scale-up procedure showed in flash point measurements, which initially were 40 ºC and 80 ºC for F-biofuel and A-biofuel, respectively. This is explained with ineffective evaporation process of large sample quantities using rotary evaporator and 1 L evaporative flask with approximately 200 g final product load. Evaporation process in the same

conditions was repeated for smaller samples of about 10 g in 50 mL flasks and after additional mass decrease of 2.5% and 0.7% for F-biofuel and A-biofuel, respectively, the flash point values were as reported in Table 7.

4. Conclusion

Scale-up process of biofuel synthesis in chemical interesterification reaction using rapeseed oil and methyl formate or methyl acetate shows no considerable differences in synthesis procedure and composition of products. The differences in realization of process are observed only at reactant excess evaporation step, the rotary evaporator and vacuum drying oven cannot ensure full remove of all light components and their presence is detected via decrease of component sum, determined by gas chromatography and decrease of flash point measurements.

In reactions with methyl formate, biofuel containing 93% FAME was obtained, corresponding to standard EN 14214 and ASTM D6751 limits for following tested fuel properties: flash point, density, viscosity, and acid value. In reactions with methyl acetate, biofuel containing 72% FAME and 14% triacetin was obtained with fuel characteristics near to EN 14214 requirements.

Biofuel synthesis via interesterification leads to higher product mass yield, excess reagent could be recovered, and only waste stream is potassium phosphates containing precipitates, which could be used as fertilizer. Biofuel obtained in chemical interesterification reaction of rapeseed oil with methyl formate is cleaner and more perspective than biofuel obtained in similar reaction with methyl acetate. Moreover, this reaction produces promisingly valuable by-product – glycerol formate. Before commercial use of pure new biofuels, that does not complain with current standard requirements, new standards could emerge [8], [31]. Such fuels could be used as additives to petrol diesel.

Acknowledgements

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