

University of Groningen

Novel highly integrated biodiesel production technology in a centrifugal contactor separator device

Kraai, G. N.; Schuur, B.; van Zwol, F.; van de Bovenkamp, H. H.; Heeres, H. J.

Published in:
Chemical Engineering Journal

DOI:
[10.1016/j.cej.2009.04.047](https://doi.org/10.1016/j.cej.2009.04.047)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kraai, G. N., Schuur, B., van Zwol, F., van de Bovenkamp, H. H., & Heeres, H. J. (2009). Novel highly integrated biodiesel production technology in a centrifugal contactor separator device. *Chemical Engineering Journal*, 154(1-3), 384-389. <https://doi.org/10.1016/j.cej.2009.04.047>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



Novel highly integrated biodiesel production technology in a centrifugal contactor separator device

G.N. Kraai, B. Schuur, F. van Zwol, H.H. van de Bovenkamp, H.J. Heeres*

Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ARTICLE INFO

Article history:

Received 19 November 2008

Received in revised form 31 March 2009

Accepted 17 April 2009

Keywords:

Biodiesel

Pure plant oils

Centrifugal contactor separator

CINC V02

ABSTRACT

The base catalyzed production of biodiesel (FAME) from sunflower oil and methanol in a continuous centrifugal contactor separator (CCS) with integrated reaction and phase separation was studied. The effect of catalyst loading (sodium methoxide), temperature, rotational frequency and flow rates of the feed streams was investigated. An optimized and reproducible FAME yield of 96% was achieved at a feed rate of 12.6 mL min^{-1} sunflower oil and a sixfold molar excess of MeOH (3.15 mL min^{-1}) containing the catalyst (1 wt% with respect to the oil). A jacket temperature of 75°C and a rotational frequency of 30 Hz were applied. The productivity under those conditions ($61 \text{ kg}_{\text{FAME}} \text{ m}_{\text{liquid}}^{-3} \text{ min}^{-1}$) was slightly higher than for a conventional batch process. The main advantage is the combined reaction–separation in the CCS, eliminating the necessity of a subsequent liquid–liquid separation step.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Concerns for the environment combined with the current high crude oil prices have stimulated the interest in biofuels from renewable resources [1–3]. In January 2007 the European Commission published the New Energy Policy for Europe, targeting a 10% share of biofuels in the transportation sector and raising the share of renewable energy to 20% by 2020 [1]. This has stimulated the production of biofuels in Europe considerably, with biodiesel being the most important example. The projected biodiesel consumption for 2007 was 3.8 MTOE, a 70% increase compared to 2006 [4].

Typically, biodiesel, also known as FAME (fatty acid methyl ester) is produced from plant or vegetable oils and fats by transesterification with an alcohol (Fig. 1) [5,6]. A wide variety of different oils and alcohols can be used for the production of biodiesel. Most frequently methanol is the alcohol of choice, although higher alcohols like ethanol, 2-propanol and 1-butanol may be applied as well [7]. Glycerol is a byproduct from the transesterification and has to be separated from the FAME after the reaction [8]. FAME production may either be catalyzed by acidic or basic catalysts. Typical examples of homogeneous base catalysts are sodium hydroxide, potassium hydroxide and sodium methoxide [9], well known examples of homogeneous acidic catalysts are sulfuric acid, phosphoric acid and hydrochloric acid [10]. Both types of catalyzed reactions have been extensively studied [11–13]. Besides homogeneous acidic

and basic catalysts, enzymes [14] and heterogeneous catalysts have been explored as well [11,15].

FAME production is most commonly performed in batch operation, although continuous processes are emerging [11,16–21]. New catalyst, reactor and process concepts for biodiesel production have been reported the last decade. An interesting example is the use of supercritical methanol [22]. In this medium, complete conversion is obtained within 5 min of reaction time without the need of a catalyst.

We here report the use of highly intensified centrifugal contactor separator (CCS) equipment (CINC V02 [23]) for biodiesel synthesis. In the CCS device reaction and separation are combined in a single apparatus, thus making it a good example of process intensification (PI). PI is currently one of the most significant trends in process engineering and aims at replacing large, energy consuming processes [24] by small, highly integrated processes to reduce the size and energy consumption of process plants. Some well known examples of PI are reactive distillation, reactive extraction and the application of micro-reactors [24,25].

The CINC V02 (Fig. 2) is basically a rotating centrifuge in a static reactor housing. The immiscible liquids are fed to the CCS where they are dispersed in the annular zone between the static housing and the rotating centrifuge. The dispersion is then transferred into the hollow centrifuge, through a hole in the bottom plate, where the phases are separated by centrifugal forces of up to $900 \times g$, making it possible to separate fluids with densities that differ only 10 kg m^{-3} . Both liquid phases are collected individually, making use of a weir system.

The CCS was originally designed for waste water cleaning in the nuclear industry [26] and has been used successfully for oil–water

* Corresponding author. Tel.: +31 50 363 4174; fax: +31 50 363 4479.
E-mail address: h.j.heeres@rug.nl (H.J. Heeres).

Nomenclature

a	specific interfacial area ($\text{m}^2 \text{m}^{-3}$)
d_d	drop diameter (m)
F_{MeOH}	methanol flow rate (mL min^{-1})
F_{oil}	sunflower oil flow rate (mL min^{-1})
k_L	mass transfer coefficient (m s^{-1})
μ_c	viscosity of the continuous phase (N s m^{-2})
N	rotational frequency (Hz)
r	radius of the rotor (m)
ρ_c	density of the continuous phase (kg m^3)
ρ_d	density of the dispersed phase (kg m^3)
T_{jacket}	jacket temperature ($^{\circ}\text{C}$)
v_s	settling velocity (m s^{-1})
ω	angular momentum (rad s^{-1})

separation [27] (e.g. for cleaning oils spills [28]), for extraction of fermentation broths [29] and several other extraction processes [30–33]. We recently demonstrated the use of the CCS for enantioselective extractions of amino acid derivatives [34] and reported process integration in the CCS by combining biphasic (bio)catalytic conversions with the separation of the catalyst and the reaction products in the device [35]. These examples clearly illustrate the potential of the CCS equipment for the combined reaction and separation for liquid–liquid systems. The use of the CCS for biodiesel synthesis was also mentioned in this communication. We here report the results of an in depth experimental study to optimize the biodiesel yield in a CCS. The effects of process variables like the temperature, the flow rates and the rotational frequency on the biodiesel yield will be provided and rationalized and the potential of the CCS for biodiesel manufacture will be discussed.

2. Methods

2.1. Materials

Methanol (99.8%) was obtained from Labscan, sodium methoxide solution 30% in methanol (5.4 M) was obtained from Fluka. D_2O (99.9%) and CDCl_3 (99.8%) were obtained from Sigma–Aldrich. Hydrochloric acid (37%) was obtained from Merck and the sunflower oil was purchased from Albert Heijn, the Netherlands.

2.2. Equipment and conditions

The experiments were performed in a CCS of the type CINC V02 (CINC stands for Costner Industries Nevada Corporation) equipped with a heating/cooling jacket, a high-mix bottom plate and a 0.925 in. weir. The CCS was operated at ambient pressure and jacket temperatures ranging from 60 to 75 $^{\circ}\text{C}$ using a Julabo MV basis temperature controlled water bath (accuracy ± 0.01 $^{\circ}\text{C}$) connected to the jacket. Two Watson–Marlow 101U/R MK2 peristaltic tube pumps were used to feed the CCS. The temperature was monitored at each of the two CCS outlets using CMA B016BT temperature sensors connected to a PC via a Coachlab II (CMA) interface. The system was

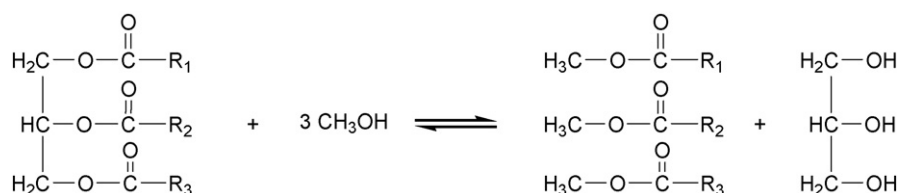


Fig. 1. The transesterification of a plant or vegetable oil or fat with methanol.

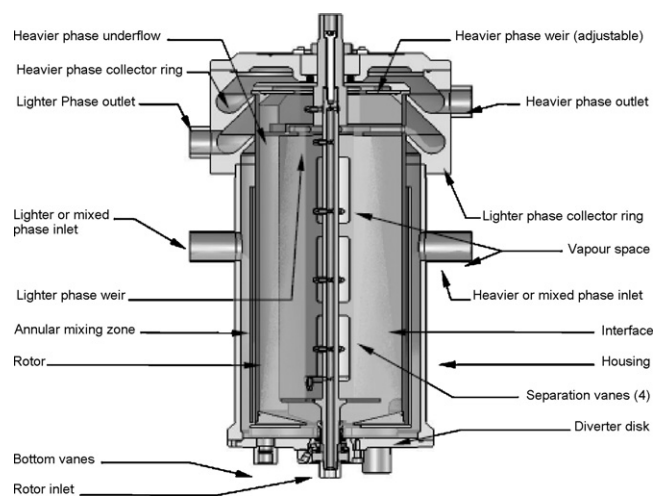


Fig. 2. Schematic cross-sectional view of the CINC (courtesy of Auxill, the Netherlands).

operated at atmospheric pressure by positioning air inlets in the liquid in and outlets. A schematic illustration of the set-up is shown in Fig. 3. The impeller in the annular zone is for illustrative purposes only. In a CINC, mixing in the annular zone is the result of rotation of the centrifuge.

2.3. Experimental procedure

The CCS was operated in a once-through mode for both liquids without recycle of the exit streams. The supply vessels containing the pure sunflower oil and the methanol with sodium methoxide, respectively were preheated to 60 $^{\circ}\text{C}$ and the water bath was set to the pre-determined temperature (60–75 $^{\circ}\text{C}$). The centrifuge was started (20–90 Hz) and the CCS was fed with pure sunflower oil (12.6–40 mL min^{-1}). The molar ratio of methanol to oil was set at 6:1 in all experiments. As soon as the oil started flowing out of the heavy phase outlet, the reaction was started by feeding the methanol and sodium methoxide solution (1% (w/w) with regard to sunflower oil) at 3.15–10 mL min^{-1} . After steady operation was achieved (typically 10–35 min), a glycerol stream with some unreacted methanol exited the CCS through the heavy phase exit. FAME with unreacted oil left the CCS through the light phase exit. The dissolved catalyst is present in both outlet phases. Samples were taken at regular intervals from the light phase outlet and analyzed using ^1H NMR.

2.4. Analytical methods

The FAME yield was determined using ^1H NMR. Hereto, a 1 mL sample of the light phase was directly quenched by adding 1 mL of 0.1 M HCl in water to neutralize the remaining sodium methoxide. The mixture was vigorously shaken and centrifuged for 10 min. A few drops were taken from the top layer and dissolved in CDCl_3 . The samples were analyzed using a 200 MHz Varian NMR. To determine the FAME yield [36], the intensity of the characteristic signal of the

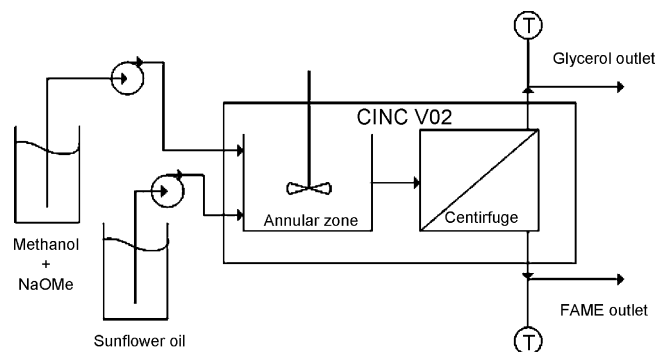


Fig. 3. Schematic representation of the CINC set-up for biodiesel synthesis. T: temperature sensors.

ester (2.3 ppm) was compared with that of the characteristic signal of the methyl end group (0.9 ppm) present in both sunflower oil and FAME.

3. Results and discussion

3.1. Exploratory experiments

The experiments were carried out with sunflower oil and NaOMe as the catalyst. Sunflower oil is readily available in high purity with a low free fatty acid number (FFA). The latter is important as a high FFA number renders the base catalyzed biodiesel synthesis cumbersome due to the formation of the sodium salts of free fatty acids (soap). The FFA number of the sunflower oil applied in this study was below 1 wt%. The molar ratio of methanol to oil was set at 6:1 in all experiments, in line with batch studies in the literature for sunflower oil and methanol [37].

In an exploratory experiment the CCS was fed with sunflower oil (40 mL min^{-1}) and a solution of NaOMe in MeOH (10 mL min^{-1} , 1% (w/w) with regard to sunflower oil). The reaction was performed with a jacket temperature of 60°C and a rotational frequency (N) of 50 Hz. The profile of the FAME yield in time is shown in Fig. 4.

It takes about 15 min to reach the steady-state FAME yield of about 65%. The liquid residence time in the CCS is estimated to be about 3.5 min, based on a total liquid hold-up of 180 mL [38] and a total liquid flow rate of 50 mL min^{-1} . Thus, steady-state is

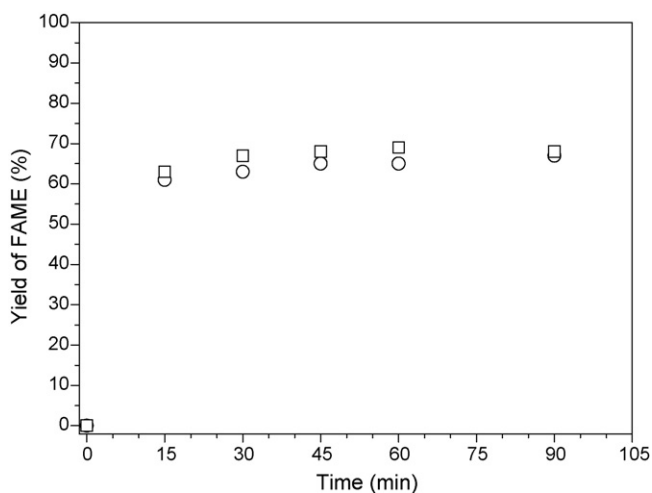


Fig. 4. FAME yield as a function of time. Conditions for both runs— $T_{\text{jacket}}: 60^\circ\text{C}$, $F_{\text{oil}}: 40 \text{ mL min}^{-1}$, $F_{\text{MeOH/NaOMe}}: 10 \text{ mL min}^{-1}$, (6:1 molar ratio of methanol to oil), $N: 50 \text{ Hz}$, and NaOMe: 1% (w/w) with regard to sunflower oil. Yield is the average steady-state yield for at least 2 h runtime.

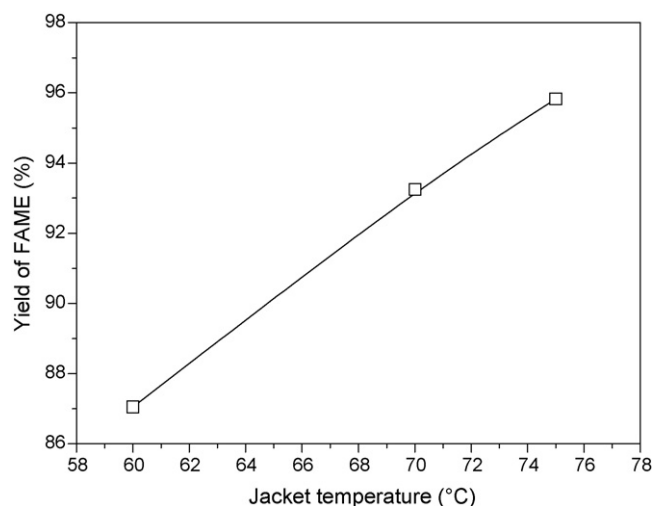


Fig. 5. Effect of T_{jacket} on the yield of FAME. Conditions— $N: 30 \text{ Hz}$, $F_{\text{oil}}: 12.6 \text{ mL min}^{-1}$, $F_{\text{MeOH/NaOMe}}: 3.15 \text{ mL min}^{-1}$ (6:1 molar ratio of methanol to oil), and NaOMe: 1% (w/w) with regard to sunflower oil, line is for illustrative purpose only. Yield is the average steady-state yield for at least 2 h runtime.

reached in just over 3 residence times. After reaching steady-state, the FAME with residual sunflower oil exited the CCS as the light phase, whereas the heavy phase consisted of glycerol in MeOH. To gain insights in the reproducibility, a second run was performed under identical conditions. The results are shown in Fig. 4 as well and imply that reproducibility is good.

These exploratory experiments clearly indicate the proof of principle of biodiesel synthesis in a CCS. In the following part of this paper, the effect of process conditions (temperature, catalyst loading, flow rates, rotational speed of centrifuge) on the biodiesel yield will be described, with the objective to obtain 95+% yield in a single run.

3.2. Effect of reaction temperature

The effect of the reaction temperature on the FAME yield was studied by adjusting the jacket temperature in the range $60\text{--}75^\circ\text{C}$, while keeping all the other variables constant ($N: 30 \text{ Hz}$, $F_{\text{oil}}: 12.6 \text{ mL min}^{-1}$, $F_{\text{MeOH/NaOMe}}: 3.15 \text{ mL min}^{-1}$, and NaOMe: 1% (w/w) with regard to sunflower oil).

The steady-state FAME yield at the lowest temperature in the range (60°C) was 87%. At 75°C , the yield increased to 96%, see Fig. 5 for details. It is well known that the FAME yield is a strong function of the temperature, with higher temperatures leading to higher yields for a given reaction time [35]. Higher jacket temperatures to further enhance the yield could not be applied due to excessive methanol evaporation.

3.3. Effect of catalyst loading

The amount of catalyst has a profound effect on the rate of biodiesel formation. Typically 1 wt% of catalyst on the oil is applied. This loading was also used in the exploratory experiments described above. A number of experiments were performed at higher catalyst loadings (1–1.3% (w/w) with regard to sunflower oil) with all other conditions at constant value ($N: 30 \text{ Hz}$, $F_{\text{oil}}: 12.6 \text{ mL min}^{-1}$, $F_{\text{MeOH/NaOMe}}: 3.15 \text{ mL min}^{-1}$, and $T_{\text{jacket}} = 60^\circ\text{C}$). Unfortunately, when using sodium methoxide intakes higher than the standard 1% (w/w) on sunflower oil, precipitation of solids was observed in the centrifuge. Analyses by NMR show that these solids are rich in fatty acids and suggest that the solids are sodium salts of the fatty acids (soap). These may be formed by saponification

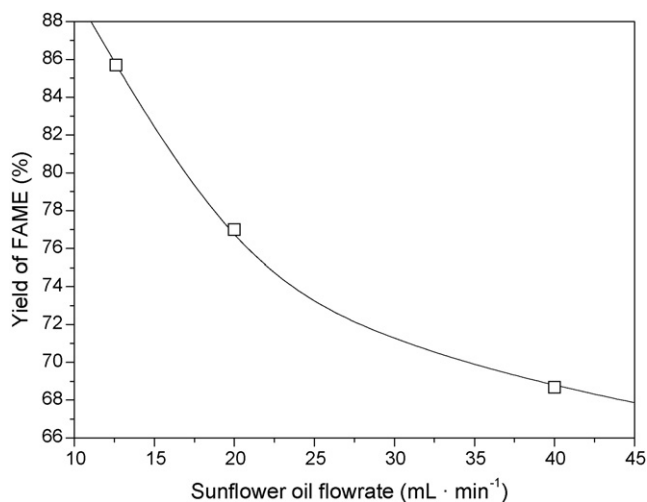


Fig. 6. Effect of flow rate variation on the FAME yield. Conditions— $F_{\text{oil}}:F_{\text{MeOH/NaOMe}}$: 4:1 (6:1 molar ratio of methanol to oil), T_{jacket} : 60 °C, NaOMe: 1% (w/w) with respect to sunflower oil, and N : 50 Hz, line is for illustrative purpose only. Yield is the average steady-state yield for at least 2 h runtime.

of the triglyceride and reaction of the remaining free fatty acids with NaOMe. Thus, yield enhancement by the application of higher intakes of catalyst is not possible due to solid soap formation in the centrifuge.

3.4. Effect of liquid flow rates

The effect of the liquid flow rates on the FAME yield was studied in the range 12.6–40 mL min⁻¹ for sunflower oil. In all cases, the methanol flow rate was 25% of the sunflower flow rate to ensure a fixed sixfold molar excess of methanol over sunflower oil [37].

The FAME yield drops when increasing the sunflower flow rate from 12 to 40 mL min⁻¹, see Fig. 6 for details. The prime reason is likely a reduction of the mean residence times of both phases in the CINC when increasing the flow rates, leading to lower conversions. Recent work by Schuur et al. [39] have shown that the liquid hold-ups at these relatively low feed rates (<100 mL min⁻¹) are essentially independent of the flow rates, implying that the mean residence time is a function of the flow rate. Further reduction of the sunflower flow rates below 12 mL min⁻¹ to increase the FAME yield is not possible due to incomplete phase separation of both outlet streams.

3.5. Effect of rotational frequency

The rotational frequency was varied from 20 to 90 Hz for two jacket temperatures (60 and 70 °C) while keeping the other parameters constant (F_{oil} : 12.6 mL min⁻¹, $F_{\text{MeOH/NaOMe}}$: 3.15 mL min⁻¹, and NaOMe: 1% (w/w) with regard to sunflower oil).

The FAME yield is a strong function of N and varied between 60 and 94% (Fig. 7). At low rotational frequencies ($N < 30$ Hz), a strong increase of the yield was found with increasing N . The yield reaches a maximum between 30 and 40 Hz. A further increase leads to a lowering of the yield. Similar trends were observed for the biphasic esterification of oleic acid with 1-butanol catalyzed by a *Rhizomucor miehei* lipase [35], where a maximum at 40 Hz was observed.

The overall sunflower conversion in this biphasic system is expected to be determined by the intrinsic kinetics of sunflower formation as well as by mass transfer effects. The trends in Fig. 7 may be rationalized by taking these two factors into account. At low rotational speed ($N < 30$ Hz), the overall conversion is likely mainly determined by mass transfer effects (mass transfer limited

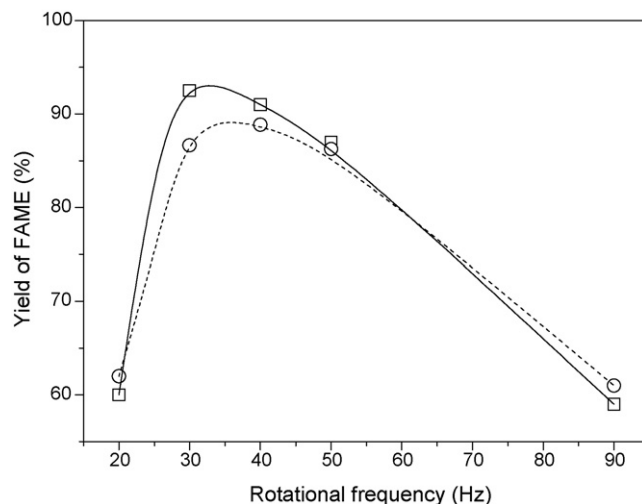


Fig. 7. Effect of the rotational frequency on the FAME yield at different temperatures. Conditions—(□) T_{jacket} : 70 °C, (○) T_{jacket} : 60 °C, F_{oil} : 12.6 mL min⁻¹, $F_{\text{MeOH/NaOMe}}$: 3.15 mL min⁻¹ (6:1 molar ratio of methanol to oil), and NaOMe: 1% (w/w) with regard to sunflower oil, lines are for illustrative purpose only. Yield is the average steady-state yield for at least 2 h runtime.

regime). The power input is rather limited, leading to relatively large droplets in the annular zone and thus to a relatively low value of the volumetric mass transfer coefficient ($k_L a$) [40–43]. The increase in the yield when going from 20 to 30 Hz is likely due to the formation of smaller droplets and a concomitant increase in the value of $k_L a$. The specific annular interfacial area for the biphasic system dichloroethane–water has been studied in detail in the CINC using an on-line laser probe (FBRM). It was shown to be highly depending on the value of N , with high N values leading to larger interfacial areas [39].

Based on this rationalize, the overall conversion rate for $N > 40$ Hz is determined solely by the intrinsic kinetics of biodiesel synthesis and the FAME yield is expected to be independent of the value of N (kinetic regime). However, this is not the case and the yield is lowered at higher N values. It is well possible that this reduction is related to the changes in the volume of the reactive phase in the CINC as a function of the value of N . For a biphasic reaction with relatively fast kinetics, the reaction only takes place in a dispersion consisting of a continuous and a dispersed phase of small droplets. In the CCS, this dispersion is found in the annular zone as well as in parts of the centrifuge. The volume of the dispersed phase in the annular zone is about constant at these low flow rates and independent of N [39]. However, the volume of the dispersed phase in the centrifuge is expected to be a function of the rate of rotation N . This may be rationalized by considering the settling velocity of individual drops in the centrifuge. In a centrifugal settler the settling velocity for individual drops is given by Eq. (1) [44]:

$$v_{s, \text{CCS}} = \frac{d_d^2 (\rho_d - \rho_c) \omega^2 r}{18 \mu_c} \quad (1)$$

The settling velocity of the droplets in the dispersed zone is thus proportional to the difference in density, the angular momentum and the squared drop diameter.

Due to the proportionality of the settling velocity with the angular momentum, we can expect that the dispersed phase volume in the centrifuge will be reduced considerably at high rotational speeds, see Fig. 8 for details. Thus, the observed reduction of the FAME yield in the kinetic regime at $N > 40$ Hz, is likely due to a strong reduction of the volume of the reactive, dispersed phase in the centrifuge of the CCS.

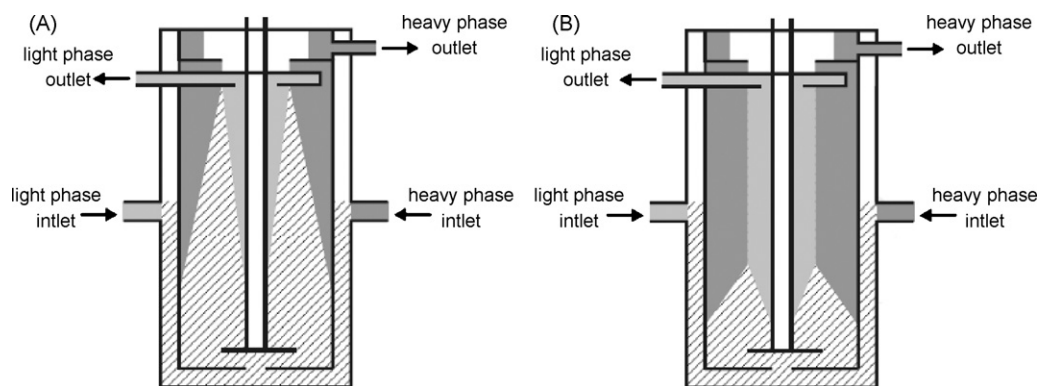


Fig. 8. Cross-sectional view of the CCS at low (A) and high rotor speeds (B). Hatched: dispersed zone, light grey: lighter phase, and darker grey: heavier phase.

3.6. FAME synthesis at optimum settings

With the effects of the most important process variables on the FAME yield established, experiments at optimum settings were performed ($N=30$ Hz, catalyst load of 1% (w/w), jacket temperature 75°C , flow of the oil and of the methanol/methoxide feed of 12.6 and 3.15 mL min^{-1} , respectively). The results for two duplicate runs are shown in Fig. 9.

After about 30 min, steady-state is reached and the FAME yield was on average 96%. Reproducibility is good, see Fig. 9 for details.

3.7. Volumetric production rate in the CCS

The volumetric production rate of FAME production in the CINC V02 at optimized settings were calculated to be $61\text{ kg}_{\text{FAME}}\text{ m}^{-3}_{\text{liquid}}\text{ min}^{-1}$. This corresponds with an annual production rate of about 5.6 ton/year. The largest CCS of the CINC type available is the CINC V20 with a maximum flow through put of 757 L min^{-1} . When assuming that the same volumetric production rate can be achieved in this CCS and taking a volumetric ratio of both devices of about 400, the productivity in the large CINC V20 is estimated to be about 2.2 kton/year.

It is of interest to compare the volumetric production rate in the CINC V02 with that for a typical batch process. Literature data imply that 98% yield is typically obtained in 20 min reaction time [45]. This corresponds with a productivity of about $40\text{ kg}_{\text{FAME}}\text{ m}^{-3}_{\text{liquid}}\text{ min}^{-1}$.

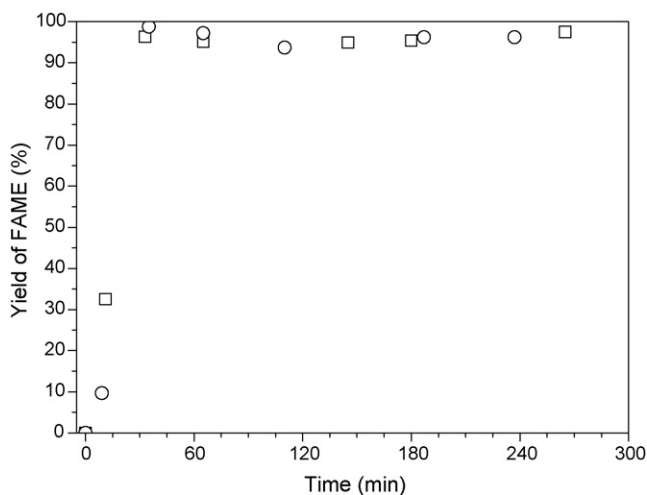


Fig. 9. The yield of FAME in time, duplicate run. ($N=30$ Hz, catalyst load of 1% (w/w), jacket temperature 75°C , flow of the oil and of the methanol/methoxide feed of 12.6 and 3.15 mL min^{-1} , respectively (6:1 molar ratio of methanol to oil), yield is the average steady-state yield for at least 2 h runtime.)

Thus, it appears that the productivity in the CINC V02 is at least comparable and likely higher than state of the art batch processes.

However, compared to batch the CCS has other advantages, the main being that a liquid–liquid separator after reaction is not required as this function is already integrated in the CCS. From the literature [46] it is known that it may take up to 2 h to obtain complete phase separation. Furthermore, the obvious advantages of continuous processes compared to batch are also valid in this case (e.g. product consistency and operator effort).

4. Conclusions and outlook

In this study, the proof of principle for the continuous biodiesel manufacture in a highly integrated CCS of the type CINC V02 is provided. As such, it demonstrates the potential of CCS equipment to be used for combined reactions and separation for biphasic (catalytic) systems. At optimum conditions a reproducible FAME yield of 96% was achieved. The volumetric production rates are at least comparable to state of the art batch processes. Further improvements are likely by hardware modifications, and particularly by modifications of the annular zone to allow for higher flow rates while maintaining a high conversion level. These studies as well as reactor engineering studies including detailed kinetics and hydrodynamics features are in progress at the moment.

Due to the compact size and flexibility in operation, the CCS equipment is likely very suitable for biodiesel production in mobile units in developing countries. A cascade of two CINC's in series, one for biodiesel production and one for a subsequent aqueous wash to remove remaining glycerol and catalyst, followed by a methanol stripper, may be a very attractive process option for further exploration and demonstration.

References

- [1] New Energy Policy for Europe, European Commission, 2007.
- [2] Ethanol 2020: A Global Market Survey, Next-Generation Trends, and Forecasts, 2008.
- [3] Biodiesel 2020: A Global Market Survey, Feedstock Trends, and Forecasts, 2008.
- [4] F. Kay-Prolea, Biofuels barometer, *Le Journal des Energies Renouvelables* 179 (2007) 63–75.
- [5] M. Balat, Production of biodiesel from vegetable oils: a survey, *Energy Sources Part A: Recov. Utilization Environ. Effects* 29 (2007) 895–913.
- [6] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Possible methods for biodiesel production, *Renew. Sust. Energy Rev.* 11 (2007) 1300–1311.
- [7] H. Sanli, A. Canakci, Effects of different alcohol and catalyst usage on biodiesel production from different vegetable oils, *Energy Fuels* 22 (2008) 2713–2719.
- [8] G. Knothe, J.H. Van Gerpen, J. Krahl, *The Biodiesel Handbook*, AOCS Press, Champaign, IL, 2005.
- [9] A. Singh, B. He, J. Thompson, J. van Gerpen, Process optimization of biodiesel production using alkaline catalysts, *Appl. Eng. Agric.* 22 (2006) 597–600.
- [10] F.R. Ma, M.A. Hanna, Biodiesel production: a review, *Bioresour. Technol.* 70 (1999) 1–15.
- [11] A.A. Kiss, F. Omota, A.C. Dimian, G. Rothenberg, The heterogeneous advantage: biodiesel by catalytic reactive distillation, *Top. Catal.* 40 (2006) 141–150.

- [12] J. van Gerpen, Biodiesel processing and production, *Fuel Process. Technol.* 86 (2005) 1097–1107.
- [13] G. Vicente, M. Martinez, J. Aracil, Integrated biodiesel production: a comparison of different homogeneous catalysts systems, *Bioresour. Technol.* 92 (2004) 297–305.
- [14] C.C. Akoh, S.W. Chang, G.C. Lee, J.F. Shaw, Enzymatic approach to biodiesel production, *J. Agric. Food Chem.* 55 (2007) 8995–9005.
- [15] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, Heterogeneous catalysts for biodiesel production, *Energy Fuels* 22 (2008) 207–217.
- [16] S. Di Bonaventura, Process and Reactor for Production of Biodiesel, 2008, 2007-BR173.
- [17] M.A. Dube, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor, *Bioresour. Technol.* 98 (2006) 639–647.
- [18] S. Hama, H. Yamaji, T. Fukumizu, T. Numata, S. Tamalampudi, A. Kondo, H. Noda, H. Fukuda, Biodiesel-fuel production in a packed-bed reactor using lipase-producing *Rhizopus oryzae* cells immobilized within biomass support particles, *Biochem. Eng. J.* 34 (2007) 273–278.
- [19] A.P. Harvey, M.R. Mackley, T. Seliger, Process intensification of biodiesel production by using a continuous oscillatory flow reactor, *J. Chem. Technol. Biotechnol.* 78 (2003) 338–341.
- [20] J.C. Thompson, B.B. He, Biodiesel production using static mixers, *Trans. ASABE* 50 (2007) 161–165.
- [21] P. Zhang, B. Wen, Microreactor technology for biodiesel production, in: Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6–10, 2008, IEC-097.
- [22] J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, Biodiesel Production Technology, 2004, NREL/SR-510-36244.
- [23] D.H. Meikrantz, L.L. Macaluso, H.W. Sams, C.H. Schardin, A.G. Federici, Centrifugal separator, 08/779,592 (1998).
- [24] A. Stanckiewicz, J.A. Mouljijn, Re-engineering the Chemical Processing Plant; Process Intensification, Marcel Dekker, Inc., New York, 2004.
- [25] B.P. Mason, K.E. Price, J.L. Steinbacher, A.R. Bogdan, D.T. McQuade, Greener approaches to organic synthesis using microreactor technology, *Chem. Rev.* 107 (2007) 2300–2318.
- [26] G. Bernstein, D. Grosveno, J.F. Lenc, N.M. Levitz, High-capacity annular centrifugal contactor, *Nucl. Technol.* 20 (1973) 200–202.
- [27] K.T. Klasson, P.A. Taylor, J.F. Walker, S.A. Jones, R.L. Cummins, S.A. Richardson, Modification of a centrifugal separator for in-well oil–water separation, *Sep. Sci. Technol.* 40 (2005) 453–462.
- [28] A. Jha, Is it true Kevin Costner is helping to clean up oil spills, *Guardian* (2003), <http://www.guardian.co.uk/film/2003/jul/31/science.features>.
- [29] J.Z. Zhou, W.H. Duan, X.Z. Zhou, C.Q. Zhang, Extraction of hydrocortisone from the fermentation liquor with annular centrifugal contactors, *Sep. Sci. Technol.* 41 (2006) 573–581.
- [30] J.F. Birdwell, J. McFarlane, R.D. Hunt, H. Luo, D.W. DePaoli, D.L. Schuh, S. Dai, Separation of ionic liquid dispersions in centrifugal solvent extraction contactors, *Sep. Sci. Technol.* 41 (2006) 2205–2223.
- [31] J.Q. Xu, W.H. Duan, X.Z. Zhou, J.Z. Zhou, Extraction of phenol in wastewater with annular centrifugal contactors, *J. Hazard. Mater.* 131 (2006) 98–102.
- [32] J. Zhou, W. Duan, X. Zhou, C. Zhang, Application of annular centrifugal contactors in the extraction flowsheet for producing high purity yttrium, *Hydrometallurgy* 85 (2007) 154–162.
- [33] J.Q. Zhu, J. Chen, C.Y. Li, W.Y. Fei, Centrifugal extraction for separation of ethylbenzene and octane using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid as extractant, *Sep. Purif. Technol.* 56 (2007) 237–240.
- [34] B. Schuur, J. Floure, A.J. Hallett, J.G.M. Winkelman, J.G. de Vries, H.J. Heeres, Continuous chiral separation of amino acid derivatives by enantioselective liquid–liquid extraction in centrifugal contactor separators, *Org. Process Res. Dev.* 12 (2008) 950–955.
- [35] G.N. Kraai, F. van Zwol, B. Schuur, H.J. Heeres, J.G. de Vries, Two-phase (bio)catalytic reactions in a table-top centrifugal contact separator, *Angew. Chem. Int. Ed.* 47 (2008) 3905–3908.
- [36] L.C. Meher, D.V. Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, *Renew. Sust. Energy Rev.* 10 (2006) 248–268.
- [37] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable-oils, *J. Am. Oil Chem. Soc.* 61 (1984) 1638–1643.
- [38] B. Schuur, W.J. Jansma, J.G.M. Winkelman, H.J. Heeres, Determination of the interfacial area of a continuous integrated mixer/separator (CINC) using a chemical reaction method, *Chem. Eng. Process.* 47 (2008) 1484–1491.
- [39] B. Schuur, G.N. Kraai, J.G.M. Winkelman, H.J. Heeres, Hydrodynamic studies in a centrifugal contactor separator; liquid hold-up, residence time distribution, phase behavior and drop size distribution, *Chem. Eng. Process.*, submitted for publication.
- [40] R. Clift, J.R. Grace, M.E. Weber, Bubbles, Drops and Particles, Academic Press, London, 1978.
- [41] E.E. Michaelides, Particles, Bubbles & Drops: Their Motion, Heat and Mass Transfer, World Scientific, New Jersey, 2006.
- [42] J.D. Thornton, Science and Practice of Liquid–Liquid Extraction, Clarendon Press, Oxford, 1992.
- [43] K.R. Westerterp, W.P.M. van Swaaij, A.A.C.M. Beenackers, Chemical Reactor Designing and Operation, John Wiley & Sons, New York, 1984.
- [44] R.H. Perry, D.W. Green, J.O. Maloney, Perry's Chemical Engineers' Handbook, McGraw-Hill, New York, 1997.
- [45] J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, Biodiesel Prod. Technol. (2004), NREL/SR-510-36244.
- [46] A. Demirbas, Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey, *Energy Convers. Manage.* 44 (2003) 2093–2109.