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Research Article

Experimental and modelling studies on continuous synthesis and refining of biodiesel in a dedicated bench scale unit using centrifugal contactor separator technology

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Continuous synthesis and refining of biodiesel (FAME) using a laboratory scale bench scale unit was explored. The unit consists of three major parts: (i) a continuous centrifugal contactor separator (CCCS) to perform the reaction between sunflower oil and methanol; (ii) a washing unit for the crude FAME with water/acetic acid consisting of a mixer and a liquid–liquid separator; and (iii) a FAME drying unit with air. The continuous setup was successfully used for a 4 h runtime without any operational issues. The CCCS was operated at an oil flow rate of 32 mL/min, rotational speed of 35 Hz, 60°C, a catalyst concentration of 1.2% w/w and a methanol flow rate of 10 mL/min. The flow rate of water (containing 1% w/w acetic acid) for the biodiesel washing unit was 10 mL/min (20°C); the air flow rate (5% humidity) was set at 12 L/min. After 4 h runtime, approximately 7 kg of refined FAME was produced from a cumulative sunflower oil feed of 7.07 kg. The ester content of the refined FAME was 98% w/w (GC). Other relevant product properties were also determined and most were shown to meet the ASTM specifications. The refining section was modelled and optimised using ASPEN software.

Practical applications: Synthesis and refining of sunflower biodiesel was successfully performed in a dedicated bench scale unit using centrifugal contactor separator technology. Besides for large scale biodiesel production, this technology has particularly potential to be applied in small mobile biodiesel units due to the compact size, robustness, flexibility in operation and high volumetric productivity of the CCCS devices.

Keywords: Continuous centrifugal contactor separator / FAME / Refining

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1 Introduction

Biodiesel, a substitute to diesel fuel, can be produced from various virgin plant oils as well as waste cooking oils [1, 2]. Global biodiesel production grew at an average annual rate of

17% in the period 2007–2012 [3]. In the US, the biodiesel industry recorded a total volume of nearly 5.67 million tons in 2013 which exceeds the 2.52 million tons/annum target set by the EPA's Renewable Fuel Standard. The production of biodiesel in Europe has also increased dramatically in the period 2000–2011 [4], driven by the EU objective of a 10% biofuels share in the transportation sector by 2020 [5].

Conventional biodiesel production involves the transesterification of a triglyceride with methanol and a homogeneous catalyst [6, 7]. Various studies have been conducted to gain insights in the process parameters affecting the transesterification reaction [7, 8]. New reactor and process concepts have been explored [9, 10]. Recently, we have proposed a new reactor configuration for the continuous synthesis and refining of biodiesel. It involves the use of a continuous centrifugal contactor separator (CCCS), a device that integrates mixing, reaction and separation of liquid–

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Abbreviations: τ_{wash} , residence time of FAME–water mixture in the wash column; $\tau_{\text{dry, L}}$, residence time of FAME in the drying column; $\tau_{\text{dry, G}}$, residence time of air in the drying column; **FAME**, fatty acid methyl esters; F_{A} , air flow rate (mL/min); F_{O} , oil flow rate (mL/min); F_{M} , methanol flow rate (mL/min); F_{W} , water flow rate (mL/min); $F_{\text{W/FAME}}$, water to FAME flow ratio (–); V_{FAME} , volume of FAME (mL)

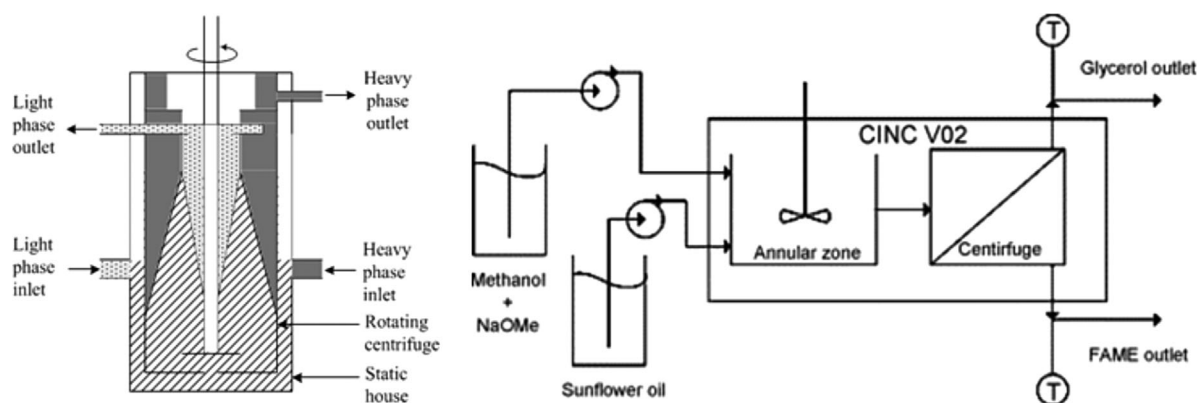


Figure 1. Cross-sectional view of the CCCS (left) and a schematic representation of the CCCS set-up for biodiesel synthesis (right) [13].

liquid systems and as such is an interesting example of process intensification [11–13].

The CCCS (Fig. 1) basically consists of vessel containing a hollow rotating centrifuge. The immiscible liquids (pure plant oil and methanol for this study) enter the device in the annular zone between the mantle and the rotating centrifuge, where they are intensely mixed. The mixture is then transferred into the hollow centrifuge through a hole in the bottom of the centrifuge. Here, the product phases (biodiesel and glycerol) are separated by centrifugal forces (up to $900\times g$), allowing excellent separation of the fluids. The volumetric productivity ($\text{kg}_{\text{FAME}} \cdot \text{m}^{-3} \cdot \text{h}^{-1}$) in a single CCCS was shown to be slightly higher than for a conventional batch process [11]. However, the main advantage compared to batch operations is the combined reaction–separation in the CCCS, eliminating the necessity of a subsequent liquid–liquid separation step. As such, the use of the CCCS integrates biodiesel synthesis and glycerol–biodiesel separation in a single unit.

We have shown the proof of principle for a CCCS (type CINC V02) to obtain fatty acid methyl esters (FAME) from sunflower oil and methanol with a reproducible yield of 96 mol% and a volumetric production of $2050 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}} \cdot \text{h}$ [11]. We have also modified the CCCS type CINV V02 to achieve a higher biodiesel volumetric production rate at a given FAME yield ($2470 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}} \cdot \text{h}$ for 94 mol% yield). Proof of principle for the synthesis and subsequent refining of FAME in a cascade of two CCCS devices has also been demonstrated [13]. Phase separation between the biodiesel and water in the crude biodiesel washing unit (a second CCCS) was excellent at low flow rates. However, we observed that the throughput was limited to an oil flow rate of 16 mL/min. At higher flow rates, the refined FAME was hazy and still contained small water droplets. This limited the overall productivity for the synthesis and refining of biodiesel in a cascade of CCCS.

We here report the continuous synthesis and subsequent refining (acetic acid/water wash) and drying of biodiesel (FAME) using a laboratory scale bench scale unit. The unit consist of three major parts: (i) a CCCS to perform the

reaction between sunflower oil and methanol; (ii) a wash unit for the crude FAME (water/acetic acid) consisting of a mixer and settler; and (iii) a FAME drying unit (air). The refining of FAME in the bench scale unit was modelled using Aspen and the results are compared with the experimental data.

2 Materials and methods

2.1 Materials

The sunflower oil was purchased from Deli XL (Reddy), the Netherlands. The fatty acid composition, acid value, water content and phosphorus content of the oil has been determined and is reported in [13]. The oil was analysed by GC and shown to consist mainly of linoleic acid (57.4%), oleic acid (30.2%), palmitic acid (8.4%) and stearic acid (4.0%). Methanol (absolute, pro analysis) was obtained from Emsure. Sodium methoxide solution (25%) in methanol and CDCl_3 (99.8%) were obtained from Sigma–Aldrich. n-Heptane (99+) was obtained from Acros Organics while (S)-(–)-1,2,4-butanetriol (97.5%), 1,2,3-tridecanolylglycerol (99.9%) and N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) were purchased from Supelco Analytical.

2.2 Synthesis of FAME in a CCCS

The synthesis of FAME was performed in a modified CCCS type CINC V02. The diameter of the outer mantle was enlarged from 6 to 11 cm with the intention to achieve higher biodiesel volumetric production rates at a given FAME yield [13]. The unit was equipped with a heating jacket using water as the heating medium. The reactor temperature reported is the water temperature in the jacket. A standard bottom plate with curved vanes was used for all experiments. The rotor was operated counter clockwise. A weir size of 0.925” was used for all experiments.

The sunflower oil and methanol solution containing the appropriate amount of the sodium methoxide catalyst were

preheated to 60°C and the jacket temperature was set to 60°C. The rotor (35 Hz) and the oil feed pump (32 mL/min) were started. As soon as the oil exited the heavy phase outlet, the actual reaction was initiated by feeding a sodium methoxide in methanol solution (1.2% w/w NaOMe with regard to the oil) to the second inlet at a flow rate of 10 mL/min. During a run, samples were taken from the crude FAME exit. The samples (0.5 mL) were quenched with 0.1 M HCl (0.5 mL) in water and analysed with $^1\text{H-NMR}$ (*vide infra*).

2.3 Continuous washing of FAME in a stirred vessel and a liquid–liquid separator

Crude FAME produced in the CCCS was pumped to a 1 L stirred vessel at a flow rate of 40 mL/min. Either RO water or slightly acidic water (formic acid, citric acid or acetic acid) was separately fed to the vessel at a 0.5:1 ratio (water to FAME), while stirring at 175 rpm. The outlet stream was fed to the bottom of a liquid–liquid separator (55 cm high and 6.3 cm diameter) at a flow rate between 50 and 120 mL/min (depending on the water to FAME flow ratio). The liquid–liquid separator was initially filled with either RO water or slightly acidic water until a level of 15 cm below the top. After a certain time (depending on the flow rate), the washed FAME exited the liquid–liquid separator at the top. At the same time, a valve was operated at the bottom of the liquid–liquid separator to drain the water phase at a flow rate of approximately 10–80 mL/min (depending on the water to FAME flow ratio) to maintain a constant liquid level in the liquid–liquid separator.

2.4 Continuous drying of FAME in a bubble column

The FAME from the wash section was dried continuously with air (5% relative humidity) in a bubble column of 70 cm high and 6.3 cm diameter. The column was filled with Raschig rings (height, 1.1 cm; diameter: 0.8 cm). The FAME was fed to the bubble column at the top at a flow rate of 40 mL/min. Air (5% relative humidity) entered the column at the bottom at a

flow rate of 8–12 L/min using a sparger (glass filter P1, with a diameter of 4 cm and pore size of 100–160 μm).

2.5 Continuous operation of the bench scale unit

Figure 2 shows a schematic representation of the lab bench scale unit for the continuous synthesis and refining of FAME. The start-up procedure and further operation will be described in the following. The sequence was initiated with FAME synthesis in a modified CCCS type CINC V02 in a set-up described above (Section 2.2). Periodically, samples were taken from the crude FAME exit flow (point A in Fig. 2), and the samples were analysed by $^1\text{H-NMR}$ (*vide infra*). The crude FAME was fed to a 1 L vessel equipped with a 5.7 cm diameter magnetic rod for stirring. Simultaneously, acidic water (1%w/w acetic acid) was fed to the vessel at a flow rate of 20 mL/min. The wash step was performed at room temperature with a stirring speed of 175 rpm. The liquid volume of the vessel was maintained at about 240 mL by removing the FAME–water mixture at a flow rate of 60 mL/min. This stream was fed to a column filled with water and Raschig rings. As soon as the FAME–water mixture entered the column, the outlet valve at the bottom of the column was opened and an aqueous bottom stream was removed at a flow rate of 20 mL/min. At point B (refer to Fig. 2), samples were taken from the wet FAME exit flow and these were analysed ($^1\text{H-NMR}$ (*vide infra*) and Karl–Fischer titration to determine the water content).

The washed FAME was dried in a column (70 cm high and 6.3 cm diameter) equipped with a P1 pore size sparger and filled with Raschig rings. The air was pre-heated to 95°C by passing it through a water bath before entering the drying column at a flow rate of 12 L/min. In the initial stage of operation, the column was filled with the washed FAME till 80% maximum level. Subsequently, the level was maintained constant by removal of the dried FAME at the bottom of the column by manually opening/closing a valve. At point C (refer to Fig. 2), samples were taken from the dried FAME exit and the water content of the samples was determined using a Karl–Fischer titration.

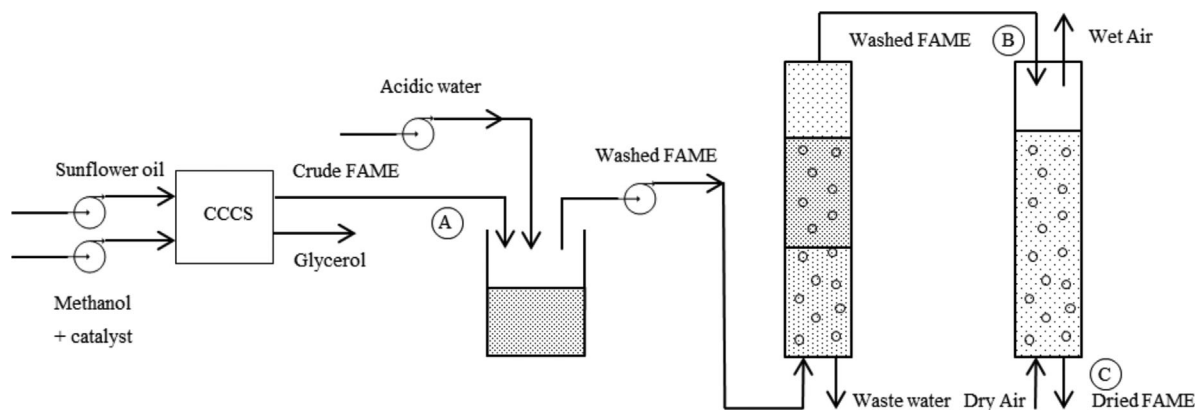


Figure 2. Schematic representation of the continuous bench scale unit.

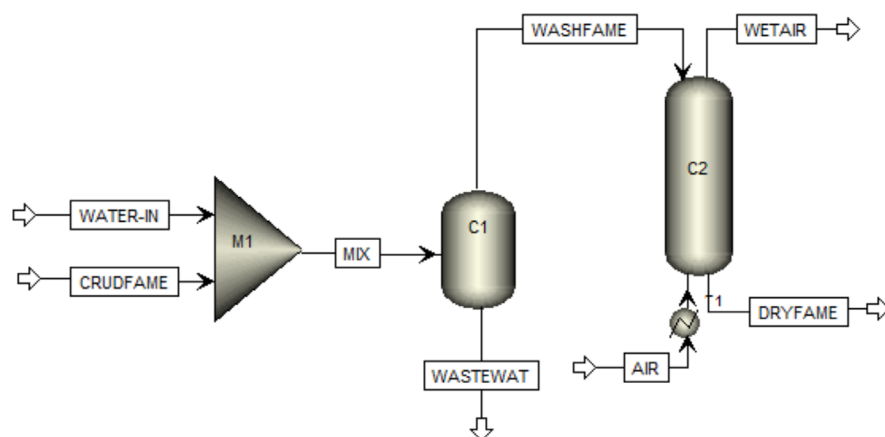


Figure 3. Aspen PLUS model for the refining section of the in a dedicated bench scale unit.

2.6 Analytical methods

Detailed descriptions of GC and other analytical methods (water content, acid value, flash point, cloud point and pour point) are given elsewhere [12]. All measurements were performed at least in duplicate and the average values are reported. The phosphorus and sodium content of the

sunflower oil and biodiesel products were determined by ASG Analytik-Service GmbH, Neuss, Germany according to the methods described in EN 14107 and EN 14108, respectively.

Table 1. Specifications of the refining units in the Aspen model

Unit	Variable/Block	Data/Method
Mixer M1	Temperature	20°C
	Pressure	1 atm
	Valid phases	Liquid
Decanter C1	Temperature	20°C
	Pressure	1 atm
	Phase split	Fugacities of two liquids
	Valid phases	Liquid–liquid
Absorber C2	Liquid coefficients	UNIFAC
	Pressure drop	Not specified
	Calculation type	Equilibrium
	Stages	5
	HETP	12 cm
	Filling	Ceramic Raschig rings 15 mm
	Condenser	None
	Reboiler	None
Dist D1	Aspen Plus “block”	RadFrac
	Number of stages	15
	Feed stage	2
	Condenser	Total
	Reflux	1.2
Dist D2	Distillate to feed ratio	0.1 mass
	Aspen Plus “block”	RadFrac
	Number of stages	15
	Feed stage	8
	Condenser	Total
Dist D2	Reflux	1.5
	Distillate to feed ratio	0.2 mass
	Aspen Plus “block”	RadFrac

2.7 Aspen modelling for FAME refining

The refining model for FAME (water wash and drying with air) was developed using the Aspen Plus 7.3 software (Fig. 3) and consists of a mixer M1 simulating the mixing in the stirred vessel and a decanter C1 simulating phase separation in the liquid–liquid separator. The drying stage was modelled by an absorption column (C2, “RadFrac” with no reboiler or condenser).

Individual model components were methanol, water, air, glycerol and methyl oleate. The latter is a well established model component for FAME [14] of which the relevant physical properties are available. The component properties were estimated using a UNIFAC model as suggested by the Aspen Plus Biodiesel Model manual [14]. The operating conditions for the wash and drying section were set as those used in the experiments. The specifications of each unit are shown in Table 1.

2.8 Definitions of FAME yield, volumetric production rate and residence time

The FAME yield was determined by $^1\text{H-NMR}$ measurements of the product phase by comparing the peak areas of the characteristic signal of the methyl ester group of the FAME (δ 3.6 ppm) with respect to the characteristic signal of the methyl end groups of the fatty acid chains (δ 0.9 ppm). The volumetric production rate of FAME is defined as the amount of FAME produced per (reactor or liquid) volume per time. Definitions of yield and volumetric production rate are described elsewhere [13].

The residence time is defined as the fluid hold up in the reactor or wash/drying column divided by the flow rate into

Table 2. Overview of residence times definitions used in this study

Symbol	Description
τ_{CCCS}	τ in the CCCS
τ_{wash}	τ of FAME–water mixture in the washing column
$\tau_{\text{dry,L}}$	τ of FAME in the drying column
$\tau_{\text{dry,G}}$	τ of air in the drying column

the reactor or column (Table 2).

$$\text{Residence time} = \frac{V}{F} \left(\frac{\text{mL}}{\text{mL/min}} \right) \quad (1)$$

where V is the fluid hold up (mL) and F is the volumetric flow rate (mL/min).

Here, the fluid hold up is either based on the total hold-up of both phases or an individual phase. Similarly, the volumetric flow rate may be based on the total flow rate or an individual flow rate. For the synthesis of FAME in the CCCS, V is defined as the total liquid hold up of the FAME–glycerol mixture in the CCCS when the system is operated at steady state.

For the liquid–liquid separator in the wash section, the residence time is based on the input flow rate of the water/FAME dispersion and the total liquid hold up of both phases in the column. The latter was determined after the continuous run by draining and measuring the FAME–water mixture inside the column.

For the continuous drying of FAME in the bubble column with air, both the gas and liquid residence times were determined. The residence time of FAME in the drying column was defined as the liquid hold up in the column divided by the volumetric FAME flow rate; the residence time of air in the drying column is the gas hold up divided by the air flow rate. The liquid and gas hold up in the column were determined experimentally. At steady state operation, the height of the FAME–air mixture ($h_l + h_a$) was measured. This height multiplied by the cross sectional area of the column is the sum of the liquid and gas hold up. The air inlet and FAME inlet and outlet stream were closed and the height of the remaining liquid in the column (h_l) was measured. This value multiplied by the cross-sectional area of the column gives the liquid hold up. For a column filled with the Raschig rings, the voidage of the filled column has to be considered, which was 82% v/v.

3 Results and discussion

Continuous synthesis and refining of FAME were investigated in an integrated bench scale unit. In the initial phase of the project, the three sections of the bench scale unit (reaction, washing and drying) were studied separately; the

last part is dedicated to studies in the integrated bench scale unit. The synthesis of FAME was carried out in a CCCS operated at the optimum conditions previously determined in our group [13]. The crude FAME was washed with water/acetic acid in a continuous set up consisting of a stirred vessel followed by a liquid–liquid phase separator. The wash section was optimised and modelled with Aspen. Finally, the refined FAME was dried continuously with dry air in a bubble column. The drying unit was optimised and modelled with Aspen as well. The continuous synthesis and refining of FAME was carried out in an integrated bench scale unit at the optimum conditions as determined for the individual units. The integrated unit was modelled using Aspen plus software to establish mass balances and to optimise the process.

3.1 Synthesis of FAME in a CCCS

Systematic studies on the synthesis of FAME using sunflower oil and methanol in a CCCS have been previously reported in detail [13]. A regression model has been developed to estimate the optimum conditions for the methanolysis of sunflower oil in the CCCS. At these optimum conditions (oil flow rate of 31 mL/min, rotational speed of 34 Hz, catalyst concentration of 1.2% w/w and a methanol flow rate of 10 mL/min), the FAME yield is 94 mol% ($^1\text{H-NMR}$) with a productivity of $2470 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}} \cdot \text{h}$. In the current study, slightly modified conditions were used for the synthesis of FAME in a CCCS. The oil flow rate was set at 32 mL/min whereas the methanol flow rate was set at 10 mL/min. The catalyst concentration was 1.2% w/w with a rotational speed of 35 Hz. At these conditions, a FAME yield of $94 \pm 2 \text{ mol\%}$ ($^1\text{H-NMR}$) was obtained with a productivity of $2530 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}} \cdot \text{h}$. A further increase in the oil flow rate resulted in the decrease of the FAME yield. Hence, an oil flow rate of 32 mL/min was selected as the base case for operation of the continuous bench scale unit (*vide infra*). With this input flow rate, the output volumetric flow rate of crude FAME is between 35 and 38 mL/min. As such, the flow rate of the crude FAME for the experimental studies in the washing and drying unit (discussed in the following sections) was set at 40 mL/min.

3.2 Continuous washing of FAME in a stirred vessel and a liquid–liquid separator

The crude FAME produced in the CCCS has an ester content of $98 \pm 0.5\% \text{ w/w}$ (GC-FID), a total glycerol content of approximately $1 \pm 0.03\% \text{ w/w}$, an acid value of $0.07 \pm 0.01 \text{ mg KOH/g}$ and a water content of $0.01 \pm 0.005\% \text{ w/w}$. However, significant amounts of methanol ($3.3 \pm 0.2\% \text{ w/w}$) and sodium ions (34 mg/kg) were present. In this section, a FAME washing procedure with water/organic acid in a stirred vessel followed by liquid–liquid separation (Fig. 2) will be discussed.

The crude FAME is initially mixed with water/organic acid in a stirred vessel before being separated in the liquid–liquid separator. Operating conditions and particularly the water to FAME ratio (0.25:1–2:1) and type of organic acid (formic acid, citric acid and acetic acid) were varied to determine the conditions for highest methanol and sodium removal. The flow rate of crude FAME into the stirred vessel was set constant at 40 mL/min. This value was selected as it is the anticipated flow rate of the crude FAME coming from the CCCS (see Section 3.1). The flow rate of water varied from 10 to 80 mL/min. The residence time in the stirred vessel was about 4 min (based on total flow rate of 40 mL/min FAME and 40 mL/min water). Initially, the column was filled with either RO water or slightly acidic water. Subsequently, the FAME–water mixture was fed at a volumetric flow rate of 50–120 mL/min (depending on the water to FAME ratio) into the bottom of the liquid–liquid separator. After a certain time (depending on the flow rate), the washed FAME exited the column at the top.

3.2.1 Effect of water to FAME ratio on amount of methanol removed

A number of experiments was performed with a water to FAME ratio between 0.25 and 2 while all other conditions were constant (F_{FAME} : 40 mL/min, 175 rpm, 20°C) and the results are shown in Fig. 4. After reaching a steady state, methanol recovery levels were between 95 and 99%. The amount of methanol removed at steady state is a function of the water to FAME ratio. At the lowest ratios, the percentage methanol removed is lower than for the highest ratio. This agrees with the results obtained from the modelling of the wash section with Aspen that will be discussed in a later section.

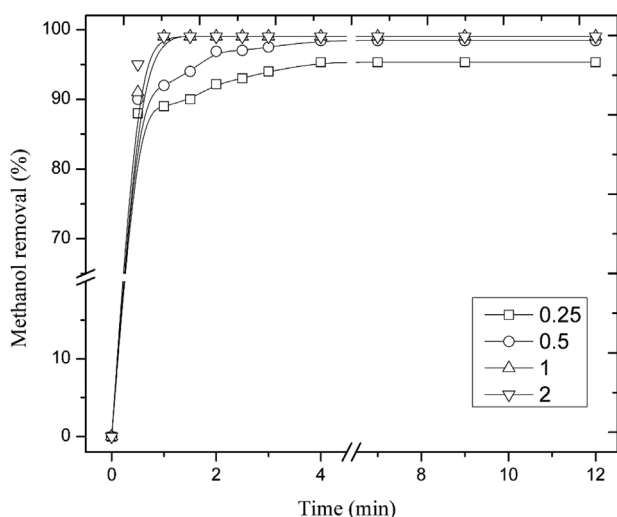


Figure 4. Methanol removal versus run time in a stirred vessel/liquid–liquid separator for different water to FAME flow ratios.

At all water to FAME ratios, except the lowest, the sodium content (2 mg/kg), acid value (0.11–0.14 mg KOH/g) and water content (0.2–0.21%w/w) in the outlet FAME stream were essentially similar. At the lowest ratio (0.25: 1 water: FAME ratio), the sodium content was much higher (10 mg/kg). Combined with the methanol removal data, a minimum water to FAME ratio of 0.5 is required for efficient removal of the methanol and sodium ions from the crude FAME.

3.2.2 Effect of organic acids

The addition of an organic acid to the water phase was investigated, as the presence of acids is known to reduce the tendency for emulsion formation in agitated vessels, particularly at longer run times [15]. For this purpose, 1% w/w of an organic acid (formic acid, acetic acid or citric acid) was added to the water phase. The water to FAME ratio was set at 0.5 and the flow rate of FAME was 40 mL/min (175 rpm, 20°C).

Emulsion formation was not observed for the runs lasting at least 2 h. As expected, the wash of the crude FAME with slightly acidic water increased the acid value from 0.11 mg KOH/g for water to 0.30 mg KOH/g (water with citric acid). Slightly lower acid values were found for the treatment with aqueous formic acid (0.21 mg KOH/g) and acetic acid (0.28 mg KOH/g). The water content of the refined FAME after the treatment was between 0.25 and 0.28%w/w for both acids, which is close to the value for water only. However, when citric acid was used, the water content increased from 0.25 to 0.56%w/w. This may be due to the higher solubility of citric acid in the FAME, rendering the FAME slightly more hydrophilic. Addition of organic acid did not have an effect on the removal of methanol from the crude FAME. Based on availability and safety aspects [16], acetic acid was selected as the organic acid of choice for further use in the continuous integrated bench scale unit.

In conclusions, the most suitable experimental conditions for the work-up of crude FAME (40 mL/min) in a continuous setup consisting of a stirred vessel and a liquid–liquid separator are the use of a water/acetic acid mixture (1%w/w) at a flow rate of 20 mL/min (residence time of 4 min in the stirred vessel and residence time of 9 min in the liquid–liquid separator, based on total flow rate), a temperature of 20°C and a stirring speed in the stirred vessel of 175 rpm.

3.2.3 Modelling of the FAME wash section with Aspen

The continuous work-up of the crude FAME was modelled using ASPEN Plus. The model consists of a mixer M1, simulating the stirred vessel and a decanter C1 for the phase separation column (refer to the washing section in Fig. 3). Detailed specifications for the mixer (M1) and decanter (C1) are given in Table 1.

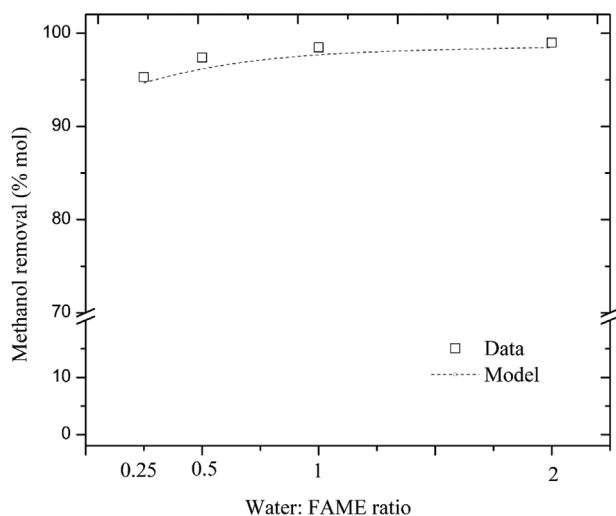


Figure 5. Experimental data and Aspen model predictions for the methanol removal from FAME at different water to FAME flow ratios (F_{FAME} : 40 mL/min, 20°C, 175 rpm).

The percentage of methanol removal versus the ratio of water to FAME (0.25–2) was modelled and the result is shown in Fig. 5. Clearly, good agreement between model and the experimental data at steady state are obtained. Thus, we can conclude that the FAME wash experiments are performed in the equilibrium regime, as modelled by Aspen, and not in the kinetic regime. As such, the selected residence times and stirring speeds in the stirred vessel are sufficient to achieve good mass transfer rates and to reach physical equilibrium. The percentage of methanol removal increased from 95 to 98% as the water to FAME ratio was increased from 0.25 to 1.

3.3 Continuous drying of FAME with air in a bubble column

The wet FAME from the wash unit was dried continuously with air (5% humidity) in a bubble column either with or without Raschig rings as shown in the drying section of Fig. 2. The wet FAME used in this study had a water content of 0.27%w/w and was fed at a flow rate of 40 mL/min. The effect of air flow rate (8–12 L/min) and column temperature (20–40°C) were studied. The run time for the experiments was set at 60 min, and as such about 2400 mL of wet FAME was used for each experiment. An overview of the ranges of process variables and the base case is provided in Table 3.

3.3.1 Effect of air flow rate on column performance

A typical profile of the water content in the FAME exiting the drying column versus the run time is given in Fig. 6. The initial water content in the outlet was 0.10%w/w and

Table 3. Base case and range of variables for the continuous drying of FAME in a bubble column

Variable	Base case	Range
F_{FAME} (mL/min) ^a	40	Constant
F_{A} (L/min) ^a	8	8–12
T (°C)	20	20–40

^a F_{FAME} : FAME flow rate, F_{A} : air flow rate.

decreased with time before reaching a steady state after approximately 10 min. The air flow rate has a significant effect on column performance and the water content of the FAME in the outlet was reduced from 0.084 to 0.07%w/w as the air flow rate was increased from 8 to 12 L/min (Table 4, no Raschig rings).

Slightly better performance was observed in the presence of Raschig rings. At an air flow rate of 12 L/min, which corresponds to an air to FAME ratio of 300, 78%w/w of the water is removed from the FAME which corresponds to a final water content of 0.06%w/w.

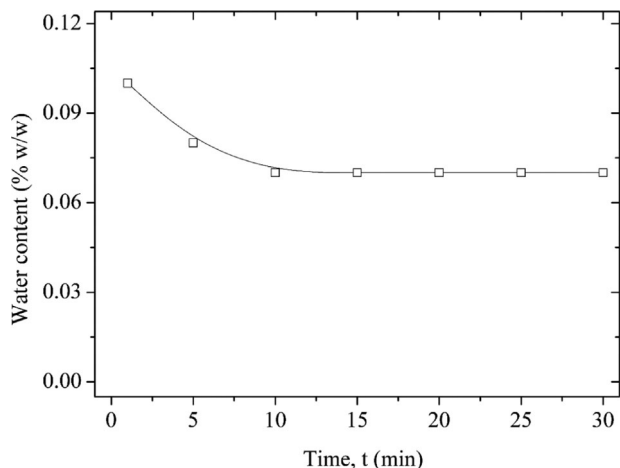


Figure 6. Water content for outlet FAME versus run time for a continuous experiment (F_{FAME} : 40 mL/min, F_{A} : 12 L/min, no Raschig rings).

Table 4. Effect of air flow rate on the water content of the dried FAME and percentage of water removal^a

F_{A} (mL/min)	$F_{\text{A}}/F_{\text{FAME}}$ (–)	Water content (%w/w)	% Water removal
8×10^3	200	0.084	69
10×10^3	250	0.076	72
12×10^3	300	0.070	74

^a F_{FAME} = 40 mL/min, 20°C, no Raschig rings.

3.3.2 Effect of temperature on the water content of the FAME

The effect of column temperature was investigated by using heated air (95°C) prior to entering the column. For these particular experiments, the FAME flow rate was set at 40 mL/min whereas the airflow rate was 12 L/min. At these conditions, the temperature in the bottom the drying column was 40°C. The measured water content of the dried FAME was 0.04%w/w, which implies 85%w/w water removal. This value is considerably lower than for an experiment at room temperature (0.06%w/w).

3.3.3 Modelling of the drying section with Aspen

The experimental results for the drying section at room temperature (no Raschig rings) were modelled using Aspen Plus (drying section of Fig. 3). The model consists of an absorption column C2 (“RadFrac” with no reboiler or condenser), see Table 1 for detailed specifications. The percentage of water removal as a function of the air flow rate for the experiments and the Aspen model is given in Fig. 7. Good agreement between the experimental data and the model was observed. The percentage of water removal increases from 55 to 74%w/w as the air flow rate increased from 5 to 12 L/min. At 12 L/min, the water content of the dry FAME is approximately 0.07%w/w.

3.4 Continuous synthesis and refining of FAME in a dedicated bench scale unit

Continuous synthesis and refining of FAME was performed in a dedicated bench scale unit (Fig. 2). The unit consist of

three major units: (i) a reactor (a CCCS); (ii) a FAME wash section consisting of a mixer and liquid–liquid separator; and (iii) a drying unit. The methanolysis reaction of sunflower oil was undertaken in the CCCS using sodium methoxide as a catalyst. After reaction/separation in the CCCS, the crude FAME stream was washed with acidic water to remove the excess of methanol and catalyst. The FAME/water dispersion was separated in a column and subsequently the FAME was dried in a bubble column using air. The inlet sunflower oil flow rate was set at 32 mL/min with an excess of methanol (7.5:1 molar excess to oil and 1.2%w/w of catalyst regarding to the oil). The temperature of the CCCS was maintained at 60 °C and counter-clockwise rotation was applied (rotational speed of 35 Hz). A 0.5:1 ratio of water to FAME was used for the washing section, operated at room temperature. The water/FAME mixture was mixed in a stirred vessel at 175 rpm before being separated in the column. An air flow rate of 12 L/min was used for the drying unit and the temperature at the bottom of the column was 40°C.

The continuous setup was operated for 4 h without operational issues. After the run, approximately 7 kg of refined FAME was produced from a cumulative sunflower oil feed of 7.07 kg, which is close to the theoretical maximum. Samples were taken at three points for analyses of relevant FAME properties (see Fig. 2). The FAME yield versus run time at the outlet of the CCCS is shown in Fig. 8, revealing that stable operation was obtained in the CCCS after 1 h operation.

The relevant properties of crude FAME, washed FAME and dried FAME when the set-up was operated at steady state are shown in Table 5. After reaction/separation in the CCCS, a FAME yield of 94 ± 2 mol% (¹H-NMR) was obtained giving to a FAME productivity of $2530 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}} \cdot \text{h}$. The crude FAME was washed with water (containing 1% w/w acetic acid), resulting in a

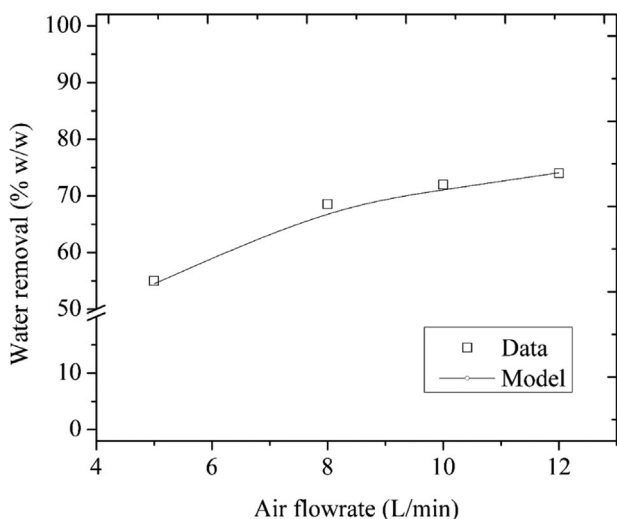


Figure 7. Comparison between experimental data and Aspen model predictions for drying of FAME at different air flow rates (F_{FAME} : 40 mL/min, 20°C, no Raschig rings).

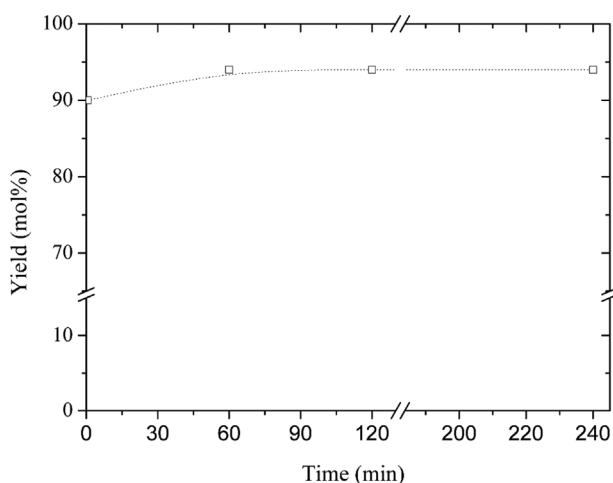


Figure 8. FAME yield (mol%) in the outlet of the CCCS (oil flow rate of 32 mL/min, methanol flow rate of 10 mL/min, 1.2%w/w of catalyst concentration, 60°C, 35 Hz).

Table 5. Properties of crude and refined FAME obtained in the continuous setup

	Bench scale unit ^a	Cascade of CCCS devices ^b
Methanol content (% w/w)		
Crude FAME	3.3	2.8
Washed FAME	0.12	1.3
Dried FAME	0.11	–
Water content (%w/w)		
Crude FAME	0.01	0.03
Washed FAME	0.27	0.22
Dried FAME	0.04	–
Acid value (mg KOH/g)		
Washed FAME	0.28	0.32
Dried FAME	0.3	–

^aResults of this study (oil flow rate: 32 mL/min, methanol flow rate: 10 mL/min, water flow rate: 20 mL/min, air flow rate: 12 L/min, FAME yield: 94 mol%, volumetric production rate: 2530 kg_{FAME}/m³_{reactor} · h).

^bAbduh *et al.* [13] (oil flow rate: 32 mL/min, methanol flow rate: 8 mL/min, water flow rate: 20 mL/min, FAME yield: 93 mol%, volumetric production rate: 2500 kg_{FAME}/m³_{reactor} · h).

reduction of the methanol content from 3.3 to 0.12 ± 0.01% w/w. The water content of the FAME increased from 0.01 to 0.27 ± 0.03%w/w during the wash step. Further drying of the wet FAME with air (5% humidity) gave a FAME with a water level of 0.04 ± 0.005%w/w.

Table 5 also shows a comparison between the results obtained in this study with those for the synthesis and refining of sunflower biodiesel in a cascade of two CCCS devices [13].

The FAME yield (93–94 mol%) and volumetric production rate of the produced FAME (2500–2530 kg_{FAME}/m³_{reactor} · h) were essentially similar, as well as the water content and acid value of the washed FAME (water content: 0.22 versus 0.27%w/w and acid content: 0.28 versus 0.32 mg KOH/g, respectively). However, the methanol content of the washed FAME reported in this study (0.12%w/w) is an order of magnitude lower than for a cascade of two CCCS devices (1.3%w/w). This is likely due to longer residence times in the washing section of the bench scale unit described in this work.

Relevant properties of the refined FAME after drying with air are shown in Table 6. When possible, the properties were compared to the biodiesel standards of ASTM D 6751 and EN 14214. All properties, except the viscosity (6.2 as compared to 6 mm²/s by ASTM D 6751) and free glycerol content (0.04 as compared to 0.02%w/w required by ASTM D 6751) are well within the specifications. The viscosity of FAME from sunflower oil has reported to be 4.584 mm²/s by Barbosa *et al.* [17] and 4.16 mm²/s by Demirbas [18], which are both lower than our value and within the ASTM norm. So far, we do not have a sound explanation for the relatively high viscosity. A possible explanation is related to the relatively high amount of free glycerol in the FAME. It has been reported in the literature that the viscosity of FAME is a function of the glycerol content and increases with higher glycerol contents [19].

3.4.1 Modelling of the refining section of the continuous bench scale unit with Aspen

An Aspen Plus model was developed for the continuous wash and drying section of the process (see Fig. 3) and the results are shown in Table 7. The simulation were performed using

Table 6. Property of refined FAME in comparison with the ASTM D 6751 and EN 14214 standards

Property	Unit		Specifications	
			ASTM D-6751	EN 14214
Ester content	%w/w	98	–	96.5 min
Density at 15°C	kg/m ³	888	–	860–900
Viscosity at 40°C	mm ² /s	6.2	1.9–6.0	3.50–5.00
Flash point	°C	174°C	93 min	101 min
Cloud point	°C	1.0°C	By report	–
Pour point	°C	–3.0°C	–	–
Water content	%w/w	0.04	0.06 max	500 max
Acid value	mg KOH/g	0.3	0.5 max	0.5 max
Methanol content	%w/w	<0.11	0.2 max	0.20 max
Monoglyceride content	%w/w	0.24	0.4 max	0.80 max
Diglyceride content	%w/w	0.04	–	0.20 max
Triglyceride content	%w/w	0.10	–	0.20 max
Free glycerol	%w/w	0.04	0.02 max	0.02 max
Total glycerol	%w/w	0.12	0.24 max	0.25 max
Na content	mg/kg	4	5 max	5 max
P content	mg/kg	1	10 max	10 max

Table 7. Comparison between model and experimental values of relevant properties of refined FAME^a

Variable	Simulated value	Actual value
Methanol content (%w/w)	0.02	0.11
Water content (%w/w)	0.04	0.04
Ester content (%w/w)	99	98
Density at 15°C (kg/m ³)	872	888
Acid value (mg KOH/g)	0.5	0.3

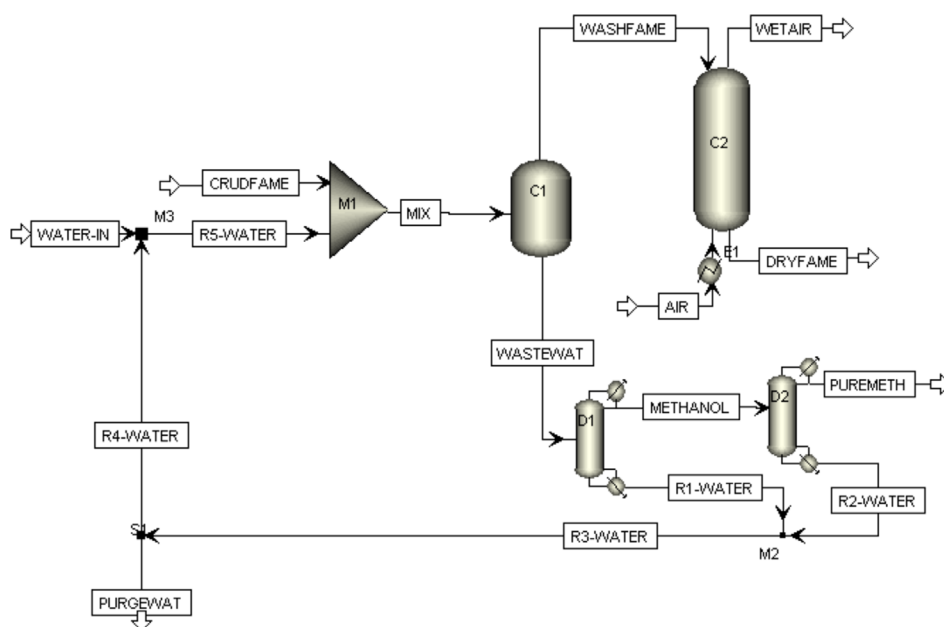
^aWashing: $F_{\text{FAME}} = 40 \text{ mL/min}$, $F_{\text{Water}} = 20 \text{ mL/min}$, 40°C, 1%w/w acetic acid, drying: $F_{\text{A}} = 12 \text{ L/min}$, 40°C.

water containing 1%w/w acetic acid in the washing section and air with a 5% relative humidity for the drying section. Agreement between the model and experimental data for the water content of the dried FAME is very good (0.04%w/w).

Other modelled properties such as the ester content, density and acid values also resemble the experimental data reasonably well. However, the model predicts a residual amount of methanol in the refined FAME (0.02%w/w), which is a factor of 5 lower than the experimental one (0.11%w/w, Table 7). A possible explanation is the use of a single model component to simulate the FAME properties or inaccurate thermodynamic properties of the individual components in the simulation. Nevertheless, it seems that the model can be used for further process design.

3.5 Process optimization using Aspen

The Aspen Plus model (Fig. 3) for the refining section of crude FAME was extended with a methanol and water recovery section (Fig. 9) with the objective to minimise methanol and water consumption in the FAME process. For

**Figure 9.** Aspen PLUS model for the refining of FAME with recycle water.**Table 8.** Compositions of methyl oleate, methanol, water and acetic acid in the streams modelled by Aspen PLUS for the refining of FAME with recycle water^a

Component	Mass Flow (kg/h)						
	Crude FAME	Water in	Air	Dry FAME	Pure methanol	Purge water	R5-water
Methyl Oleate	95.7	0	0	98.9	~0	~0	~0
Methanol	3.3	0	0	0.02	3.2	0.003	0.01
Water	0.01	2.74	0.78	0.04	0.003	2.49	57.9
Air	0		259	0.08	0	0	0
Acetic acid	~0	0.07		0.04	~0	0.02	0.02

^aAssuming 100 kg/h of crude FAME as the basis.

this purpose, the model is extended with a work-up section for the water stream exiting the wash section. This stream contains significant amounts of methanol that have potential for recycle to reduce the variable methanol costs in the process. For this purpose, two distillation columns are added (D1 and D2). This results in a methanol stream suitable for recycle in the reactor section and a water stream (with acetic acid) that may be reused in the refining section.

The results of the simulation are given in Table 8 for a crude FAME input of 100 kg/h. The water recycle reduces the amount of required water (WATER-IN) from 50 to 2.7 kg/h. The amount of acetic acid may also be reduced from 0.5 to 0.07 kg/h. The pure methanol stream (PUREMETH) contains 99% of methanol and may be recycled for the synthesis of FAME, saving approximately 20% of the fresh methanol needed for the trans-esterification of the sunflower oil.

4 Conclusions and future outlook

Continuous production and refining of FAME in a dedicated bench scale unit has been studied experimentally. The setup was operated for 4 h without operational issues. A total of 7 kg of refined FAME was produced with relevant properties well within the specifications, except the viscosity and free glycerol content. The latter indicates that the washing procedure has to be improved, e.g. by applying higher water to crude FAME ratio's in the wash section. The refining part of the bench scale unit was modelled using Aspen, and agreement between experimental data and the Aspen model was very satisfactory. The model can be used for process optimisation and scale up purposes. The use of a CCCS device for reaction/separation instead of a conventional combination of a stirred vessel and phase separator has several advantages. The CCCS devices are compact, robust and flexible in operation. The devices are commercially available in various sizes and throughputs and allow for continuous operation even at small scale. In addition, the use of a glycerol–biodiesel separation unit is eliminated, thereby reducing the number of unit operations. The proposed integrated process for the continuous production and refining of FAME is particularly suitable for mobile biodiesel units.

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