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Steam Distillation of Acidulated Soapstock and FAME Synthesis

Lauma Laipniece, Valdis Kampars
Institute of Applied Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University
3/7 Paula Valdena Street, LV-1048, Riga, Latvia
Lauma.Laipniece@rtu.lv; Valdis.Kampars@rtu.lv

Abstract **-** Use of rapeseed soapstock to produce biodiesel is a sustainable choice, because it deals with waste stream use in biofuel synthesis and lowers the use of food grade oil as fuel feedstock. Rapeseed soapstock was acidulated, and fatty acid and glycerides containing acid oil was separated from water phase. Steam distillation – a mild purification method – was used to separate fatty acids from acid oil. Distilled fatty acids were subjected to sulfuric acid catalyzed esterification with methanol. The chosen reaction conditions were: 65 °C temperature, molar ratio of MeOH to FFA 20:1, 7.5 mol% H_2SO_4, and a reaction time 1 h. Esterification of distilled fatty acids proceeded with 98.3–98.5% conversion to FAME and product yield 93–95% from theoretical. The esterification reaction conditions were determined using lauric acid as model compound, the catalyst concentration was adjusted to be less than usually reported, so to avoid oxidation and side reactions. Use of ultrasound assisted synthesis was elaborated by comparing reaction of lauric acid at 25 °C temperature in ultrasonic bath and with stirring. Reaction was faster with stirring than use of ultrasound.

Keywords**:** soapstock, biodiesel, fatty acids, esterification, steam distillation, ultrasound

1. Introduction

Production and use of renewable energy or fuels are important research topics nowadays [1]–[6]. Renewable fuel for transport is biodiesel, green diesel (HVO), bioethanol, biobutanol, biomethane, and others [6], [7]. Biodiesel in most cases is fatty acid methyl esters (FAME) produced by chemical conversion from vegetable oils or other triglycerides [1], [2]. Use of food grade vegetable oils is not sustainable choice, therefore best technologies are sought to use non-edible oils, algal oil [2], waste cooking oil [8], yellow and brown grease [9], animal fat [9], and waste streams from oil refining [10], [11] as fatty material source for biodiesel production.

Rapeseed production is increasing in Latvia [12] and by production of rapeseed oil also amount of waste streams from oil refining is increasing. Gums or soapstock (SS) is one of these side-products – a heavy emulsion of water (32–67%), glycerides (12–13%), soaps (10–28%), and other components, but it needs processing prior to biodiesel synthesis due to high water content and non-saponifiable ingredients [10]. Two types of SS constituents are suitable for biodiesel synthesis: free fatty acids (FFA) from soaps, and fatty acid glycerides [10]. Three methods are used for SS processing: full hydrolysis of glycerides with further esterification of FFA [13], [14], separation of FFA from glycerides followed by acid catalyzed esterification of FFA and base catalyzed transesterification of glycerides [15]–[17], and acidulation or soap-splitting prior to biodiesel synthesis *via* acid catalyzed esterification and transesterification [14], [18]. The latter option – acid catalyzed transesterification is much slower in relatively mild conditions [1].

When separation of FFA from SS is employed without full hydrolysis, two innovative techniques are used: separation by gravity of soybean soapstock water phase, soap emulsion, and glyceride and phosphatide extract in diethyl ether [17], and short path distillation of acid oil from rapeseed soapstock separating FFA and glycerides [15], [16]. Steam distillation is a good large scale purification method of fatty acids [19], [20], however it is not reported to separate FFA from soapstock.

FAME synthesis is most reported using FFA esterification with methanol and H_2SO_4 as homogenous acid catalyst [10] and it is true for SS separated FFA (see Table 1). The reported conditions are contradictory – the highest yield is obtained using less reagent, time, and temperature (Table 1, entry 3), but the reaction conditions are optimized for the minimum acid value and somehow the composition and the acid value of obtained product are not reported [15]. Haas et. al. and Pantoja et. al. obtained similar yield using the same long reaction time of 14 h and temperature, but substantially different reagent ratios [13], [14]. But only Pantoja et. al. reported FAME content of 96.6% and a conversion of 99.9% for their biodiesel [13]. On the other hand, Haas et. al. reported higher FFA content of product and suggested washing by the cost of 5% product loss or second esterification step [14]. H_2SO_4 is used in relatively high concentrations up to 17% despite its corrosive properties. High amounts of catalyst H_2SO_4 leads to oxidation of unsaturated fatty acids and appearance of brown coloring [10], [21].

Table 1: Reported reaction conditions of acid catalyzed esterification reactions of fatty acids.

Entry	Substrate	Procedure	MeOH:FFA molar ratio*	Catalyst H_2SO_4, mol%*	Time, h	Tempe-rature, °C	Yield, %	Reference
1	Soybean SS FFA	Conventional heating and stirring	1.8:1	17	14	65	89	Haas et. al. [14]
2	Soybean SS FFA	Conventional heating and stirring	5:1	8.5	5	85	92.1	Jin et. al. [17]
3	Rapeseed SS FFA	Conventional heating and stirring	2.7:1	8.7	1.42	60	96.5	Shao et. al. [15]
4	Buriti SS FFA	Conventional heating and stirring	18:1	11	14	65	92	Pantoja et. al. [13]
5	Palm fatty acid distillate	Ultrasonic bath and mechanical stirring	7:1	14	2.5	40	98	Deshmane et. al. [22]
6	Oleic acid	Ultrasonic bath	3:1**	14	2	60	~90	Hanh et.al. [23]

* The reported esterification reagent proportions are recalculated to molar ratios of MeOH to FFA and mol% of catalyst if given otherwise.

**EtOH is used instead of MeOH

Ultrasound is used to speed up chemical reactions, specially heterogenous ones [24], [25]. Homogeneous reactions may also be influenced, the effect is due to cavitation energy [24]. Ultrasound is widely used in biodiesel synthesis from microalgae using it in various stages of processing and transesterification reaction [25]. FAME for biodiesel is synthesized using ultrasound in acid catalyzed esterification reaction rarely. Deshmane et. al. explored esterification of palm fatty acid distillate and obtained high yield in batch process [22] (see Table 1, entry 5). Authors compared mechanical stirring with ultrasound aided mechanical stirring and concluded, that when reaction mixture from homogeneous becomes heterogeneous, then the effect of macroscale mixing by stirrer and microscale mixing by ultrasound together enhances reaction speed [22]. Hanh et. al. explored synthesis of ethyl oleate and found out that after 2 h at 60 °C conversion of acid is around 90% in ultrasound, but around 75% with stirring [23]. Reported yield of ethyl esters and methyl esters in the same conditions are usually similar, but reagent and catalyst ratios are very high in general organic chemistry approach possibly ruling out differences in reaction efficiency [26], [27]. Till now methyl ester synthesis is not compared in one research using ultrasound and without use of ultrasound.

In our work, we explored the possibility to separate fatty acids from acidulated soapstock *via* steam distillation and to use them in synthesis of fatty acid methyl esters as biodiesel. The objective of this study was to find reaction conditions at MeOH boiling temperature with short reaction time and low catalyst concentration and to elaborate the efficiency of ultrasound in FAME synthesis by acid catalyzed esterification.

2. Experimental Procedures and Methods

2.1. Materials

Soapstock (SS) was obtained from Bio-Venta Ltd. Moisture and volatile compounds content is 72.15 ± 0.23 % from SS mass, and accordingly dry matter content is 27.85 ± 0.23 %. Soxhlet extraction, of acidified and dried SS was performed using cyclohexane as extraction solvent. Extract was 22.85% from the wet SS, containing 0.05% glycerol, 1.2% monoglycerides (MG), 7.4% diglycerides (DG), 29.9% triglycerides (TG), and 40.7% free fatty acids (FFA). The average molar mass of FFA is 283 g/mol.

Lauric acid (70%, A7012, Palm-Oleo Sdn. Bhd.) is a mixture of lauric acid and myristic acid (71.7% and 27.5% respectively, according to gas chromatography), which contains also dodecane, tetradecane, and other acids in negligible quantities. The acid content of the lauric acid material is 99.2 wt% and the average molar mass is 208.8 g/mol. Methyl laurate (99.1%) was obtained from esterification product by column chromatographic purification on silica gel with hexane.

Commercial grade reagents were used without additional purification: H_2SO_4 (97%, Fluka), MeOH (99.8%, Chempur), stearic acid (98.7%, Reahim).

Ultrasonic bath Bandelin Sonorex (160/640 W power, 35 kHz frequency) was used and the water temperature in it was manually adjusted during the reaction at 23–27 °C.

2.2. Analytical methods

Quantitative GC analysis of samples was carried out on Analytical Controls biodiesel analyzer based on Agilent Technologies gas chromatograph 7890A. FAME, monoglycerides (MG), diglycerides (DG), triglycerides (TG), and glycerol were quantified using calibration curves from ERM-EF001 biodiesel (Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, FAME 98.9%), monoolein (Sigma-Aldrich, ≥99%), diolein (Sigma-Aldrich, ≥99%), rapeseed oil (Iecavnieks & Co Ltd., TG 97.5%), and glycerol (Sigma-Aldrich, ≥99%), respectively, using internal standards 1,2,4-butanetriol (Alfa Aesar, 96%) and tricaprin (TCI Europe, 98%). In sample preparation *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (Alfa Aesar, 97%), pyridine (Lach-Ner, 99.5%), and CH_2Cl_2 (Chempur, 99%) were used. Analysis was carried out on DB5-HT column (15 m, 0.32 mm ID, 0.10 µm), TPI splitless injector. Oven and injector 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 flame ionization detector (FID) temperature was set to 390 °C. Standard deviation for FAME was 1.9 wt.% and not higher than 0.5 wt% for all other analyzed compounds.

Qualitative analysis of substrates and products of model experiments was performed with Shimadzu Nexis GC-2030 gas chromatograph equipped with Shimadzu GCMS-QP2020 NX mass spectrometer (MS) and FID. Separation was accomplished with Restek Rtx®-5MS (30 m, 0.25 mmID, 0.1 µm) column, temperature program: 30 °C for 5 min, then 10 °C/min ramp to 300 °C and hold for 5 min. 1 µL of sample was injected with split ratio 100, carrier gas helium flow 1.47 mL/min, FID temperature was 300 °C, MS operates in scanning mode 10–500 Da.

Content of methyl laurate was measured using FTIR method on a PerkinElmer Spectrum 100 spectrometer connected with Universal ATR Sampling Accessory. Methyl laurate and lauric acid were used for calibration, baseline was set from 1820 to 1580 cm^{-1}. Standard deviation of measurements was 3.0 wt%. The acid value and FFA content were determined according to the EN 14104 standard method.

The experiment results have an uncertainty which arises from accuracy and precision of measurements, calibration of the instruments, deviations in operating conditions, and actions of scientists. Linear regression was used for sample composition results of standard solution measurements by GC and standard mixture analysis by FTIR. Experiments were performed several times and averaged. Each analytical measurement was carried out twice and the average value was calculated and used.

2.3. Experimental procedures

Esterification of model acid at boiling temperature. The lauric acid (30.97 g, 0.15 mol acid) and the majority of MeOH (121.2 mL, 3.0 mol, 20 equiv.) were heated to 65 °C, and solution of conc. H_2SO_4 (1.22 mL, 15 mol% or 0.61 mL, 7.5 mol%) in the remaining MeOH was added to it. The reaction mixture was boiled for 5 h, samples (15 mL) were removed from the reaction mixture after 10, 20, 30 min, 1, 2, 3, 4 h from the onset of the reaction. Aqueous Na_2CO_3 (50 mL, 4% or 2%) was added to samples, the ester layer was washed twice with dist. H_2O and dried by distillation in a rotary evaporator at 60 °C for 1 h. Total yield 29.91 g (using 15 mol% of the catalyst) and 29.85 g (using 7.5 mol% of the catalyst).

Acid oil (AO) synthesis. 50% aqueous H_2SO_4 (12 mL) was added to SS (200 g) and stirred, pH should be ≤ 2. The mixture was heated at 80 °C for 1 h, then transferred to the separating funnel and left to separate overnight. The sediment and water layer were removed to yield 55.31 g (28% from SS) of AO.

Steam distillation of FFA. The steam generator and heater were prepared hot. Two-neck round-bottom 250 mL flask with AO (55.31 g) was placed on heater, steam inlet tube was connected. Steam distillation was carried out without prolonged exposure of the mass containing fatty acids to high heat. The collected fatty acids and water were warmed, until the fatty acids melted, and separated into a separating funnel, dried in a rotary evaporator at 70 °C for 1 h. Yield 13.88 g of FFA (7.3% from SS, 25% from AO).

FFA esterification. Distilled FFA (10.00 g) and MeOH (26.7 mL, 20 equiv. to FFA) were heated to reflux and conc. H_2SO_4 (134 µL, 7.5 mol% from FFA) was added. The resulting mixture was refluxed for 1 h and stirred at the same rate for all tests. Aqueous Na_2CO_3 (15 mL, 2% solution) was added, and resulting two phases separated, the ester layer was washed twice with dist. H_2O (10 mL) and dried by distillation in a rotary evaporator at 70 °C for 1 h. Yield 9.92 g of biodiesel (95% from theoretical).

3. Results and Discussion

3.1. Experiments with model compounds

We started research on esterification reactions of fatty acids with model studies. Stearic acid was first selected because of its availability in laboratory and the length of its carbon chain. We chose to test the esterification response using 20 equivalents of MeOH and 15 mol% of H_2SO_4 calculated from the amount of the fatty acids of rapeseed oil [9], [28]–[32]. Expression of catalyst amount in mol% was preferred over wt% since the molar mass of the model acid is slightly different from the average molar mass of the rapeseed oil FFA, and it denoted the real ratio of reactants and catalyst therefore is the best for comparison purposes.

Both stearic acid and methyl stearate are solid substances at room temperature. Therefore, heating was required in the product neutralization and washing steps to keep the reaction product in a liquid state. A sample of the reaction product was tested with GC-MS and it consisted only of stearic acid and methyl stearate, this means that no significant quantities of impurities were forming in the reaction, therefore the products were characterized by titrating the acid content. The esterification reaction is more rapid than initially expected using stearic acid and 20 equivalents of MeOH with 15 mol% of H_2SO_4 and the initially selected sample withdrawal intervals did not accurately reflect the behavior of the reaction. The conversion of stearic acid reached 97.9% within half an hour, half of the remaining acid reacted in the next 30 min and continuing to boil the reaction mixture did not change the acid content, which was within the range of 1.0–1.2%.

We continued our studies using another model acid: lauric acid, which methyl ester is a liquid. The substrate is a mixture of lauric and myristic acids (71.7% and 27.5%, respectively). Only acids and their corresponding esters (in the same ratio) were detected by GC-MS in the reaction products. The selectivity of ester formation is 100%. The ester content is determined by the FTIR-UATR method, the acid content by titration. The chromatographic results corresponded to that obtained by titration.

Experiments have been performed using 20-fold MeOH excess and boiling temperature, but the effects of the catalyst concentration on response behavior have been assessed using 15.0 and 7.5 mol% of H_2SO_4 (see Table 2). Lauric acid reacted with MeOH very rapidly, reaching the lowest acid content after 20 and 60 minutes using 15.0 and 7.5 mol% of the catalyst, respectively. However, lower acid content than 1.1–1.2% could not be achieved by this method, the acid content corresponded to acid number of 3.1–3.4 mg KOH/g, which is 7 times the allowed value of the biodiesel standard EN 14214.

Table 2: Esterification progress of lauric acid with MeOH (molar ratio to FFA 20) at 65 °C temperature.

Entry	Time, min	15.0 mol% H_2SO_4			7.5 mol% H_2SO_4		
		Acid, wt%	Ester, wt%	Sum, wt%	Acid, wt%	Ester, wt%	Sum, wt%
1	10	1.5	96.7	98.2	6.6	92.9	99.5
2	20	1.1	97.9	99.0	1.8	96.9	98.7
3	30	1.1	98.4	99.5	1.3	96.0	97.3
4	60	1.2	96.9	98.1	1.1	98.4	99.5
5	120	1.2	97.3	98.5	1.1	98.7	99.8
6	180	1.2	96.5	97.7	1.2	95.9	97.1
7	240	1.2	96.8	98.0	1.2	97.0	98.2
8	300	1.2	97.7	98.9	1.2	99.1	100.3

The effects of ultrasound application were tested using lauric acid esterification with 20 equivalents of MeOH and 7.5 mol% catalyst at 25 °C. Low temperature was chosen instead of previously tested 65 °C, because esterification reactions occur in ultrasound even at ambient temperature [27], and slight differences in reaction rate would be easier to see, when reactions are moderately fast. We compared two processes when closed vials were immersed in an ultrasound bath or reaction was stirred with magnetic stirrer (see Fig. 1). In contrast to the anticipated, reaction was significantly faster using stirring than ultrasound. The esterification reaction was significantly slower than at the boiling point, but it was possible to reach the same 1.2% acid content in 5 h. The reaction mixture was homogeneous all 5 h, the reason for not promoting effect of ultrasound could be the weak power of used ultrasound bath and little effect on homogeneous reactions in general.

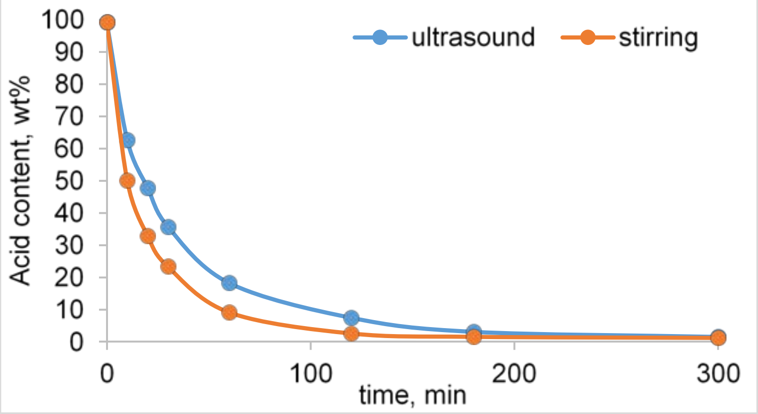

Fig. 1: Acid content of the esterification product using ultrasound or stirring. Reaction conditions: 25 °C, molar ratio of MeOH to FFA 20:1, 7.5 mol% H_2SO_4.

Reaction conditions for esterification of SS derived FFA were selected as follows: 65 °C temperature, molar ratio of MeOH to FFA 20:1, 7.5 mol% H_2SO_4, and a reaction time no more than 1 h, when the chemical equilibrium is established, and conversion has reached 98.9%.

3.2. Esterification of distilled fatty acids

Acidulation of soapstock yielded 28–29 wt% acid oil (AO) using well elaborated method [13]. Initially acidified SS formed a hard-to-mix mass that liquidified by heating. After removal of aqueous phase and sediment, AO is obtained which consisted essentially of FFA and triglycerides (see Table 3). Yield of AO depends mostly on water content of the particular batch of SS. Steam distillation of fatty acids is a mild distillation method utilizing relatively low temperature and avoiding decomposition of FFA. AO was viscous upon steam distillation and formed high-rising foam, which partially polluted distillate, therefore the distillate nevertheless contained MG, DG, and TG and was darker in color than expected. Yield of distilled FFA could be expressed in three ways: 47–51% from FFA in AO, 23–25% from mass of AO, and 6.8–7.3% from mass of SS. For laboratory scale experiments other distillation techniques could be more useful like wiped film short path distillation [15], [16].

Measures were taken to avoid pollution of distillate by AO, but it was only partially successful. As a result, two significantly different batches of FFA were obtained, named FFA1 and FFA2.

Table 3: Composition by GC and acid value of rapeseed soapstock derived AO, steam distilled FFA, and synthesized FAME samples.

Sample	Glycerol, wt%	MG, wt%	DG, wt%	TG, wt%	FFA, wt%	FAME, wt%	Sum, wt%	Acid value, mg KOH/g
AO	0.10	1.1	4.8	29.8	48.7	0.0	84.4	96.5
FFA1	0.0	0.9	2.3	5.4	82.2	0.0	90.9	162.9
FFA2	0.0	0.6	2.0	4.1	88.8	0.0	95.5	175.7
FAME1	0.0	0.6	1.9	3.9	1.4	83.8	91.5	2.7
FAME2	0.0	1.4	1.7	2.8	1.3	89.3	96.5	2.6
FAME3	0.0	0.7	1.3	2.3	0.8	91.3	96.3	1.5

The reaction conditions selected in the modelling studies have been used to implement the fatty acid esterification reaction. Esterification of both FFA1 and FFA2 proceeded with 98.3–98.5% conversion of FFA to FAME and 93–95% yield from theoretical, giving products FAME1 and FAME2, respectively. From the chromatographic results (Table 3) followed that glycerides had possibly reacted in acid catalyzed transesterification, because their content has decreased. Conversion of distilled FFA was lower than model compound probably due to presence of 4–9% of impurities, which were not identified and quantified. The esterification reactions of FFA were homogeneous at the beginning, but they became heterogeneous after 10–15 min. The influence of phase separation on reaction efficiency is disputable. Heterogeneous system could slow mass transfer between phases, but the reaction between FFA, methanol, and sulfuric acid is taking place in homogeneous phase. Glycerides with FAME are separating in the second liquid phase, although this process may decrease available concentration of FFA and increase side product water concentration in reaction phase, leading to lower conversion.

Both products of FFA esterification had FAME and FFA contents not corresponding to biodiesel standard EN 14214. To further increase the content of FAME and decrease contents of other components, a second esterification experiment was proposed. FAME2 was repeatedly subjected to esterification using the same reaction conditions and reagent ratios to FFA content. FAME3 was obtained with 91% yield from mass of starting material with decreased FFA, MG, DG, and TG content, but increased FAME content (Table 3). Nevertheless, FAME3 did not meet the requirements of the standard.

4. Conclusions

Steam distillation of laboratory scale is not sufficiently effective for fatty acid separation from acid oil derived from rapeseed soapstock, the yield is just about half of the fatty acids present in acid oil and overflow of distillable matter could not be fully avoided. However, steam distillation is well-known large-scale purification method and could be used with better effect on large scale. We tested sulfuric acid catalyzed esterification reaction with methanol using lauric acid and showed that ultrasound did not speed up the reaction compared with stirring and that using half of the initial amount of acid yielded the same high 98.9% conversion to methyl esters. The reaction conditions were set to 65 °C temperature, molar ratio of MeOH to FFA 20:1, 7.5 mol% H_2SO_4, and a reaction time 1 h. Distilled fatty acids reacted in chosen reaction conditions with similar conversion but higher residual FFA content probably due to impact of impurities. The yield of product biodiesel was 93–95% from theoretical. The offered method is high-yielding and could be used on purified fatty acids.

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