Research Article

Synthesis and refining of sunflower biodiesel in a cascade of continuous centrifugal contactor separators

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The synthesis of fatty acid methyl esters (FAME) from sunflower oil and methanol was studied in a continuous centrifugal contactor separator (CCCS) using sodium methoxide as the catalyst. The effect of relevant process variables like oil and methanol flow rate, rotational speed and catalyst concentration was investigated and modelled using non-linear regression. Good agreement between experiments and model were obtained. At optimised 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 was 94 mol% at a productivity of 2470 kg $_{FAME}$/m$^3_{reactor}$.h. Proof of principle for the synthesis and subsequent refining of FAME in a cascade of two CCCS devices was also obtained. Relevant properties of the refined FAME obtained using this technology were determined and were shown to meet the ASTM specifications.

Practical application: Synthesis and refining of sunflower biodiesel was successfully performed in a cascade of two CSSS devices. 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: Biodiesel / Continuous centrifugal contactor separator / Methanol / Refining / Regression model / Sunflower oil

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1 Introduction

The total global biofuel production level has reached almost 74.6 million ton in 2011 [1]. Biodiesel, besides bioethanol, is an important first generation biofuel and is produced from triglycerides like virgin plant oils and waste cooking oils [2–4]. In the US alone, the biodiesel industry recorded a total volume of nearly 5.67 million ton in 2013 which exceeds the 2.52 million ton/annum target set by the EPA's Renewable Fuel Standard [5]. The production of biodiesel in Europe has also increased dramatically in the period 2000–2011, and is considered of high importance to meet the EU objective of a 10% biofuels share in the transportation sector by 2020 [6].

Conventional biodiesel production involves the trans-esterification of a triglyceride with methanol and a homogenous catalyst [7, 8]. The effect of process variables on the trans-esterification reaction has been studied in detail [2–4, 9, 10]. In addition, new reactor and process concepts have been explored [11, 12]. Recently, we have proposed a new reactor configurations for continuous biodiesel synthesis. It involves the use of a Continuous Centrifugal Contactor Separator (CCCS), a device that integrates mixing, reaction and separation of liquid-liquid systems and as such is an interesting example of process intensification [13–15].

The CCCS (Fig. 1) consists of a hollow rotating centrifuge in a static house. The immiscible liquids (here a pure plant oil and methanol) enter the device in the annular zone between the static house 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

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Abbreviations: C, Catalyst concentration [%w/w with respect to the oil]; **FAME,** Fatty acid methyl esters; **FAEE,** Fatty acid ethyl esters; **F_O,** Oil flow rate [mL/min]; **F_M,** Methanol flow rate [mL/min]; **F_W,** Water flow rate [mL/min]; **$F_{W/FAME}$,** Water to FAME flow ratio [–]; **N,** Rotational speed [Hz]; **T,** Temperature [°C]

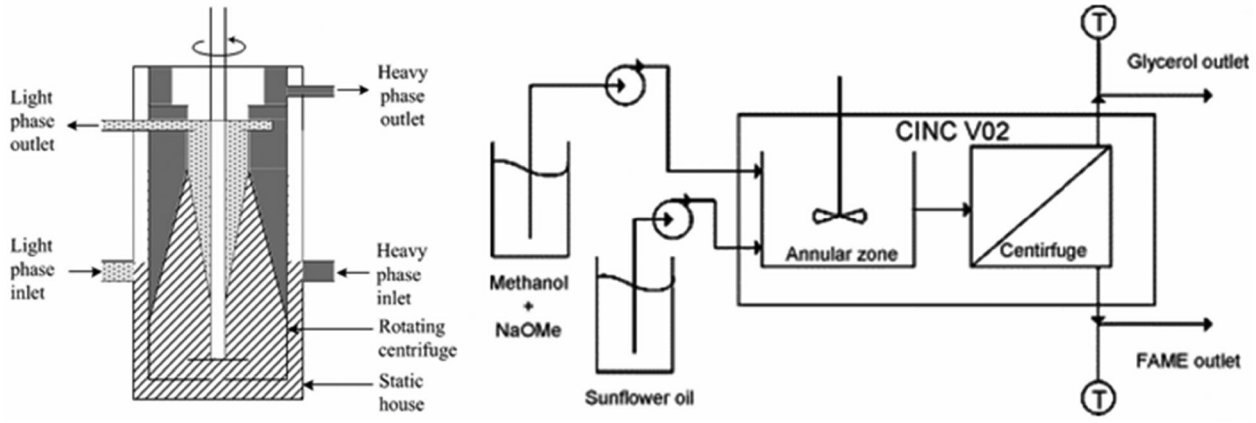

Figure 1. Cross sectional view of the CCCS (left) and a schematic representation of the CCCS set-up for biodiesel synthesis (right) [13].

and glycerol) are separated by centrifugal forces (up to 900 g), allowing excellent separation of the fluids.

We have shown the proof of principle for a CCCS (type CINC V02) to obtain FAME from sunflower oil and methanol with a reproducible yield of 96 mol% and a volumetric production of 2050 $kg_{FAME}/m^3_{reactor}$.h [13]. In addition, fatty acid ethyl esters (FAEE) from *Jatropha curcas* L. oil and ethanol could also be prepared using a modified CCCS device with a reproducible FAEE yield of 98 mol% and a volumetric production rate of 2270 $kg_{FAEE}/m^3_{reactor}$.h [15]. The use of the CCCS has two main advantages compared to conventional stirred vessels, viz. i) the crude FAME/FAEE is in situ separated from the glycerol layer by the action of centrifugal forces and not in a separate separation vessel and ii) the volumetric production rates exceed those in stirred tanks, likely due to higher mass transfer rates as a result of the presence of very fine droplets of the dispersed phase, giving rise to high volumetric mass transfer coefficients (k_La) [16].

Crude FAME requires refining before it meets the product specification set by the biodiesel industry. Washing with water is the most commonly used refining technique [17–19]. Haas et al. [20] proposed two sequential washing steps using NaCl in water followed by a washing with aqueous $NaHCO_3$.Karaosmanoglu et al. [21] tested three different methods and compared performance: washing with distilled water (50–80°C), dissolution in petroleum ether followed by washing with water, and neutralization with H_2SO_4. The best refining method in terms of biodiesel purity and refining cost was shown to be a washing step with water at 50°C.

In this paper, a systematic study on the continuous synthesis and refining of FAME from sunflower oil and methanol using a cascade of two CCCS devices, one for the synthesis of FAME and the other one for the subsequent washing/refining of FAME, is reported. The first part describes an experimental study to optimise relevant process conditions in the CCCS with the objective to obtain a high FAME yield in combination with a high volumetric production rate. High volumetric production rates are advantageous as they allow the use of smaller reactors for a given FAME production and as such lower the investment costs for FAME production considerably. For this purpose, the standard CCCS was modified, viz. the annular volume was enlarged with the intention to allow the use of higher flow rates at similar liquid residence times, which is expected to enhance the volumetric production rate at a given FAME yield. A total of forty experiments were performed and the experimental FAME yields and volumetric production rates were modelled using multi-variable non-linear regression. Such quantitative data are not available for biodiesel synthesis in a CCCS device. The second part describes a study on the use of the CCCS unit for the refining of crude FAME using a water wash at elevated temperatures, with the objective to obtain biodiesel with product properties within the international specifications. Such refining studies using the CCCS to the best of our knowledge not been reported. Finally, the combined use of two CCCS devices in series, one for reaction and one for refining, was studied experimentally, and this is an absolute novelty of this paper.

2 Materials and methods

2.1 Materials

The sunflower oil was purchased from Albert Heijn, The Netherlands. Methanol (99.8%) was obtained from Labscan. Sodium methoxide solution (25%) in methanol, trimethylsulfonium hydroxide solution (0.25 M in methanol), tert-butyl methyl ether (anhydrous, 99.8%), D_2O (99.9%) and $CDCl_3$ (99.8%) were obtained from Sigma-Aldrich.

2.2 Synthesis of FAME in a batch reactor

The batch experiments were performed in a 250 mL glass batch reactor equipped with a heating/cooling jacket

connected to a thermostated water bath. Stirring was performed with a six-blade Rushton turbine with an impeller of 1.4 cm diameter, placed 0.5 cm from the bottom and baffles were present to enhance mixing. The temperature and rotational speed were varied between 20–60°C and 3–10 Hz, respectively. Samples were taken at fixed intervals during the reaction. The samples (0.5 mL) were quenched with 0.1 M HCl (0.5 mL) in water and analyzed with ^{1}H-NMR (vide infra).

2.3 Synthesis of FAME in a CCCS

The synthesis of FAME was performed in a modified CCCS type CINC V02. The diameter of the outer house was enlarged from 6 to 11 cm with the intention to achieve higher biodiesel volumetric production rates at a given FAME yield. 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 can either be operated clock or counter clockwise which affects the mass flow rate from the annular to the centrifugal zone in the CCCS and as such affects the liquid hold-up in the annular zone. For the systematic studies on the effect of process conditions on FAME yield, the rotor was operated counter clockwise. For all other CCCS experiments (FAME refining and the use of two CCCS devices in series for synthesis and refining), the rotor was operated 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 and the oil feed pump 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 to the second inlet. 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 analyzed with ^{1}H-NMR (vide infra).

2.4 Refining of FAME in a CCCS

The refining of FAME was performed in a standard CCCS type CINC V02 equipped with a heating/cooling jacket and a standard bottom plate with curved vanes. A weir size of 0.95″ was used for all experiments. The rotor was operated in the clockwise direction. The crude FAME and reverse osmosis (RO) water were preheated to the pre-set temperature (between 50–75°C). The jacket temperature was set at the pre-determined value (between 50–75°C). Subsequently, the rotor (20–40 Hz), the crude FAME feed pump (12 mL/min) and RO water feed pump (6–48 mL/min) were started. During a run, samples were taken from the FAME outlet and the samples were analyzed using ^{1}H-NMR, Karl-Fischer- and acid value titration.

2.5 Synthesis and refining of FAME in a cascade of CCCS

Synthesis and refining of FAME was performed in a cascade of two CCCS. The rotor of both CCCS units were set to rotate in a clockwise direction. In a typical experiment, the sunflower oil and methanol/sodium-methoxide solution were preheated to 60°C, while the jacket temperature was set and maintained at 60°C. The rotor (35 Hz) and the oil feed pump (16 mL/min) were started. As soon as the oil started to exit the heavy phase outlet of the first CCCS, the reaction was initiated by feeding the sodium methoxide in methanol solution (1%w/w NaOMe with respect to the oil) at a flow rate of 4 mL/min. The rotor (35 Hz) of the second CCCS unit and the RO water feed pump (10 mL/min) were started as soon as the crude FAME entered the second CCCS unit. The RO water was preheated to 50°C and the jacket temperature of the second CCCS unit was set at 50°C. During a run, samples were taken from the FAME outlet of the first CCCS. The samples (0.5 mL) were quenched with 0.1 M HCl (0.5 mL) in water and analyzed with ^{1}H-NMR (vide infra). Samples were also taken from the refined FAME outlet of the second CCCS and were analyzed using ^{1}H-NMR, Karl-Fischer- and acid value titration.

2.6 Drying procedure for refined FAME

500 mL of refined FAME was placed in a 1 l vessel. Dry air (5% relative humidity) was introduced at a flow rate of 5 L/min for 30 min through a sparger placed at the bottom of the vessel. The product was collected and analysed.

2.7 Statistical analyses and optimization

Non-linear multi-variable regression was used to model the experimental date and for this purpose the Design Expert Version 7.0.0 software package was used. The following equation was used:

$$y = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{4} b_{ii} x_i^2 + \sum_{i=j}^{3} \sum_{j=i+1}^{4} b_{ij} x_{ij} + e \quad (1)$$

where y is a dependent variable (FAME yield and FAME productivity), x_i and x_j are the independent variables (oil flow rate, methanol flow rate, catalyst concentration, and rotational speed), b_0, b_i, b_{ii}, and b_{ij} are regression coefficients of the model whereas e is the model error.

The regression equations were obtained by backward elimination of non-significant coefficients. A coefficient was considered statistically relevant when the P value was less than 0.05. The optimum conditions for the synthesis of FAME in the CCCS were determined using the numerical optimization function provided in the software package.

2.8 Analytical methods

The FAME yield was determined using ^{1}H-NMR as described by Kraai et al. [13]. The fatty acid composition of the oil was analyzed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard (HP) 5890 series II Plus device. Detailed descriptions of the GC method and other analytical methods for water content, acid value, flash point, cloud point, and pour point are given elsewhere [15]. The phosphorus and sodium content of the sunflower oil and biodiesel products were determined by ASG Analytik-Service GmbH, Neusass, Germany according to the methods described in EN 14107 and EN 14108, respectively.

2.9 Definition of yield and volumetric production rate

The FAME yield and volumetric production rate are relevant outputs of the experiments. The FAME yield was determined by ^{1}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 (δ 0.9 ppm).

$$\text{FAME yield} = \frac{\text{methyl ester peak area}}{\text{methyl end group peak area}} \times 100\% \ (\text{mol}\%) \quad (2)$$

The reported FAME yield for a continuous experiment is the average FAME yield of the samples after the device reached steady state.

The volumetric production rate of FAME is defined as the amount of FAME produced per (reactor or liquid) volume per time.

$$\text{Volumetric production rate} = \frac{3\Phi_{\text{oil}} Y \left(\frac{MW_{\text{FAME}}}{MW_{\text{oil}}}\right) \rho_{\text{oil}}}{V} \quad \left(\frac{kg_{\text{FAME}}}{m^3 \cdot h}\right) \quad (3)$$

where Φ_{oil} is volumetric flow rate of the sunflower oil (m^3/h), ρ_{oil} is oil density (kg/m^3), Y is FAME yield (mol%), V is volume (m^3), MW_{FAME} is molecular weight of FAME (kg/mol), and MW_{oil} is molecular weight of oil (kg/mol)

The volumetric production rate may either be defined on the basis of the geometric reactor volume (V_R) of the CCCS or the actual measured liquid hold-up (V_L) in the device (sum of the liquid hold-up in the annular zone and centrifuge). The geometrical volume of the modified CCCS used in this study is 650 mL. Typical values for the V_L are 210 mL and 400 mL for clockwise and counter clockwise, respectively (6:1 molar ratio of methanol to oil, 1%w/w of catalyst concentration with respect to the oil, oil, and methanol flow rate of 16 mL/min and 4 mL/min respectively, 60°C, 35 Hz).

3 Results and discussion

3.1 Screening experiments in a batch reactor

Exploratory experiments were performed in a batch reactor using sunflower oil, methanol, and sodium methoxide as the catalyst to gain insights in the optimum reaction conditions for high FAME yield and particularly the temperature and stirring rate. This information is valuable input to set the range of conditions to be used for the subsequent continuous CCCS experiments. The batch experiments were carried out with commercial sunflower oil. The fatty acid composition was determined (GC) and the oil was shown to consist mainly of linoleic acid (57.4%), oleic acid (30.2%), palmitic acid (8.4%), and stearic acid (4.0%). These values are within the range reported in the literature for sunflower oil viz.60–72% for linoleic acid, 16–32% for oleic acid, 6–6.7% for palimitic acid and 3.2–5.1% for stearic acid [22, 23]. The acid value was 0.07 mg KOH/g oil, corresponding to an FFA value of 0.04%. The water content of the oil was 0.04%v/v while the phosphorus content was below 1 mg/kg. All values are well below the standards for plant oils [7, 9], and therefore the oil was not purified prior to a trans-esterification reaction.

A series of experiments with this oil in a batch set-up was performed in a temperature range of 20–60°C, while keeping other relevant conditions constant (6:1 molar ratio of methanol to oil, 1%w/w of catalyst with respect to oil, 10 Hz). The effect of reaction temperature on the FAME yield is presented in Fig. 2. As expected, temperature has a marked effect on the FAME yield and the highest rates were obtained at 60°C. This is mainly a kinetic effect, though mass transfer rates are also known to be positively affected as the solubility of methanol in the reactive oil/FAME phase

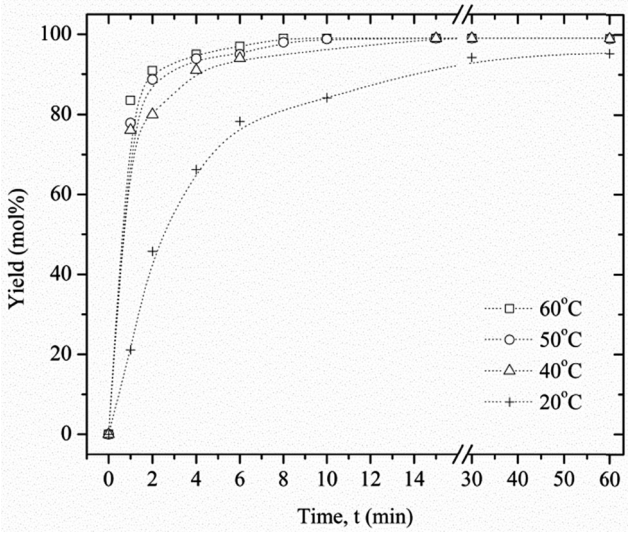

Figure 2. Effect of temperature on FAME yield in batch (6:1 molar ratio of methanol:oil, 1%w/w catalyst concentration, 10 Hz).

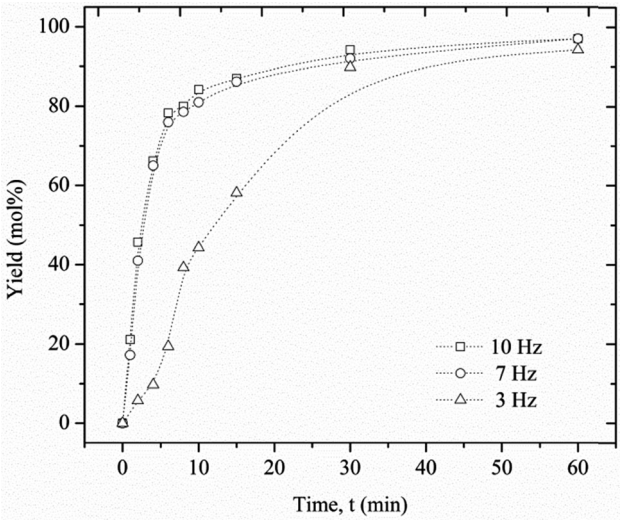

Figure 3. Effect of rotational speed on FAME yield in batch (6:1 molar ratio of methanol:oil, 1%w/w catalyst concentration, 20°C).

increases [24, 25]. As such, the experiments in the CCCS were carried out at 60°C.

Figure 3 shows the effect of stirring speed (3–10 Hz) on the FAME yield versus time while keeping other relevant reaction conditions constant (6:1 molar ratio of methanol: oil, 1%w/w catalyst concentration with respect to the oil, 20°C). At the lowest stirring speed (3 Hz), a lower FAME yield was observed, especially in the initial stage of the trans-esterification reaction. This is caused by mass transfer limitations. At lower stirring speeds, the volumetric mass transfer coefficient (k_La) is reduced leading to lower mass transfer rates of the reactants between the phase boundary [26]. When using stirring speeds above 7 Hz, the FAME yield is essentially independent on the stirring rate, indicating that mass transfer limitations do not play a major role above 7 Hz and that the experiments were carried out in the kinetic regime. As such, these data indicate that the overall rate of FAME synthesis may in some cases be mass transfer limited and this should be taken into account for the continuous CCCS experiments.

Table 1. Process conditions for the screening and systematic study for themethanolysis of sunflower oil in a modified CCCS[a)]

Variable	Screening	Systematic study
Molar ratio of methanol:oil	6:1	6–8:1
Catalyst concentration, C (%w/w)	1.0	0.5–1.5
Oil flow rate, F_o (mL/min)	16	32–60
Methanol flow rate, F_M (mL/min)	4	8–21
N (Hz)	35	30–60
T (°C)	60	fixed at 60
Run time (min)	120	30–60

[a)]Counter clock wise operation of the rotor.

3.2 Initial screening experiments in a CCCS device

Initial screening experiments in the modified CCCS device were carried out for sunflower oil methanolysis using sodium methoxide as the catalyst at conditions close to those found earlier in our group to be optimal for biodiesel synthesis in the unmodified CCCS [13]. Compared to the standard CCCS, the modified CCCS has an enlarged diameter of the outer house (from 6 to 11 cm), allowing for larger liquid hold ups. The experimental conditions are given in Table 1 (screening conditions), the results are provided in Table 2. A typical profile of the FAME yield versus runtime for the modified CCCS is given in Fig. 4. After about 5 min, steady state was achieved with, in this particularly experiment, a FAME yield of 97 mol%. When comparing the performance of the modified CCCS with the standard one (clockwise rotor operation), it is clear that the modified CCCS allows for higher inlet flow rates (16 mL/min for the oil) than the original

Table 2. Volumetric production rates for standard and modified CCCS

	CCCS[a)]	CCCS[b)]	Modified CCCS	Modified CCCS
F_o[c)] (mL/min)	12.6	12.6	16	16
F_M[c)] (mL/min)	3.15	3.15	4	4
Rotational direction	Clockwise	Clockwise	Clockwise	Counter clockwise
Geometrical volume (mL)	322	322	650	650
Typical liquid hold-up in the device (mL)	180	180	210	400
FAME yield (mol%)	96	96	97	97
Volumetric production rate ($kg_{FAME}/m^3_{reactor}.h$)	2050	2080	1300	1300
Volumetric production rate ($kg_{FAME}/m^3_{liquid}.h$)	3670	3730	4040	2120

[a)]Kraai et al. [13].
[b)]This study.
[c)]F_O, Oil flow rate; F_M, Methanol flow rate.

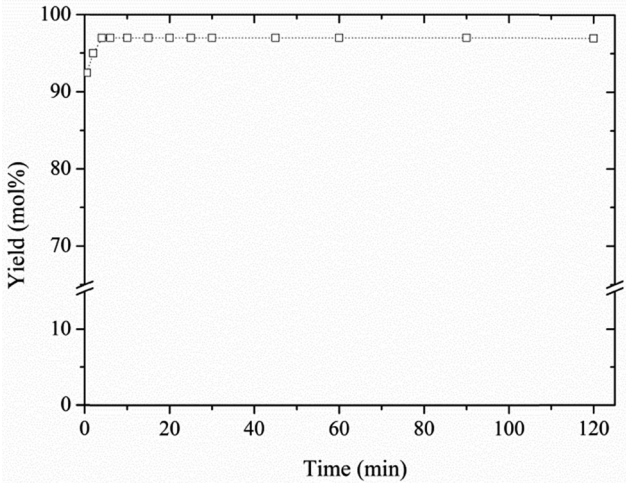

Figure 4. FAME yield (mol%) for a typical experiment in a modified CCCS (6:1 molar ratio of methanol to oil, 1%w/w of catalyst concentration, oil flow rate of 16mL/min, methanol flow rate of 4 mL/min, 60°C, 35 Hz).

one (12.6 mL/min) to obtain similar (high) FAME yields. This positive finding is the result of a larger annular liquid hold-up in the modified CCCS compared to the unmodified version (experimentally determined, see Table 2 for details), which allows the use of higher flow rates while maintaining the required residence time for high FAME yields. As such, the volumetric production rate in the modified CCCS based on liquid hold-up in the device is about 10% higher than for the unmodified version (4040 versus about 3700 $kg_{FAME}/(m^3_{liquid}.h)$).

However, in terms of reactor volume, the volumetric production rate obtained for the modified version is lower; 1300 $kg_{FAME}/m^3_{reactor}.h$ as compared to 2080 $kg_{FAME}/m^3_{reactor}.h$ for the unmodified version. This is due to the larger geometrical volume of the modified CCCS as compared to the standard CCCS (650 mL compared to 322 mL). Hence, a systematic study regarding relevant process conditions (oil and methanol flow rate, catalyst concentration, and rotor speed) was performed to optimize the FAME yield and volumetric production rate of sunflower oil methanolysis in the modified CCCS.

3.3 Systematic studies on the effect of process variables on CCCS performance

Systematic studies on FAME synthesis were performed in a modified CCCS type CINC V02 with sunflower oil, methanol and sodium methoxide as the catalyst. The objective was to obtain high FAME yields in combination with high FAME productivities. As such, the experiments were typically carried out at much higher sunflower and methanol flow rates than for the screening experiments discussed above. In addition, the rotor was operated in a counter clockwise manner as this was shown to lead to a higher liquid volume in the annular zone (120 mL) than for clock wise operation (45 mL, comparative experiment at a 6:1 molar ratio of methanol to oil, 1%w/w of catalyst concentration with respect to the oil and an oil and methanol flow rate of 16mL/min and 4 mL/min, respectively, 60°C, 35 Hz). An overview of the ranges of process variables for the systematic study is given in Table 1. Based on the batch data, the reaction temperature was set at 60°C for all experiments. The run time for the experiments varied between 30 and 60 min, depending on the oil flow rate (a total of about 2000 mL of oil feed was used for each experiment).

One of the experiments was carried out six times to determine the reproducibility of the experimental set-up. The standard deviation regarding the FAME yield was 0.8% absolute, indicative that reproducibility is good.

The results for all experiments are given in Table 3. The FAME yield ranged between 14 and 94 mol%, the FAME productivity between 330–3930 $kg_{FAME}/m^3_{reactor}.h$. The highest FAME yield (94 mol%) within the experimental window was obtained at an oil flow rate of 32 mL/min (10 mL/min methanol), a rotational speed of 35 Hz and catalyst concentration of 1.25%w/w with respect to the oil. The highest volumetric production rate was found for an oil flow rate of 60 mL/min, rotational speed of 30 Hz and catalyst concentration of 1.5%w/w with respect to the oil, though the FAME yield at these conditions is far from quantitative (78 mol%).

Good phase separation of the biodiesel phase and the glycerol rich layer in the outlets was observed for experiments when the FAME yield exceeded 50%. Below these values (i.e., at high flow rates, high rotational speeds, and low catalyst concentrations) partial separation of the biodiesel phase and glycerol phase was observed.

3.4 Model development

The experimental data given in Table 3 were used as input for the development of a multi-variable non-linear regression model for both the FAME yield and the volumetric production rate.

3.4.1 Regression model for FAME yield

The coefficients for the regression model for the FAME yield are provided in Table 4 and relevant statistical data are given in Table 5. The p-value of the model is very low ($<10^{-4}$) which indicates that the model is statistically significant. The parity plot (Fig. 5) shows that the fit between the model and experimental data is very good. The effects of the process variables on the FAME yield are provided in the three-dimensional response surface plots provided in Fig. 6. These clearly show a complicated interplay between process variables and FAME yield. The FAME yield is a function

Table 3. Experimental and modelled FAME yield and productivity in the modified CCCS at a wide range of operating conditions[a)]

Run	F_O[b)] (mL/min)	N[b)] (Hz)	C[b)] (%w/w)	F_M[b)] (mL/min)	FAME Yield (mol%)		Productivity ($kg/m^3_{reactor}.h$)	
					Data	Model	Data	Model
1	40	30	1.5	14	84	87	2820	2890
2	40	40	1.5	14	84	86	2820	2960
3	36	35	1.25	11	89	91	2690	2770
4	40	40	1	14	78	80	2620	2760
5	36	35	1.25	11	88	91	2660	2770
6	36	35	1.25	11	89	91	2690	2770
7	40	30	1	14	83	84	2790	2730
8	32	40	1.5	9	88	90	2370	2430
9	36	35	1.25	10	88	90	2660	2740
10	36	30	1.25	11	88	90	2660	2710
11	36	35	1	11	86	88	2600	2690
12	32	40	1	11	90	87	2420	2490
13	32	30	1.5	9	90	91	2420	2440
14	36	35	1.5	11	91	91	2750	2780
15	32	30	1	11	92	94	2470	2560
16	36	35	1.25	11	88	91	2660	2770
17	40	40	1.5	11	85	88	2860	3030
18	36	35	1.25	11	90	91	2720	2770
19	32	40	1.5	11	90	89	2420	2430
20	40	40	1	11	81	81	2720	2730
21	40	30	1	11	79	82	2650	2710
22	32	40	1	8	86	87	2310	2420
23	36	40	1.25	11	86	88	2600	2720
24	32	30	1	8	89	91	2390	2490
25	32	30	1.5	11	91	93	2450	2440
26	40	30	1.5	11	85	85	2860	2950
27	36	35	1.25	13	88	90	2660	2760
28	32	35	1.25	10	94	94	2530	2580
29	40	35	1.25	12	86	88	2890	2970
30	36	35	1.25	11	89	91	2690	2770
31	30	60	0.5	10	12	13	330	500
32	45	45	0.5	12	49	52	1850	1950
33	45	45	1	8	65	69	2460	2520
34	45	30	1	12	74	77	2800	2870
35	45	60	1	12	38	39	1440	1640
36	60	30	0.5	21	38	45	1920	2030
37	60	30	1.5	21	78	81	3930	4010
38	60	45	1	16	69	75	3480	3570
39	60	60	0.5	10	14	15	700	730
40	60	60	1.5	11	69	74	3480	3560

[a)]Counter clockwise rotor operation.
[b)]F_O, Oil flow rate; N, Rotational speed; C, Catalyst concentration; F_M, Methanol flow rate.

of the rotor speed and the model predicts the existence of an optimum rotational speed (Fig. 6a). Such optima have also been observed for sunflower oil methanolysis in an unmodified CCCS (maximum between 30 and 40 Hz [13]) and jatropha oil ethanolysis (30 and 35 Hz [15]). These trends may be rationalised by considering the fact that the overall sunflower conversion and associated FAME yield is expected to be a function of both the intrinsic kinetics and mass transfer effects. At low rotational speeds (< 30 Hz), the FAME yield is likely limited by mass transfer and higher rotational speeds in this regime lead to higher values for the volumetric mass transfer coefficient (k_La) and thus higher FAME yields. At higher rotational speeds (> 40 Hz), the reaction is expected to occurr in the kinetic regime, where mass transfer limitation

Table 4. Coefficients for the regression model for FAME yield (mol%)[a]

Variable	Coefficient
Constant	148.07
F_O	−6.27
N	2.41
C	1.95
F_M	4.74
F_O.N	0.07
F_O.C	1.0
F_O. F_M	0.16
N.C	0.67
N. F_M	−0.10
F_M^2	−0.31
N^2	−0.07
C^2	−22.3

[a]F_O, Oil flow rate (mL/min); N, Rotational speed (Hz); C, Catalyst concentration (%w/w with respect to the oil); F_M, Methanol flow rate (mL/min).

Table 5. ANOVA for the FAME yield of sunflower oil methanolysis in a CCCS

	SS	DF	MS	F	*p*-value	R^2 values	
Model	15638	12	1303	785	< 0.0001	R^2	0.99
Error	44.8	27	1.66			$R^2_{adjusted}$	0.99
Total	15682	39				$R^2_{predicted}$	0.98

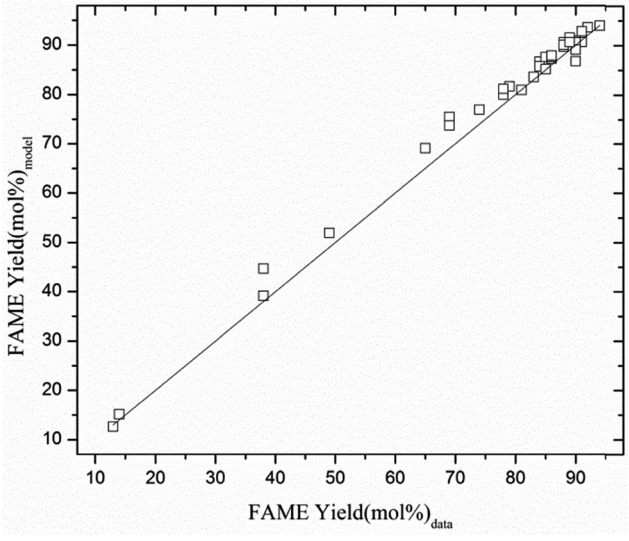

Figure 5. Parity plot for the regression model for FAME yield.

does not play a major role. However, the FAME yield drops dramatically when increasing the rotational speed from 40 to 70 Hz and this is not expected when the reaction is carried out in the kinetic regime. This drop is likely due to a strong reduction of the hold-up of the dispersed phase in the CCCS, leading to lower liquid residence times and as such alowering of the FAME yield.

It is of interest to compare the performance of the modified and unmodified CCCS. In an unmodified CCCS device, Kraai et al. [13] obtained a FAME yield of 71 mol% at a sunflower flow rate of 32 mL/min (6:1 molar ratio of methanol to oil, 1%w/w of catalyst concentration, 60°C, 50 Hz). When using the modified CCCS with a similar sunflower oil flow rate, a much higher FAME yield (94 mol%) was obtained (7:1 molar ratio of methanol to oil, 1%w/w of catalyst concentration, 60°C, 35 Hz). This is a positive effect of the enlargement of the annular zone, allowing for larger inlet flow rates while maintaining the liquid residence time required for high FAME yields.

3.4.2 Regression model for volumetric production rate of FAME

The effect of process conditions on the volumetric production rate is best described by a model of which the coefficients are given in Table 6. ANOVA data are provided in Table 7 and reveal that the model describes the experimental data very well (low *p*-value, high *R*-squared values). This is also illustrated by a parity plot with the experimental and modeled FAME volumetric production rates (Fig. 7). A visualisation of the effect of process variables on the volumetric production rate is given in Fig. 8. All process variables affect the volumetric production of FAME. As expected and in line with the definition of the volumetric production rate (Eq. 3), it increases at higher oil flow rates. Higher catalyst concentrations lead to higher FAME yield (vide supra) and as such also lead to higher volumetric production rates. Similar to the FAME yield, the FAME productivity is also highly influenced by the rotational speed and an optimum is observed.

3.4.3 Optimization

A numerical optimization function was used to predict the highest FAME yield in the modified CCCS within the range of variables used in this study. According to the model, the highest FAME yield (95 mol%) is attainable at an oil flow rate of 30 mL/min (12 mL/min methanol), a rotational speed of 30 Hz and catalyst concentration of 1.3%w/w with respect to the oil. At these conditions, the oil and methanol flow rates are at the lowest end of the ranges used in the design of experiments (Table 1). Higher FAME yield are possible by a further lowering of the flow rates, e.g., to 97 mol% at 16 mL/min, see the screening experiment reported in Table 2.

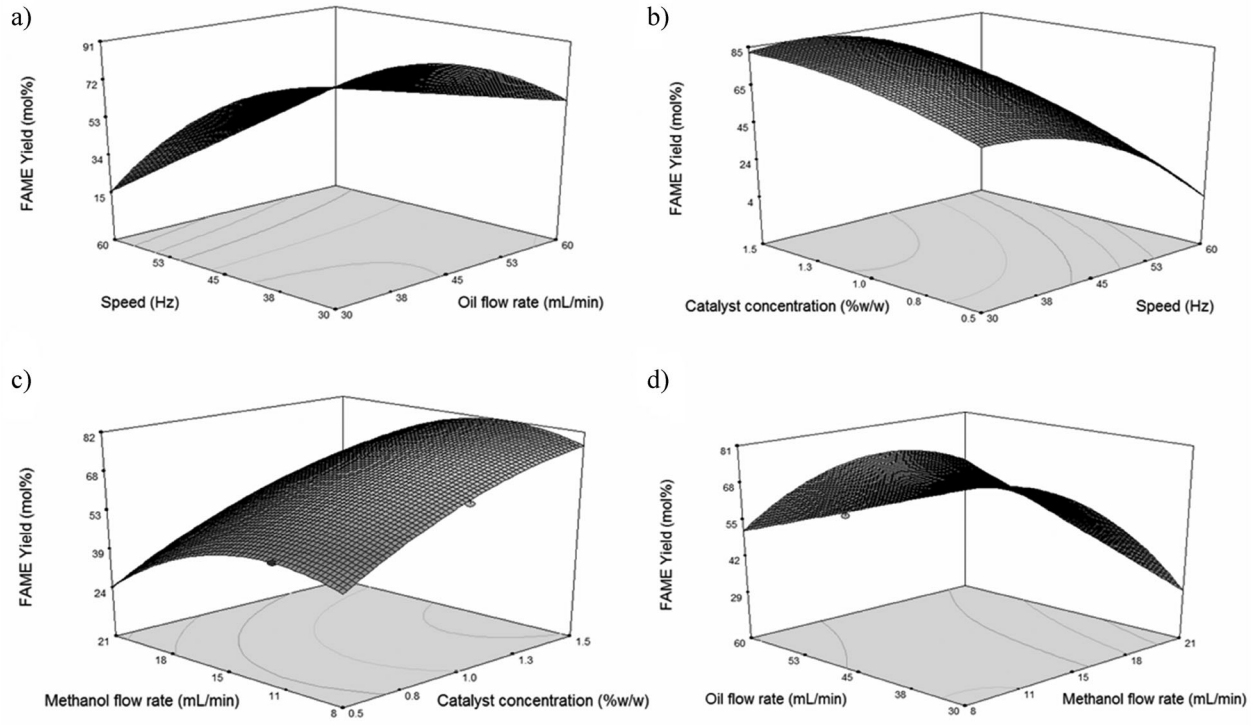

Figure 6. Response surfaces showing the interaction between two parameters on the FAME yield (a) speed and oil flow rate (methanol flow rate (F_M): 14.5 mL/min, catalyst concentration (C):1%w/w) (b) catalyst concentration and speed (oil flow rate (F_O): 45 mL/min, methanol flow rate (F_M): 14.5 mL/min) (c) methanol flow rate and catalyst concentration (oil flow rate (F_O): 45 mL/min, rotational speed (N): 45 Hz) (d) oil and methanol flow rate (catalyst concentration (C):1%w/w,rotational speed (N): 45 Hz).

Subsequently, the model was used to determine the optimum conditions for the highest volumetric production rate with a FAME yield exceeding 90%. According to the model, the best conditions are an 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 modelled FAME yield is 94 mol% at a productivity of 2470 kg $_{FAME}/m^3_{reactor}$.h. The latter is about 25% higher than earlier reported by us using the unmodified CCCS (Table 2) [13], showing the potential of the modified CCCS for further scale up studies.

Table 6. Coefficients for the regression model for FAME productivity ($kg_{FAME}/m^3_{reactor}.h$)[a]

Variable	Coefficient
Constant	2166.05
F_O	−137.65
N	115.42
C	1278.83
F_M	155.77
F_O.N	1.06
F_O.C	85.85
F_O. F_M	3.66
N.C	11.96
C. F_M	−45.05
F_M^2	−10.29
N^2	−2.45
C^2	−620.57

[a]F_O, Oil flow rate (mL/min); N, Rotational speed (Hz); C, Catalyst concentration (%w/w with respect to the oil); F_M, Methanol flow rate (mL/min).

3.5 Product properties of the crude FAME

Relevant product properties of the crude FAME from run 28 (FAME yield of 94%) were determined. The water (0.02%v/v), and P content (1 mg/kg) are low. However, the methanol and Na contents are both high, 24 mol% and 42 mg/kg, respectively. In the following section, the application of a second CCCS to refine the crude FAME will be reported.

Table 7. ANOVA for the FAME productivity of sunflower oil methanolysis in a CCCS

	SS	DF	MS	F	*p*-value	R^2 values	
Model	4441	11	404	908	< 0.0001	R^2	0.99
Error	12.5	28	0.44			$R^2_{adjusted}$	0.99
Total	4454	39				$R^2_{predicted}$	0.98

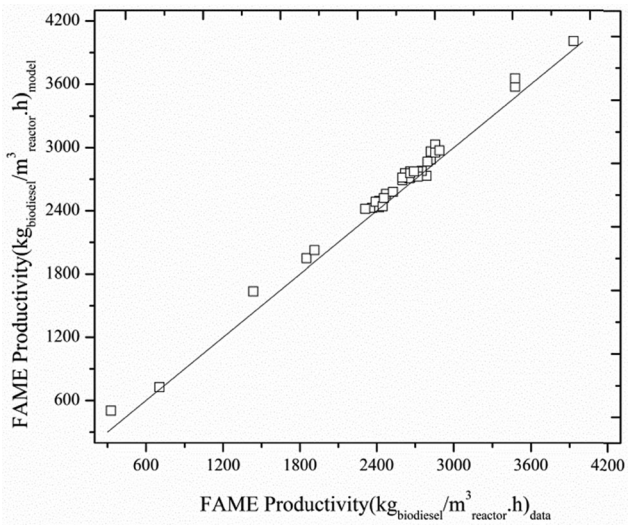

Figure 7. Parity plot for the regression model for volumetric FAME production rate.

3.6 FAME refining in a CCCS

The refining of FAME was performed with RO water in a standard CCCS type CINC V02 with clockwise operation of the rotor. The effect of the rotational speed (20–40 Hz), temperature (50–75°C) and flow ratio of water to biodiesel (0.5–4 to 1) on relevant properties of the refined FAME were assessed, including the acid value and residual methanol, sodium, and water content. The flow rate of the crude FAME was set at a constant value of 12 mL/min for each experiment and an experiment was run for at least 120 min. An overview of the ranges of process variables and the base case is provided in Table 8.

Table 8. Base case and range of variables for the refining of crude FAME in a CCCS

Variable	Base case	Range
F_{FAME} (mL/min)	12	constant
F_W/F_{FAME}	1	0.5–4
F_W (mL/min)	12	6–48
N (Hz)	30	20–40
T (°C)	75	50–75

F_{FAME}, FAME flow rate; $F_{W/FAME}$, Water to FAME flow ratio; F_W, Water flow rate.

A typical profile for the water content and acid value of the refined FAME versus run time is given in Fig. 9 (F_{FAME}: 12 mL/min, F_W/F_{FAME}: 0.5, 30 Hz, 50°C). At steady state operation, the water content and acid value are approximately constant at 0.22%v/v and 0.32 mg KOH/g, respectively. For

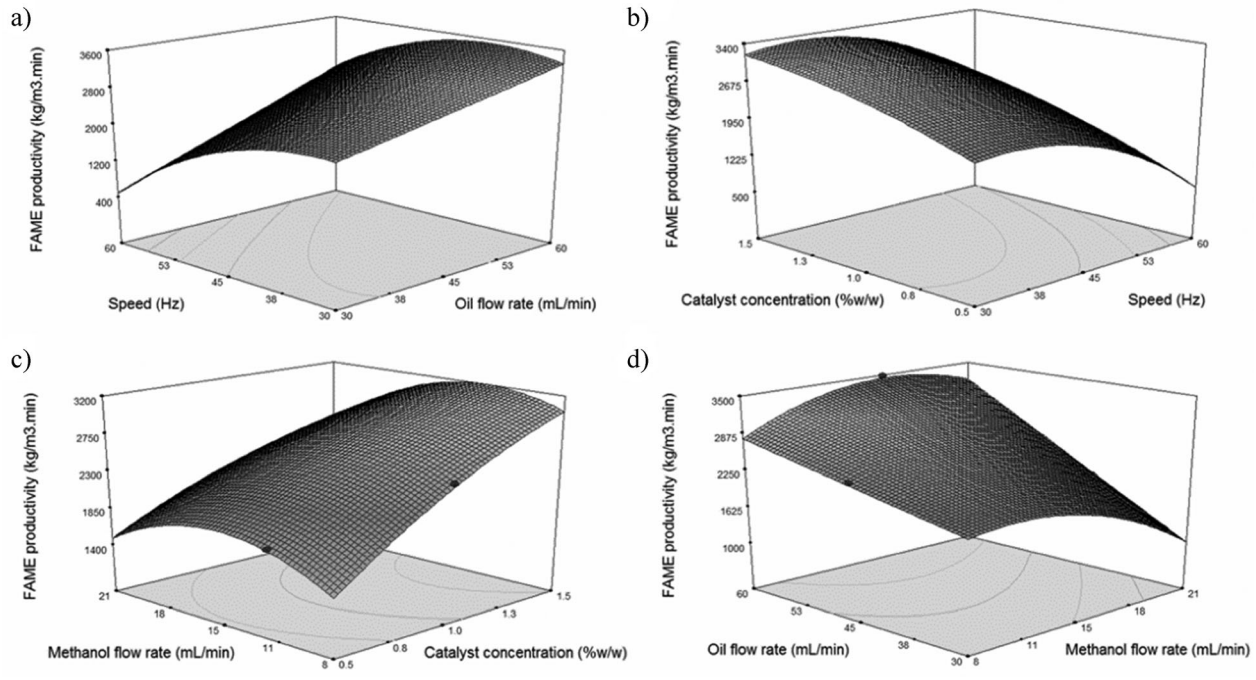

Figure 8. Response surface showing the interaction between two parameters on the FAME productivity (a) speed and oil flow rate (methanol flow rate (F_M): 14.5 mL/min, catalyst concentration (C):1%w/w) (b) catalyst concentration and speed (oil flow rate (F_O): 45 mL/min, methanol flow rate (F_M): 14.5 mL/min) (c) methanol flow rate and catalyst concentration (oil flow rate (F_O): 45 mL/min, rotational speed (N): 45 Hz) (d) oil and methanol flow rate (catalyst concentration (C): 1%w/w, rotational speed (N): 45 Hz).

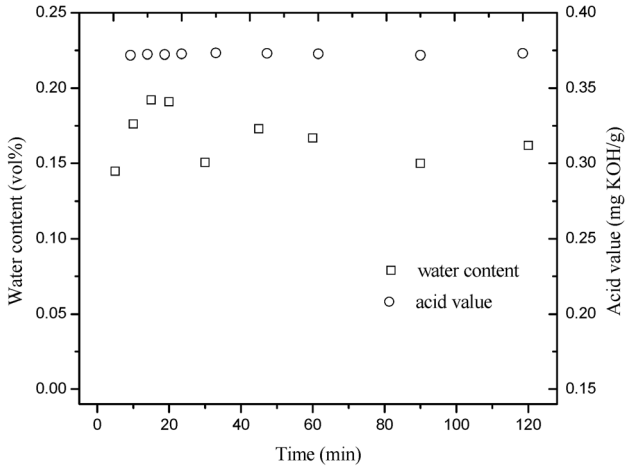

Figure 9. Water content (% v/v) and acid value (mg KOH/g) versus time for a FAME refining experiment in a CCCS (FAME flow rate (F_{FAME}): 12mL/min, Water to FAME flow rate (F_W/F_{FAME}): 0.5, 30Hz, 50°C).

all experimental settings, the results (not shown here for brevity) showed that the quality of the refined FAME in terms of methanol, water and sodium content as well as acid value do not differ considerably. In all cases, methanol was not detectable in the refined FAME. The Na content was below 0.5 mg/kg, and as such satisfies the biodiesel specification. As expected, the water content increased almost ten times, from 0.02 to approximately 0.2%v/v which is close to the equilibrium solubility of water in FAME [27].

3.7 Synthesis and refining of FAME in a cascade of CCCS devices

Continuous synthesis and subsequent refining of FAME was performed in a cascade of two CCCS devices. The CCCS units were connected in series without an intermediate buffer vessel as shown in Fig. 10. The first CCCS device for FAME synthesis was a modified CCCS, whereas the refining was performed in a standard CCCS type CINC V02. Clockwise rotation of the rotor was applied for both CCCS devices.

Three separate experiments with different oil flow rates (16–48 mL/min) were performed while other process parameters were kept constant. The operating temperature was set at 60°C for the first and 50°C for the second CCCS whereas the rotational speed was 35 for the first and 30 Hz for the second CCCS unit. The methanol flow rate (containing 1%w/w sodium methoxide catalyst with respect to the oil) was coupled to the oil flow rate to ensure a fixed methanol to oil molar ratio of 6. The water inlet flow rate in the second CCCS was set at such a value to ensure a constant water to crude FAME feed flow ratio of 0.5 in the second CCCS unit. Sampling was performed at the outlet of the first CCCS unit to determine the FAME yield, methanol and water content of the crude FAME. The run time for the experiments varied between 30 and 90 min, depending on the oil flow rate (a total of about 1500 mL of oil feed was used for each experiment).

The results for all experiments are given in Table 9. Good separation between the crude FAME phase and the glycerol rich layer in the outlets of the first CCCS was observed for all experiments The FAME yield after the first CCCS unit ranged from 91 to 97 mol%. The highest FAME yield (97 mol %) was obtained at an oil flow rate of 16 mL/min (Table 9). Increasing the oil flow rate from 16 to 48 mL/min led to a decrease in the FAME yield (91 mol%) due to shorter liquid residence times at higher flow rates, and in line with the systematic study described in 3.4. As a result, the amount of the unreacted methanol in the crude FAME increased from 23 to 33 mol%. Higher oil flow rates do not have a significant effect on the water content of the crude FAME (0.03%v/v).

Phase separation performance in the second CCCS is a strong function of the crude FAME inlet flow rate, which is coupled to the oil flow rate to the first CCCS. At an oil flow

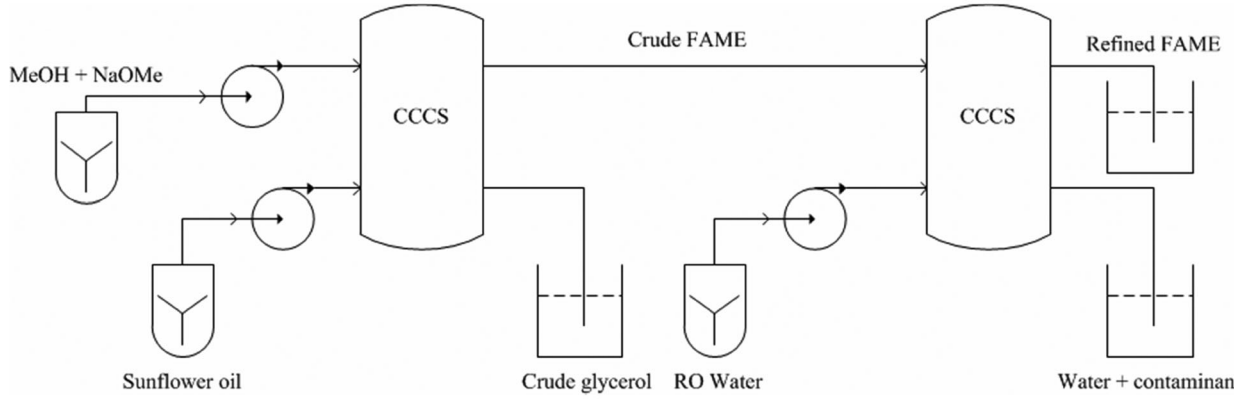

Figure 10. Schematic representation of continuous synthesis and refining of sunflower biodiesel in a cascade of two CCCS devices.

Table 9. Properties of crude and refined FAME obtained in a cascade of two CCCS devices[a)]

Flow rate (mL/min)				Methanol content (mol%)		Water content (%v/v)		Acid value (mg KOH/g)
F_O[d)]	F_M[d)]	F_W[d)]	FAME yield[b)] (mol%)	Crude FAME	Refined FAME	Crude FAME	Refined FAME	Refined FAME
16	4	10	97	23	n.d.[c)]	0.03	0.12	0.32
32	8	20	93	26	12	0.03	0.22	0.32
48	12	30	91	33	16	0.03	0.37	0.31

[a)]Conditions: CCCS 1: 1% w/w of catalyst concentration, 6:1 molar ratio of methanol to oil, 60°C, 2100 rpm; for CCCS 2: 50°C, 1800 rpm, flow ratio of water to FAME of 0.5.
[b)]FAME yield measured at the outlet of the first CCCS unit.
[c)]n.d, not detected based on ^{1}H-NMR measurements.
[d)]F_O, Oil flow rate; F_M, Methanol flow rate; F_W, Water flow rate.

rate of 16 mL/min in the first CCCS, phase separation between the refined FAME and water layer in the second CCCS was excellent and the FAME phase was clear and transparent and did not contain small water droplets. Methanol in the crude FAME was not detectable, indicating also good separation performance. Hence, combined reaction and refining of the crude FAME in a cascade of two CCCS devices was performed successfully and refined FAME with a low methanol and sodium content could be obtained in the continuous setup. However, at higher flow rates ($F_O > 16$ mL/min), phase separation between the refined FAME and water phase in the second CCCS was cumbersome and the refined FAME was hazy and still contained small water droplets. As such, the refining step is not effective yet for oil flow rates exceeding 16 mL/min and further optimization (e.g., by CCCS modifications and weir size variation) is required.

3.8 Properties of the refined FAME obtained in a cascade of two CCCS devices

Relevant properties of the refined FAME after a drying step with air are shown in Table 10. When possible, the properties were compared to the biodiesel standard set according to ASTM D 6751 and EN 14214. It can be concluded that the mono-, di-, tri-, and free glycerine content as well as sodium and phosphorus content are below the maximum values. The water content, acid value, and flash point are also within specification.

Table 10. Property of refined FAME in comparison with the ASTM D 6751 and EN 14214 standards

		Specification Limit	
Characteristic	Refined FAME	ASTM D 6751	EN 14214
Ester content	99%w/w	–	96.5%w/w min
Monoglyceride content	0.6%w/w	–	0.80%w/w max
Diglyceride content	0.09%w/w	–	0.20%w/wmax
Triglyceride content	0.02%w/w	–	0.20%w/wmax
Free glycerine	0.01%w/w	–	0.02%w/wmax
Water content	0.04%v/v	0.05%v/v max	500mg/kg max
Methanol content	n.d.[a)]	–	0.20%w/w max
Na content	0.5 mg/kg max	5 mg/kg max	5 mg/kg max
P content	1 mg/kg	0.001%w/w max	10 mg/kg max
Kinematic viscosity (40°C)	6 mm^2/s	1.9–6.0 mm^2/s	3.5–5.0 mm^2/s
Flash point	150°C	130°C min	120°C min
Cloud point	0°C	–	–
Pour point	−6°C	–	–
Acid value	0.32 mg KOH/g max	0.5 mg KOH/g max	0.5 mg KOH/g max

[a)]n.d, not detected (^{1}H-NMR measurements).

4 Conclusions

Proof of principle for sunflower oil methanolysis and subsequent product refining in a cascade of two CCCS devices has been provided. In the first CCCS unit, a reproducible FAME yield of 97 mol% was obtained. Further refining of the crude FAME in the second CCCS unit with water was successful and after a drying step with air, purified FAME was obtained with product properties within international specifications. Device modifications and particularly the use of a larger annular zone led to significantly improved volumetric production rates in the first CCCS (up to 2470 kg $_{FAME}/m^3_{reactor}$.h) while maintaining high FAME yields. The cascade of two CCS devices used here has several advantages compared to conventional FAME technology. The CCCS devices are compact, robust, and flexible in operation. In addition, they allow for continuous operation even at small scale and are commercially available in various sizes and throughputs. As such, they are particularly suitable for mobile biodiesel units. The design and construction of such a small scale integrated unit is in progress and the results will be reported in due course.

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The authors have declared no conflict of interest.

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