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Optimization of Biodiesel Production over Chicken Eggshell-Derived CaO Catalyst in a Continuous Centrifugal Contactor Separator

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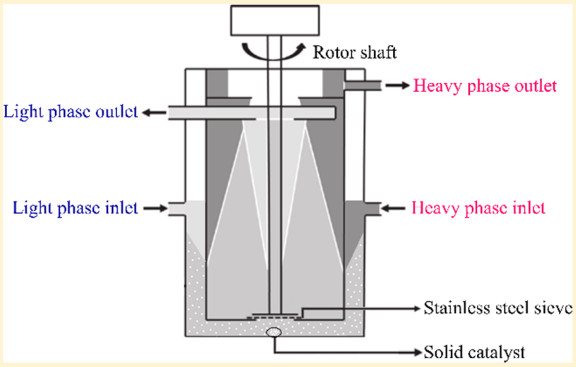
S *Supporting Information*

ABSTRACT: Solid calcium oxide (CaO) catalyst was prepared via the calcination of chicken eggshells as an environmentally friendly waste resource and incorporated in a continuous centrifugal contactor separator (CCCS) for intensified biodiesel synthesis. Biodiesel or fatty acid methyl esters (FAME) were produced via the transesterification of sunflower oil (containing 5 wt % tetrahydrofuran as a cosolvent) with methanol under 60 °C and separated from the glycerol and catalyst phases continuously in the CCCS. The influence of reaction parameters on biodiesel production was well modeled by response surface methodology. At an oil flow rate of 9 mL/min, an alcohol to oil molar ratio of 11:1, and a weight hourly space time (defined as the catalyst weight over the oil mass flow rate) of 0.050 h, an optimized FAME yield of 83.2% with a productivity of 638 $kg_{FAME}/(m^3_{reactor}\cdot h)$ was achieved. CaO catalyst was reused without significant activity loss for at least four cycles.



1. INTRODUCTION

Limited oil reserves and its unbalanced distribution across countries, along with the environmental detriments derived from the heavy use of fossil fuels, are some key issues to be well addressed within the context of societal and environmental challenges. Intensive research has thus focused on the development of alternative fuels to surmount these issues.[1−3] In this regard, biodiesel (typically fatty acid methyl esters) has been identified as a suitable renewable fuel with superior properties in comparison with diesel no. 2. Transesterification is the common route for producing biodiesel from different sources of triglycerides (e.g., vegetable oils, animal fats, and extracted oil from microalgae).

Different types of homogeneous and heterogeneous catalysts have been used in the transesterification reaction for biodiesel production, the former being more dominant. Although homogeneously catalyzed reactions (e.g., using mainly alkali and acid catalysts) take place faster under moderate reaction conditions compared with heterogeneously catalyzed ones,[4] a number of drawbacks are present. A high level of free fatty acid usually present in animal fats or waste cooking oils can be converted to soap via reaction with homogeneous alkali catalyst through the saponification reaction. This side reaction not only consumes the catalyst leading to a potential reduction of the biodiesel yield but also renders difficulties when it comes to the separation and purification process.[5] In addition, the application of homogeneous acid catalysts in the transesterification reaction faces some technical disadvantages (e.g., relatively slow reaction rate, equipment corrosion, requiring multiple downstream purification steps).[6−8] The above-mentioned pitfalls with homogeneous catalysts can be mitigated via a switch to the use of heterogeneous catalysts in biodiesel synthesis given the following advantages:

- It is possible to recover solid catalysts in a facile way and to reuse them. They can be used frequently in production cycles with a constant catalytic activity and can potentially reduce the biodiesel production cost.[9,10]
- The use of solid catalysts simplifies the purification process, leading to reduced energy consumption and waste minimization (e.g., by avoiding the homogeneous catalyst neutralization step and thus reducing wastewater generation).[11]

Different waste resources such as bones, ashes, rocks, and shells can be used to prepare solid base catalysts,[4,12] which add to the environmental benefits of the process. Recently, the use of natural calcium resources derived from waste biomass to produce calcium oxide (CaO) catalyst as a typical solid base

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catalyst for biodiesel synthesis has received increasing attention.[13,14] Due to its large availability, cost effectiveness, sustainability, environmentally friendiness, and being biobased resource, eggshell (consisting of more than 95% calcium carbonate, $CaCO_3$) represents a good and natural waste biomass resource to produce CaO upon calcination under high temperatures.[15] Several studies have reported that the use of CaO catalyst (derived from chicken eggshell, quail eggshell, snail shell and kaolin, shrimp shell, crab shell, oyster, mussel, clam and scallop shell, wing shell, abalone shell, and palm kernel shell) can provide a cheap way for catalyst preparation and a good catalytic activity for biodiesel synthesis, together with the additional benefit of turning waste into useful resources.[4,12−24]

Biodiesel synthesis is a typical multiphase reaction (e.g., oil and alcohol feedstocks present in different phases). Therefore, large liquid−liquid interfacial area and high mass transfer rates are preferable for an enhanced reaction efficiency at reduced reaction time, which has been addressed recently via process intensification. Although there are many reports regarding biodiesel production over solid catalysts derived from eggshells in the conventional batch or continuous stirred tank reactors,[4,16,17] fewer studies dealt with the intensification of biodiesel synthesis over heterogeneous catalysts. Typically, several process intensification methods such as ultrasonic and microwave-assisted synthesis have been investigated for biodiesel production using eggshell-derived CaO catalyst, where a better product yield than that in the conventional reactors was obtained at a shorter reaction time.[13,25] However, due to the issues remaining with these techniques such as the difficulties in scale-up and continuous flow processing, more research has yet to be performed in this field especially with the development of new process intensification methods.[13,25]

The continuous centrifugal contactor separator (CCCS) is viewed as an attractive process intensification method. The CCCS basically consists of an outer static housing and an inner rotating centrifuge, which features the use of centrifugal field to enhance mixing/reaction (in an annular zone between the static housing and the centrifuge) and separation (in the centrifuge) within a single device in a continuous flow fashion (Figure 1).[26−37] The CCCS was initially used to clean wastewater in the nuclear industry.[28] Later, its extended uses included oil−water separation[29] and liquid−liquid extraction.[30−33] The advantages of using the CCCS over conventional reactors for biodiesel production mainly include the following:

(i) The crude fatty acid methyl/ethyl esters (FAME/FAEE) can be in situ separated from the glycerol layer under the action of centrifugal forces rather than in a separate separation vessel, reducing processing steps and therefore equipment cost.

(ii) The reaction efficiency can be significantly increased due to the enhanced mass transfer rate in the annular mixing zone in the presence of a strong shear force exerted on fluids by the rotating centrifuge.[31]

Some studies have been carried out on biodiesel synthesis using the CCCS in the presence of homogeneous catalysts in the previous work of our group.[34−37] A CCCS was employed to run the transesterification of sunflower oil with methanol using sodium methoxide catalyst. An optimized FAME yield of 96% was achieved at a flow rate of sunflower oil at 12.6 mL/min and a flow rate of methanol (containing 1 wt % catalyst with respect to the oil) at 3.15 mL/min. A jacket temperature of 75 °C and a rotational frequency of 30 Hz were applied. The FAME productivity under the optimal conditions was 61 $kg_{FAME}/(m^3{}_{liquid}\cdot min)$ and was slightly higher than that obtained for a conventional batch process.[34] To increase the residence time needed for a better reaction or productivity, a modified CCCS having a larger annular zone than the standard one has been used for FAME synthesis over the same feedstock and catalyst system described above. At an oil flow rate of 31 mL/min, a methanol flow rate of 10 mL/min, a catalyst concentration of 1.2 wt %, and a rotational speed of 34 Hz, a FAME yield of 94% could be achieved at a productivity of 2470 $kg_{FAME}/(m^3{}_{reactor}\cdot h)$.[35] Moreover, ethanolysis of *Jatropha curcas* L. oil as an inedible feedstock in a CCCS was examined using sodium ethoxide as the homogeneous catalyst. A maximum FAEE yield of 98% was obtained at 60 °C reaction temperature, 35 Hz rotational frequency, 1 wt % catalyst concentration, and an oil feed rate of 28 mL/min.[36] Very recently, the CCCS was investigated to perform biodiesel synthesis over an enzyme (TransZyme A) immobilized on hard shell beads that was present in the annular zone of the device.[37] An average FAME yield of 72% was obtained at an oil flow rate of 1.8 mL/min, a flow rate of methanol−buffer mixture (60 wt % methanol) of 0.6 mL/min, and 30 °C. Higher FAME yields (e.g., 86%) could be further obtained in a cascade consisting of a continuously stirred tank reactor and a CCCS device in series.[37]

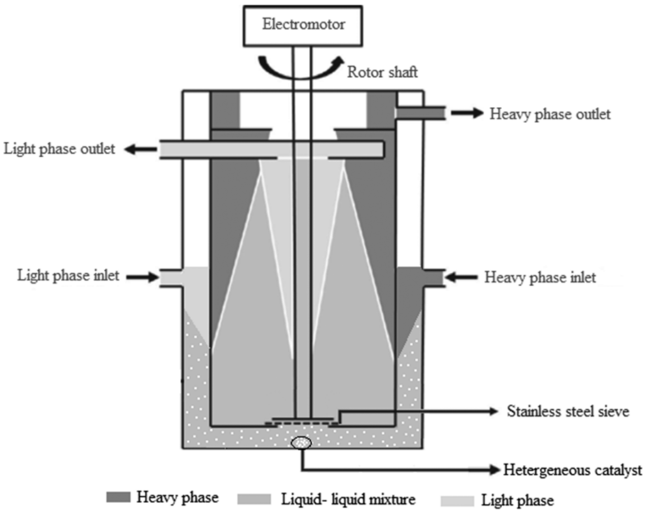

Figure 1. Schematic representation of the continuous centrifugal contactor separator for use in heterogeneously catalyzed liquid−liquid reaction. Adapted from the work of Ilmi et al.[37] (http://dx.doi.org/10.1016/j.cej.2017.03.070), used under Creative Commons Attribution 4.0 (CC BY 4.0).

In summary, although there have been various studies concerning biodiesel production using different feedstocks and catalyst systems, no study has presented the use of recyclable and stable heterogeneous catalysts derived from natural waste resources in the CCCS. Thus, the present study intends to examine the use of chicken eggshells as a waste resource for the preparation of solid CaO catalyst and its incorporation into the CCCS with the aim to determine its efficient catalysis in biodiesel synthesis. The structure, morphology, thermal stability, and crystallinity of the prepared CaO catalyst were characterized. The potential of the CCCS for the enhanced biodiesel production via the transesterification of sunflower oil

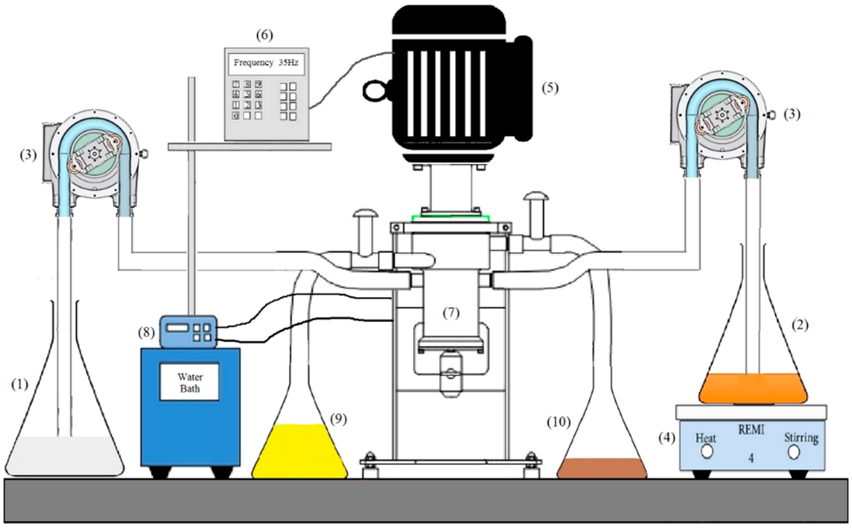

Figure 2. Schematic of the experimental setup: (1) methanol, (2) sunflower oil, (3) peristaltic pump, (4) heater-stirrer, (5) electromotor, (6) inverter, (7) CCCS, (8) heating circulator, (9) crude biodiesel, (10) crude glycerol.

with methanol (with tetrahydrofuran as a cosolvent) over this catalyst was investigated via a comparison with the batch reactor study. Statistical analysis based on response surface methodology (RSM) was performed to model the biodiesel or FAME yield in relation to several important operating parameters. The optimized results by RSM were further verified by the additional experiments. The recyclability of CaO catalyst and the contribution of homogeneous catalysis due to possible catalyst leaching were also addressed.

2. MATERIALS AND METHODS

2.1. Raw Materials. Chicken eggshells were obtained from the local company (Vogel-Bio, The Netherlands). Sunflower oil was purchased from Jumbo supermarket (The Netherlands). Methanol (anhydrous, 99.8%), tetrahydrofuran (pro anlayse), and $CDCl_3$ (99.8 atom % D) were obtained from Macron Company, Boom B.V., and Sigma-Aldrich, respectively.

2.2. Catalyst Preparation. The provided chicken eggshells were in the crushed form for the general usage. First, the eggshells were washed with distilled water to remove all the soluble impurities. Then, the cleaned eggshells were dried overnight in an oven at 100 °C to remove the excess water, followed by crushing using mechanical grinder to obtain the fine powder. The fine powder was further sieved using sieve meshes to obtain a particle size between 0.3 and 0.5 mm. Thus obtained fine powder was calcined in a muffle furnace at 900 °C for 3 h to convert $CaCO_3$ into CaO and to burn off organic residues. To avoid the contamination of the active CaO catalyst by atmospheric water moisture and carbon dioxide to form much less active hydrates and inactive carbonate,[38] the calcined samples were taken out of the furnace before its temperature dropped to room temperature and then kept in a sealed glass desiccator.[39,40]

2.3. Catalyst Characterization. The surface structure and morphology of the prepared catalysts were characterized under a scanning electron microscope (SEM) using a Philips ESEM-XL30. Micrographs were recorded at 10 nm magnification. Thermogravimetric analysis (TGA) was used to characterize the thermal stability of the eggshell samples by measuring changes in its physicochemical properties. The analysis was done by TGA Q50 V20.13 Build 39 with a ramp of 10 °C/min to 900 °C under 1 mL/min flow of nitrogen gas. X-ray diffraction (XRD) was used to gain information about the crystallinity of the samples, using a Bruker D8 Advance diffractometer, operating at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5544 Å). Data were collected using a coupled θ−2θ configuration in the 2θ range of 2−80° with a step size of 0.02° and a scan time of 1 s.

2.4. Catalyst Activation with Methanol. Before the prepared CaO catalyst was used for biodiesel production, it was activated with methanol under room temperature for 1 h in a vessel stirred at 650 rpm. This activation was found necessary based on the results of our prescreening experiments which clearly revealed the deficiency of the biodiesel yield for the initial a few hours when only a nonactivated catalyst was applied. This suggests that one active catalyst phase was likely calcium methoxide at least in the initial stage of reaction.[41]

2.5. Biodiesel Production in a Batch Reactor. The benchmarking experiments for biodiesel production were performed in a 250 mL double-jacket glass batch reactor equipped with a reflux condenser. The temperature of the reactor was maintained at 60 °C through a heating jacket coupled with a water circulator device. 100 g of sunflower oil (already preheated to the reaction temperature of 60 °C), 5 g of tetrahydrofuran (THF), certain amount of methanol (to keep the alcohol to oil molar ratio at 11:1), and 3.5 g of activated CaO catalyst were added into the reactor maintained at the reaction temperature. Stirring at 1000 rpm was performed using a six-blade Rushton turbine with an impeller, which was placed at 0.5 cm from the bottom of the reactor. The reaction was run up to 3 h, and samples were taken at different time intervals. The collected samples were centrifuged for 10 min in order to stop the reaction and to reach complete phase separation. The top FAME layer was then analyzed (cf. section 2.7).

Moreover, the explanatory experiments were performed to evaluate the contribution of homogeneous catalysis (e.g., in the presence of the possible catalyst leaching). Herein, the activated CaO of different weight was first removed from methanol via centrifugation. Then, the remaining liquid phase (i.e., methanol which likely contained the leached catalyst) was added into the batch reactor setup described above together with 100 g of sunflower oil. The alcohol to oil molar ratio, stirring speed, and reaction temperature were kept at 9:1, 650 rpm, and 60 °C, respectively. The sampling procedure remained the same as above.

2.6. Biodiesel Production in the CCCS. Figure 2 shows the experimental setup for biodiesel production in the stainless steel CCCS (of the type CINC V02; geometrical volume of ∼650 mL) in which the inner diameter of the static housing was enlarged from ∼6 to 10 cm in order to increase the residence time in the annular zone for a given flow rate. A standard (high mix) bottom plate with curved vanes was used, and the rotor was operated counterclockwise for all the experiments. The quality of separation between the light and heavy phases could be adjusted with the heavy phase weir size (∼23.5 mm in diameter used in this work[34]). At the bottom of the rotor, a very fine stainless steel sieve was used in order to keep the catalyst in the annular zone throughout the experiment (Figure 1). Further information on the CCCS geometry used in this work is shown in the Supporting Information (cf. Table S1), and more detailed structure of the CCCS can be found in the previous work of our group.[27,34] The setup was equipped with a heating jacket using water as the heating medium. The reaction temperature was set based on the recirculating water temperature inside the jacket, and both temperature values were found to be very close to each other (difference usually below 3 °C).

Prior to starting the experiment, the activated CaO catalyst (see section 2.4) was first separated from methanol in the batch vessel and then loaded into the annular zone of the CCCS. The feed to the CCCS consisted of methanol on the light phase inlet side and sunflower oil with 5 wt % THF (with respect to the oil) on the heavy phase inlet side, delivered using peristaltic pumps (Verder Company, model no. AHP-vl 246 for oil; Watson Marlow Company, model no. 101U/R for alcohol). THF was used here as a cosolvent to increase the solubility of reagents and thereby to improve mass transfer and reaction rates therein.[42,43] Moreover, due to the close boiling points of THF and methanol (∼2 °C difference), they can be easily recovered together via distillation.

In all experiments, the reaction temperature and rotational frequency of the rotor were kept constant at 60 °C and 35 Hz, respectively, based on the optimized conditions in the CCCS in the previous work of our group.[35,37] The oil flow rate was varied from 8 to 16 mL/min and the alcohol to oil molar ratio from 6:1 to 12:1. The weight of catalyst loaded in the annular zone ranged from 6.6 to 66.2 g. The total time to run each test was 90 min, and during each run, when both phase outlets reached steady state, samples were taken periodically from the light phase (crude biodiesel or FAME) outlet. The collected samples were centrifuged for 10 min to ensure that the reaction was stopped and subsequently analyzed (vide infra).

2.7. Analytical Methods. The biodiesel (FAME) yield was determined using ^{1}H NMR. A few aliquots of the prepared FAME samples were dissolved in $CDCl_3$ and analyzed with a 400 MHz Varian NMR (model AS400). When integrating the spectra, the ratio between the intensity of the methyl ester group of the FAME (peak at 3.6 ppm) and that of the methyl end group of the fatty acid chains present in both sunflower oil and FAME (peak at 0.88 ppm) was used to find the FAME yield (Y_{FAME}) as indicated in eq 1.[35,37]

$$Y_{\mathrm{FAME}}\ (\%) = \frac{\text{methyl ester peak area}}{\text{methyl end group peak area}} \times 100 \qquad (1)$$

2.8. Definitions. On the basis of the obtained FAME yield, the volumetric production rate of FAME (P_{FAME}) in the CCCS, defined as the amount of FAME produced per reactor volume per time, can be calculated by[34]

$$P_{\mathrm{FAME}} = \frac{3\phi_{\mathrm{v,oil}}\rho_{\mathrm{oil}}Y_{\mathrm{FAME}}\mathrm{MW}_{\mathrm{FAME}}}{V_{\mathrm{reactor}}\mathrm{MW}_{\mathrm{oil}}} \qquad (2)$$

Here, $\phi_{\mathrm{v,oil}}$ and ρ_{oil} are the volumetric flow rate and density of sunflower oil, respectively. V_{reactor} is estimated using the geometric volume of the CCCS. $\mathrm{MW}_{\mathrm{FAME}}$ and $\mathrm{MW}_{\mathrm{oil}}$ are the molecular weights of FAME and sunflower oil, respectively.

The average residence time the oil and alcohol mixture spent in the annular mixing zone of the CCCS (τ) is defined as

$$\tau = \frac{V_{\mathrm{L,annular}}}{\phi_{\mathrm{v,total}}} \qquad (3)$$

where $\phi_{\mathrm{v,total}}$ is the total flow rate of the light (i.e., methanol) and heavy (i.e., oil and THF) phases entering the CCCS. $V_{\mathrm{L,annular}}$ is the total liquid volume present in the annular zone during the reaction. $V_{\mathrm{L,annular}}$ was estimated roughly via the following procedure: When the CCCS reached the steady state, the fluid pumps were shut down and the valve on the bottom of the annular zone was opened simultaneously (the inner centrifuge being still rotating). The liquid−liquid−solid mixture was drained from the annular zone and solid catalysts were separated. The left total volume of both the light and heavy phases were measured as an approximation of $V_{\mathrm{L,annular}}$.[27] Under the current flow rate conditions ($\phi_{\mathrm{v,total}}$ ranging from ∼10.5 to 25.1 mL/min), $V_{\mathrm{L,annular}}$ was found to be around 350 mL. This is in good agreement with the previous work of our group which showed a very small influence of the flow rate of each phase on the total liquid volume in the CCCS.[27]

The weight hourly space time (WHST) is calculated based on the oil mass flow rate as

$$\mathrm{WHST} = \frac{m_{\mathrm{cat}}}{\phi_{\mathrm{m,oil}}} \qquad (4)$$

where m_{cat} is the weight of catalyst loaded in the annular zone of the CCCS in each experimental run and $\phi_{\mathrm{m,oil}}$ the mass flow rate of sunflower oil. WHST can be also understood as the reciprocal of the weight hourly space velocity.[37]

The catalyst concentration in the annular zone of the CCCS (w_{cat}) is defined as the percentage of the mass of catalyst with respect to the mass of the oil present therein and is roughly estimated from

$$w_{\mathrm{cat}}\ (\%) = \frac{m_{\mathrm{cat}}}{\rho_{\mathrm{oil}}V_{\mathrm{L,annular}}\left(\frac{\phi_{\mathrm{v,oil}}}{\phi_{\mathrm{v,total}}}\right)} \times 100 \qquad (5)$$

Equation 5 is based on the simple assumption that the oil phase fraction in the reaction mixture present in the annular zone is equal to its volumetric flow rate percentage in the mixture, which has to be further examined in the future hydrodynamic study.

2.9. Statistical Analysis. RSM is a powerful technique for the statistical analysis and mathematical modeling in order to optimize the process conditions based on the minimized number of experiments. The present work has followed RSM and Box−Behnken design method to conduct the statistical analysis in order to find the values of independent parameters for an optimized biodiesel yield.[44,45] Nonlinear multivariable regression was used to model the experimental data, and for this purpose the Design-Expert software (version 7.0.0, Stat-Ease Company) based on eq 6 was used.

$$y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} {x_i}^2 + \sum_{i=1}^{2} \sum_{i<j=1}^{3} b_{ij} x_i x_j + e \qquad (6)$$

where y is a dependent variable (in this work being the FAME yield and volumetric production rate of FAME). x_i and x_j are the independent variables, including the oil flow rate, alcohol to oil molar ratio, and weight hourly space time (used as a variable to indicate the influence of the catalyst weight). It can be easily seen that the higher the weight hourly space time, the greater is the amount of catalyst available for the reaction. b_0, b_i, b_{ii}, and b_{ij} are the regression coefficients of the model, whereas e is the model error. Table 1 represents the levels of the independent variables that were determined based on the literature[4,34,35] and our experimental results in the CCCS. Finally, the modeled optimum conditions for biodiesel synthesis in the CCCS were determined using the numerical optimization function provided in the software package.

Table 1. Coded and Actual Values of the Variables Used in the Experimental Design

		coded variable levels		
independent variable	unit	1	0	−1
oil flow rate ($\phi_{\mathrm{v,oil}}$)	mL/min	16	12	8
alcohol to oil molar ratio (M)		12:1	9:1	6:1
weight hourly space time (WHST)	h	0.075	0.045	0.015

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. *3.1.1. XRD Analysis.* The analysis of XRD pattern (Figure 3) proved that CaO species were the major component of the calcined chicken eggshells. The peaks observed therein at 2θ = 32.3°, 37.4°, 53.9°, 64.2°, and 67.4° correspond to the standard XRD pattern of CaO.[25] It is worth noting that the peak related to $CaCO_3$ (at 2θ = 29.7°) as observed in the natural chicken eggshells was absent in the calcined eggshells. Moreover, $CaCO_3$ was identified as inactive during triglyceride transesterification.[38] Also, the XRD pattern confirms that less active $Ca(OH)_2$, which could be typically observed at 2θ = 45−50° in the natural eggshell pattern, was not present in the calcined eggshells.[38,46]

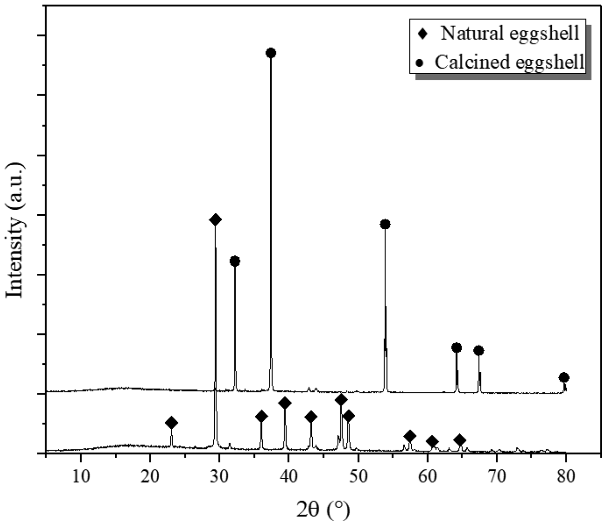

Figure 3. XRD patterns of the natural and calcined chicken eggshells.

3.1.2. SEM Analysis. The natural and calcined chicken eggshells were compared in terms of the surface morphology by SEM measurements (Figure 4). The analysis of SEM images revealed that particles at various sizes (1−10 μm) were included in the calcined chicken eggshells. Although irregular-shaped particles were mainly present in the natural eggshells, the calcination treatment resulted in more regularity in the particle shape, forming a termite nest-like structure (simply saying, macroporous structure). The studies undertaken by Tan et al.[4] and Khemthong et al.[13] showed similar results about the structure improvement after calcination and particle size.

3.1.3. TGA Analysis. Figure 5 illustrates the TGA results of the natural eggshells, emphasizing the first derivation of the TGA curve (DTG). The dominant decomposition with a 37.2% weight loss at around 640−740 °C was observed as a result of CaO production via the decomposition of $CaCO_3$ with the release of CO_2. Thus, a calcination temperature above 800 °C was considered sufficient for the complete decomposition of chicken eggshells to produce CaO. From the first weight loss below 400 °C on the DTG curve, it can be concluded that the physically absorbed water and the organic compounds were removed from the eggshell sample upon being heated above ∼400 °C.[19] It is worth noting that TGA analysis was performed on the fresh eggshells; thereby only small peaks related to the weight loss were seen at around 450−500 °C, indicating the presence of a negligible amount of $Ca(OH)_2$.[17,47]

3.2. Exploratory Results on Biodiesel Production in the Batch Reactor. Exploratory experiments to assess the biodiesel production performance have been conducted in the batch reactor. Figure 6 shows that the transesterification reaction progressed slowly in the batch reactor. A FAME yield of 92% was achieved at 2.5 h reaction time, after which a slight increase to 93% was observed at 3 h. This indicates that possibly the reaction almost reached an equilibrium at 3 h, which is consistent with the literature results.[19] The batch reactor performance here is generally comparable to the existing work with the commercial CaO catalysts,[14] showing the feasibility of chicken eggshell-derived CaO catalysts for use in biodiesel synthesis. Although the operating conditions in the batch reactor (e.g., in terms of the alcohol to oil molar ratio, catalyst amount, and stirring speed) were not further optimized, the results seem to suggest the likely presence of a mass transfer resistance between the three phases (i.e., solid catalyst and oil and alcohol phases) in the batch reactor. As a result, the reaction rate could be slowed down. It has to be mentioned that the amount of THF added as a cosolvent (5 wt %, with respect to the oil) was still much lower than the amount of methanol herein. Thus, although the addition of THF increased the miscibility of the alcohol and oil phases, the reaction mixture still existed as a two-phase system instead of a miscible single-phase system.[42,43]

3.3. Experimental Results in the CCCS. The CCCS for biodiesel production was operated at a rotational frequency of 35 Hz and a reaction temperature of 60 °C. Table 2 lists all the experimental runs and the obtained results. The oil flow rate

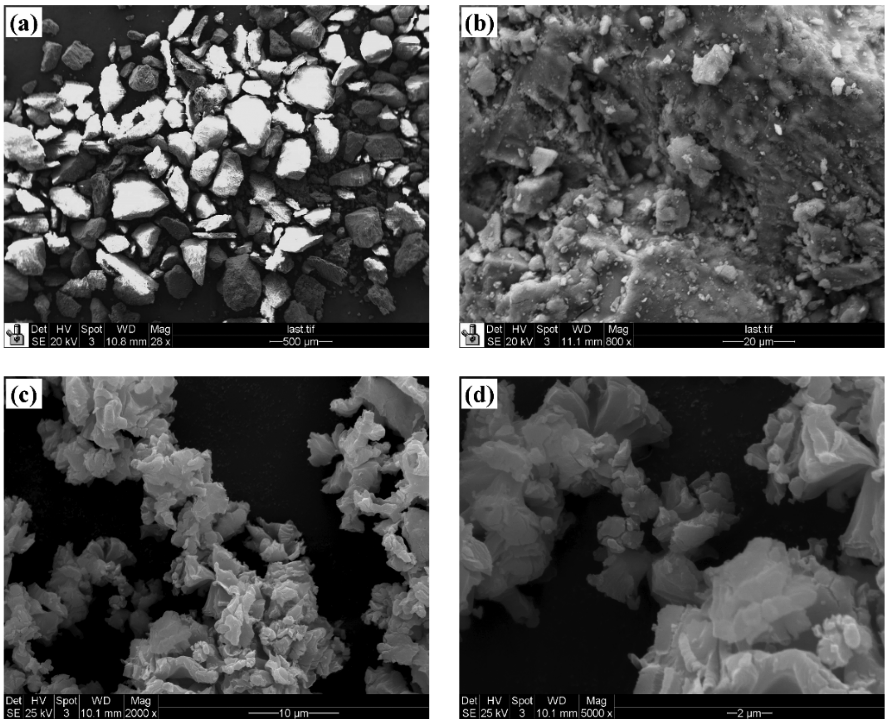

Figure 4. SEM images of the natural chicken eggshells (a, b) and the calcined chicken eggshells (c, d): (a) 28× magnification; (b) 800× magnification; (c) 2000× magnification; (d) 5000× magnification.

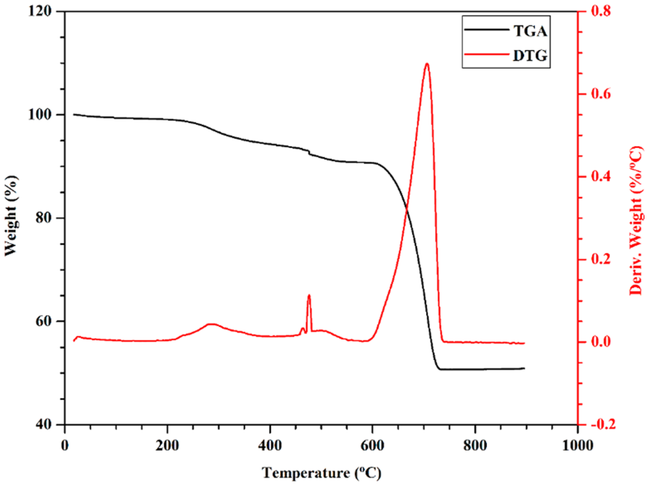

Figure 5. TGA/DTG curves of the natural chicken eggshells.

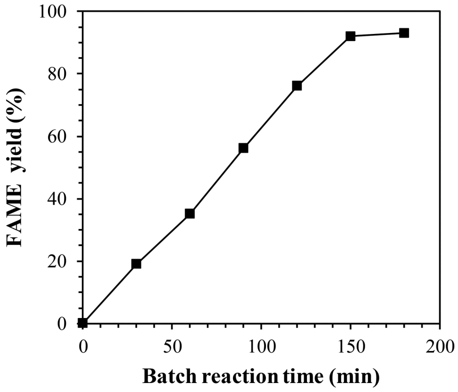

Figure 6. FAME yield versus the reaction time in the batch reactor. Operating conditions are the following: 100 g of sunflower oil, 5 g of THF, 11:1 alcohol to oil molar ratio, 3.5 g of CaO catalyst, 1000 rpm stirring speed, 60 °C.

was varied from 8 to 16 mL/min and the alcohol to oil molar ratio from 6:1 to 12:1. The weight of CaO catalyst present in the annular zone was varied from 6.6 to 66.2 g, corresponding to a WHST value (cf. eq 4) in a range from 0.015 to 0.075 h. Multiple experiments were performed, and a good reproducibility was confirmed; e.g., a very small relative standard deviation of 1.1% was found in the measured FAME yield under one typical operating condition (cf. Table 2; experimental runs 5−7, 15, and 16).

Some typical experimental data are further shown in Figure 7. For given values of WHST and alcohol to oil molar ratio, the FAME yield increased upon decreasing the oil flow rate. This is due to the increased residence time of the alcohol−oil mixture in the annular zone in which the heterogeneous reaction occurred. A higher WHST or alcohol to oil molar ratio seems to favor a higher FAME yield, indicating that adding more catalyst in the annular zone or increasing the amount of methanol in the feed might benefit the reaction. The production rate of FAME per unit weight of catalyst was found to be highest at 51.6 $kg_{FAME}/(kg_{catalyst}\cdot h)$ in the CCCS, and the corresponding FAME yield was 77% under an oil flow rate of 8 mL/min, an alcohol to oil molar ratio of 9:1, and a WHST of 0.015 h (Figure 7 and Table 2). However, the production rate of FAME per unit weight of catalyst was also found to decrease with increasing WHST in the CCCS, as can be inferred from Figure 7 that the FAME yield only increased slightly with increasing WHST for given values of the oil flow rate and alcohol to oil molar ratio. This implies that the reaction tended to be more limited by mass transfer upon increasing the catalyst loading in the CCCS. This concerns more about the liquid−solid mass transfer limitation in view of the fact that THF was added as a cosolvent to improve the

Table 2. FAME Yield and Productivity Measured in the CCCS at Different Operating Conditions

exptl run	m_{cat} (g)	$\phi_{v,oil}$[a] (mL/min)	M	WHST (h)	w_{cat}[b] (wt %)	τ (min)	Y_{FAME} (%)	P_{FAME} ($kg_{FAME}/(m^3_{reactor}\cdot h)$)
1	49.7	12	12	0.075	24.2	18.6	74	757.6
2	33.1	8	9	0.075	14.8	30.4	84	573.4
3	6.6	8	9	0.015	3	30.4	77	525.6
4	49.7	12	6	0.075	20.2	22.2	69	706.4
5	29.8	12	9	0.045	13.3	20.2	76	778.1
6	29.8	12	9	0.045	13.3	20.2	77	788.4
7	29.8	12	9	0.045	13.3	20.2	75	767.9
8	39.7	16	6	0.045	16.2	16.7	65	887.3
9	19.9	8	12	0.045	9.7	27.9	84	573.4
10	9.9	12	6	0.015	4	22.2	66	675.7
11	66.2	16	9	0.075	29.6	15.2	67	914.6
12	39.7	16	12	0.045	19.4	13.9	67	914.6
13	13.2	16	9	0.015	5.9	15.2	62	846.4
14	9.9	12	12	0.015	4.8	18.6	72	737.2
15	29.8	12	9	0.045	13.3	20.2	76	778.1
16	29.8	12	9	0.045	13.3	20.2	77	788.4
17	19.9	8	6	0.045	8.1	33.4	77	525.6

[a] In the presence of THF as a cosolvent (5 wt % with repect to the oil). [b] Estimated according to eq 5.

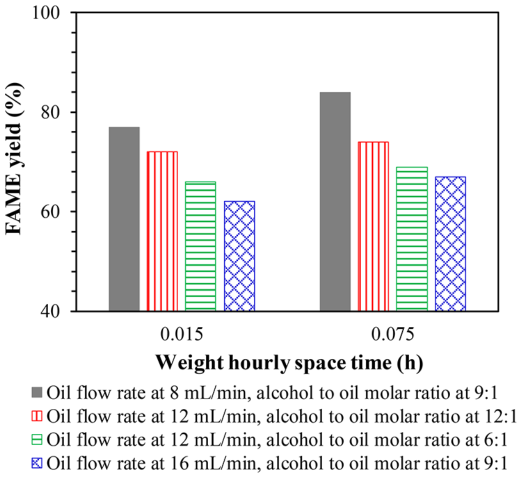

Figure 7. Typical experimental results on the FAME yield in the CCCS. Operating conditions are the following: rotational frequency of 35 Hz, 60 °C, 5 wt % THF (with respect to the oil) as a cosolvent. Other conditions are shown in the figure.

mass transfer between the immiscible alcohol and oil phases.[42,43] In-depth discussion about the precise influence of these reaction parameters will be provided in the section hereafter.

As shown in Table 2, the residence time in the annular zone of the CCCS was estimated to vary from ~13.9 to 33.4 min (cf. eq 3). The corresponding FMAE yield ranged from 62% to 84% over a catalyst concentration (w_{cat}) in a range from ~3 to 29.6 wt % (i.e., with respect to the oil; cf. eq 5). This seems to suggest that biodiesel production over the prepared CaO catalyst was more efficient in the CCCS compared with the laboratory batch reactor used in this study. To further support this suggestion, the FAME yield in both devices was compared under similar conditions. In the batch reactor, 3.5 wt % catalyst (with respect to the oil) was used, where a FAME yield of 76% was obtained at 120 min at an alcohol to oil molar ratio of 11:1 (Figure 6). A better performance was achieved in the CCCS in which a FAME yield of 77% was obtained at a residence time of ~30.4 min, an alcohol to oil molar ratio of 9:1, and a catalyst concentration of ~3 wt % (Table 2, experimental run 3). This implies an improved reactant mixing or reactant−catalyst contact in the CCCS compared with the batch process. However, it should be noted that an underestimation of the catalyst concentration using eq 5 is also possible, due to a lack of the exact knowledge of the actual oil phase fraction in the annular zone. Thus, the reaction rate enhancement in the CCCS might be also partly due to the higher catalyst concentration therein. Given the limited residence time in the CCCS, the catalyst concentration tested therein was generally higher (up to 29.6 wt % according to eq 5) than that in the batch process in order to reach a favorable FAME yield. Thus, a further optimization using RSM is also necessary to well address a better catalyst usage in the CCCS.

On the basis of the data in Table 2, the volumetric production rate of FAME in the CCCS was estimated according to eq 2 to range from 525.6 to 914.6 $kg_{FAME}/(m^3_{reatcor}\cdot h)$. For the batch process shown in Figure 6, the volumetric production rate of FAME (i.e., the weight of FAME produced per unit of reaction time divided by the entire volume of the batch reactor) was estimated to be on the order of 100−200 $kg_{FAME}/(m^3_{reatcor}\cdot h)$. Thus, the productivity in the CCCS appears to be higher than the studied batch process or at least comparable if one considers that the catalyst concentration in the batch reactor could be still increased to enhance the productivity. However, the CCCS presents the clear advantages in the continuous reaction and phase separation within one device.

3.4. Statistical Analysis for Modeling and Optimizing Biodiesel Production in the CCCS.

3.4.1. Regression Model. The RSM technique was used for a statistical analysis of the CCCS performance in order to investigate the relationship between the FAME yield and reaction parameters and to identify the operating conditions for an optimized biodiesel yield. The experimental data given in Table 2 were used as input for the development of a multivariable nonlinear regression model for both the FAME yield and its volumetric production rate. On the basis of the results derived from the statistical analysis of variance, the quadratic model was chosen as the proper model. The model p-value of <0.0001 implies that the model is significant at 99% probability level (i.e., only a 0.01% chance occurring due to noise). In this case, the oil

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flow rate ($\phi_{\mathrm{v,oil}}$), alcohol to oil molar ratio (M), weight hourly space time (WHST), M^2, WHST^2, and $\phi_{\mathrm{v,oil}} \times M$ were found as the significant model terms, given their p-values being less than 0.1000. p-values greater than 0.1000 indicate that the model terms are not significant. In order to exclude insignificant parameters, the backward elimination analysis was done. The final results of the statistical anlysis of the effective parameters are shown in Table 3.

Table 3. Analysis of Variance for Coefficients of the Model

source	sum of squares	df	mean square	F	P
model	638.74	6	106.46	86.44	<0.0001
oil flow rate ($\phi_{\mathrm{v,oil}}$)	465.12	1	465.12	377.67	<0.0001
alcohol to oil molar ratio (M)	50.00	1	50.00	40.60	<0.0001
weight hourly space time (WHST)	36.12	1	36.13	29.33	0.0003
$\phi_{\mathrm{v,oil}} \times M$	6.25	1	6.25	5.07	0.0480
M^2	28.95	1	28.95	23.50	0.0007
WHST^2	47.91	1	47.91	38.90	<0.0001
residual	12.32	10	1.23		
lack of fit	9.52	6	1.59	2.27	0.2241
pure error	2.80	4	0.70		
cor total	651.06	16			

Equation 7 shows the predicted regression equation based on the experimental data and the selected (quadratic) model in the RSM.

$$Y_{\mathrm{FAME}}\ (\%) = 45.85 - 0.97\phi_{\mathrm{v,oil}} + 7.32M + 407.68\,\mathrm{WHST} - 0.1\phi_{\mathrm{v,oil}}M - 0.29M^2 - 3742.69\,\mathrm{WHST}^2 \qquad (7)$$

In this equation, Y_{FAME} is in %, $\phi_{\mathrm{v,oil}}$ in mL/min, and WHST in h. The algebraic sign (i.e., + or −) indicates the increase or decrease of the FAME yield in relation to each independent variable. This equation is valid within the operating window of the current experiments (i.e., between variable levels +1 and −1 as indicated in Table 1). In addition, the model has emphasized the importance of the independent variables with regard to the FAME yield in the order of oil flow rate > alcohol to oil molar ratio > weight hourly space time. Figure 8 presents a good agreement between the modeled FAME yield (eq 7) and the measured value in the experiments (with a relative standard deviation of 1.2%), which corroborates the accuracy of the proposed regression model and further allows the use of model predictions for a more precise elucidation of the relationship between the FAME yield and independent variables.

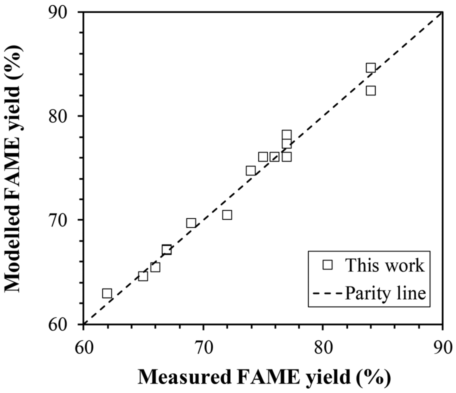

Figure 8. Measured FAME yield in the CCCS versus the model prediction by eq 7.

3.4.2. Effect of the Independent Variables on the Biodiesel Yield.

Figure 9 shows the surface plots and contour plots for the effect of interaction between the independent variables (i.e., the oil flow rate, alcohol to oil molar ratio, and weight hourly space time) on the FAME yield. According to the RSM analysis, the quadratic coefficient of the oil flow rate ($\phi_{\mathrm{v,oil}}{}^2$) was not significant in the proposed model (Table 3). Thus, a linear change exists regarding the FAME yield in relation to the oil flow rate (eq 7). As can be seen in Figure 9a and Figure 9b, the FAME yield was found to decrease linearly upon increasing the oil flow rate for given values of the alcohol to oil molar ratio and weight hourly space time. For example, at a weight hourly space time of 0.045 h and an alcohol to oil molar ratio of 9:1, an increase of the oil flow rate from 8 to 12 mL/min or from 12 to 16 mL/min could result in a decrease of the FAME yield by ~7.6%. The decreased FAME yield as a result of the increased flow rate of the oil (or equivalently, total flow rate of the oil and alcohol phases) can be attributed to the decreased mean residence time in the annular zone of the CCCS (cf. eq 3). Under the current experimental conditions, the total liquid volume present in the annular zone was found to be almost independent of the flow rate.[27] Thus, the flow rate increase resulted in a decreased effective time for the contact of oil with alcohol and catalyst, causing lower reaction yields. Kraai et al.[34] reported similar results for the effect of flow rate on the biodiesel yield.

In the regression model, the alcohol to oil molar ratio (M), its interaction with the oil flow rate ($\phi_{\mathrm{v,oil}} \times M$), and M^2 were found as the significant model terms (Table 3), where the first term has a positive impact on the FAME yield and the last two terms have a negative impact (eq 7) along with a quadratic change regarding the FAME yield in relation to M. As a result, for given values of the oil flow rate and weight hourly space time, the FAME yield would increase first with the alcohol to oil molar ratio and then tend to decrease after reaching its maximum. For example, Figure 9a and Figure 9c show that at an oil flow rate of 12 mL/min and a weight hourly space time of 0.045 h, an increase of the alcohol to oil molar ratio from 6:1 all the way to 12:1 caused the FAME yield to first increase from 70.9% to a maximum value of 76.6% at M = 10.4 and then to decrease slightly to 75.9% at M = 12 (a similar trend was found for other oil flow rate conditions). The observed initial increase of the FAME yield with increasing alcohol to oil molar ratio could be attributed to the faster transesterification reaction rate (e.g., higher molar ratios increased the methanol−oil miscibility and contact and shifted the equilibrium reaction direction more toward the FAME product side). It has been reported that increasing the alcohol to oil molar ratio above the stoichiometric ratio (3:1) improved the reaction progress.[48,49] The existence of an optimal alcohol to oil molar ratio for a maximum FAME yield could be first explained based on the fact that the high excess of methanol content beyond a specific limit in the reaction mixture gave rise to the dissolving of glycerol and alcohol in biodiesel. Under such circumstances, the formation of a separate glycerol phase was hindered by the increasing mutual solubility of the reactants. Without the formation of a separate glycerol phase, the reaction reached equilibrium,[50,51] leading to a yield loss. In

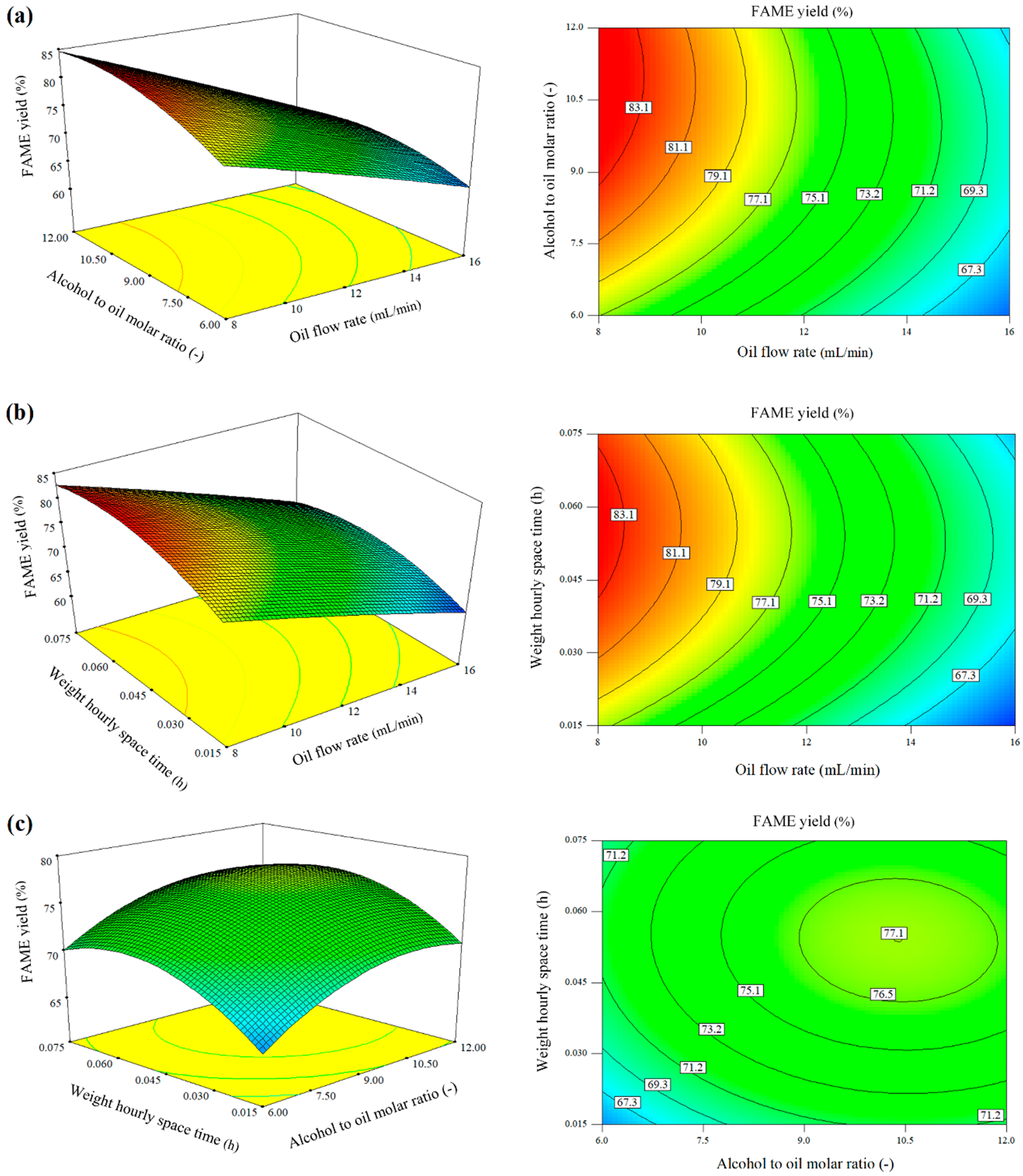

Figure 9. Surface plot and contour plot for the effect of interaction between independent variables on the FAME yield in the CCCS: (a) interaction between the oil flow rate and alcohol to oil molar ratio (the weight hourly space time being at 0.045 h); (b) interaction between the weight hourly space time and oil flow rate (the alcohol to oil molar ratio being at 9:1); (c) interaction between the weight hourly space time and alcohol to oil molar ratio (the oil flow rate being at 12 mL/min).

addition, the total flow rate of the alcohol−oil mixture increased gradually upon increasing the alcohol to oil molar ratio for a given oil flow rate. Accordingly, the mean residence time of the alcohol−oil mixture in the annular zone of the CCCS decreased (cf. eq 3), which further contributed to the FAME yield decrease.

The effect of catalyst content on the FAME yield was investigated in RSM via the weight hourly space time (WHST) as one independent variable at defined levels of 0.015, 0.045, and 0.075 h (Table 1). In the developed regression model, WHST and WHST^2 were both found as the significant model terms (Table 3), the former having a postive impact on the FAME yield and the latter having a negative impact (eq 7) along with a quadratic change regarding the FAME yield in relation to WHST. This indicates that increasing the weight hourly space time has two counterbalancing effects on the FAME yield. As revealed in Figure 9b and Figure 9c, an increase of the weight hourly space time from 0.015 to 0.045 h resulted in an increase in the FAME yield by ~5.5% for given values of the alcohol to oil molar ratio and oil flow rate. However, a maximum FAME yield was observed at a weight hourly space time of about 0.055 h, and a slight yield loss was present upon its further increase to 0.075 h. The FAME yield increase with increasing weight hourly space time could be understood by the increase of the available active catalyst sites for the reaction.[52] However, there is an optimal solid catalyst amount for biodiesel synthesis that depends on the used feedstock and applied conditions.[52−54] In the present experiments, a weight hourly space time higher than 0.055 h would lead to a FAME yield decrease. Under such conditions, the overall reaction rate might tend to be limited by liquid−liquid−solid mass transfer (or at least limited by liquid−solid mass transfer in view of the presence of THF as a cosolvent to improve liquid−liquid mass transfer). To investigate such possible mass transfer limitation, liquid−liquid−solid hydrodynamics in the annular zone needs to be made clear first, especially regarding how the presence of solid catalyst of various amount affects the alcohol−oil mixing and the reactant−catalyst contact. Due to the opaque outer housing of the CCCS (made of stainless steel), a flow pattern visualization of liquid−liquid−solid flow in the annular zone could not be performed so far and will be addressed in our future study. It is worth noting that in the stirred tank reactors, the volumetric gas−liquid or liquid−solid mass transfer coefficient has been reported first to increase with an increase of the solid or catalyst loading and then to decrease after reaching a maximum.[55,56] Thus, there might exist an optimal solid catalyst amount to ensure the desired mass transfer rate and reaction performance.

In general, Figure 9 shows that a higher FAME yield could be obtained at lower oil flow rate, and there existed the optimum values of the alcohol to oil molar ratio and weight hourly space time for a maximized FAME yield. Among the three independent variables investigated, the oil flow rate presented the most significant impact on the FAME yield and the weight hourly space time the least. Since the FAME yield was generally above 60% even at the lowest weight hourly space time (or catalyst loading) investigated, the prepared CaO catalyst was considered active enough. The results here also suggest that by a fine-tuning of the oil flow rate and alcohol to oil molar ratio, a reduced catalyst usage (e.g., for cost and environmental benefits) is also possible in order to reach the same FAME yield or productivity.

3.4.3. Effective Parameters for Biodiesel Production: The Optimization.

In order to allow a fast prediction of the maximum FAME yield and the corresponding productivity of the CCCS without doing tedious experimental screening, and thus saving experimental cost, a numerical optimization function was used to predict the optimal point based on the regression model (eq 7) with the boundary conditions illustrated in Table 4. Results of optimization showed that at the oil flow rate, alcohol to oil molar ratio, and weight hourly space time of around 9 mL/min (with additional 5 wt % THF added as a cosolvent), 11:1, and 0.050 h, respectively, the modeled FAME yield was 83.2% with a volumetric production rate of 638 $kg_{FAME}/(m^3_{reactor} \cdot h)$. These optimal operating conditions were validated by an extra experimental run in the CCCS. The difference between the optimized yield in the software and the measured value is less than 1%.

Table 4. Conditions for Biodiesel Production Optimization in the CCCS Using RSM

parameter	goal	minimum	maximum	importance
oil flow rate (mL/min)	in range	8	16	
alcohol to oil molar ratio	in range	6	12	
weight hourly space time (h)	in range	0.015	0.075	
FAME yield (%)	maximize	62	84	*****
volumetric production rate of FAME ($kg_{FAME}/(m^3_{reactor} \cdot h)$)	maximize	525.6	914.6	**

3.5. Reusability of CaO Catalyst.

Solid catalysts allow easy recovery compared with homogeneous catalysts and also need to be durable over long-term operation. To determine the reusability of the prepared CaO catalyst, the same catalyst was tested in multiple experimental runs in the CCCS. In more detail, at the end of each experiment, the reaction was stopped. Afterward, the remaining material at the bottom of the CCCS (Figure 1) that contained catalyst and the reaction mixture was collected and centrifuged. The resulting solid part was treated with methanol and THF to remove the impurities and was then dried overnight at 120 °C in the oven. The recovered catalyst was primarily activated with methanol for 1 h (cf. section 2.4) and then put again into the CCCS for the next cycle experiment. The experiments for reusability test were carried out under the optimal reaction conditions determined by the present research (cf. section 3.4.3). As Figure 10 reveals, for the first four cycles there is not an appreciable decrease of the FAME yield (remaining above 80%) if the experimental uncertainty is considered. During the fifth and sixth cycles, the biodiesel yield dropped slightly significant to less than 80%. The slight decline in the catalyst activity may be due to the formation of the inactive $CaCO_3$ and less active $Ca(OH)_2$ on the catalyst surface during the catalyst recovery from the CCCS and the subsequent drying.[38] In these steps, the hydration and especially the carbonation of CaO to some extent could have occurred since CaO was in contact with air and no further calcination at high temperatures was performed. For example, a few minutes were reported enough for CaO to chemisorb significant amounts of H_2O and CO_2 under room air.[57] Another possible reason for the catalyst activity loss is the leaching of catalyst into the reaction medium (i.e., methanol/glycerol phase and oil phase; cf. sections 3.6 and 3.7 below), which tended to gradually reduce the available solid catalyst sites over multiple tests.[47] It should be noted that some researchers have ascribed the somewhat significant activity loss of CaO (nano)catalyst in biodiesel synthesis under higher reaction temperatures than used in this work (e.g., 70 or 100 °C) to particle agglomeration as well.[38,47] Thus, the reusability

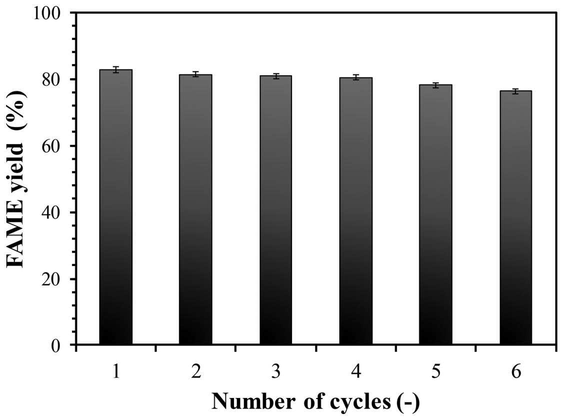

Figure 10. Reusability of eggshell-derived CaO catalysts for biodiesel production under the optimal condition in the CCCS (at the oil flow rate at 9 mL/min, alcohol to oil molar ratio at 11:1, and weight hourly space time at 0.050 h). Error bar indicates the standard deviation measured from three sample analyses in each cycle.

of CaO catalyst in biodiesel synthesis still needs to be improved in the above-mentioned various aspects, which deserves further research. Given a stable FAME yield in the CCCS for at least four cycles, the prepared CaO catalyst in this work presents at least a comparable stability with the literature results.[38,47,58,59]

3.6. Contribution of Homogeneous Catalysis. One of the main aims of the present study is to utilize CaO catalyst derived from chicken eggshells as a heterogeneous catalyst in the transesterification reaction, which requires a better understanding of the contribution of homogeneous catalysis (if present) due to the possible CaO catalyst leaching. To evaluate this contribution, the transesterification reaction was further investigated in the glass batch reactor at 60 °C in the presence of sunflower oil and methanol that has been previously used for CaO catalyst activation (cf. section 2.5). The reaction results are presented in Figure 11. The catalyst leaching and the resulted homogeneous contribution were found to exist, in view of the facts that a FAME yield of ∼10% was reached at 30 min reaction time and that the FAME yield tended to increase when the amount of CaO previously submerged in methanol (at room temperature) was increased from 1 to 3 g. No significant yield difference was found between the cases with methanol previously used for pretreating 3 and 5 g CaO catalysts, indicating that the equilibrium of catalyst dissolution was probably reached. The soluble substance that leached away from the catalyst herein could be calcium methoxide. Esipovich et al.[60] showed that the pretreatment of CaO with methanol caused the formation of calcium methoxide on the CaO surface, which reduced the induction period associated with nonpretreated CaO and thus increased significantly the catalyst activity in the transesterification reaction. Granados et al.[61] measured the solubility of CaO in methanol to be about 0.1−0.2 g/L at 25 °C. Thus, it is likely that soluble calcium methoxide was produced in methanol during the CaO catalyst activation step and therefore catalyzed the reaction homogeneously.

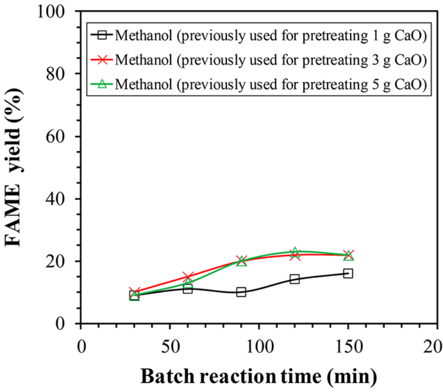

Figure 11. FAME yield in the batch reactor in the presence of only methanol (previously used for CaO catalyst activation) and sunflower oil. Operating conditions are the following: 100 g of sunflower oil, 9:1 alcohol to oil molar ratio, 650 rpm stirring speed, 60 °C. Prior to its use in the reaction test, methanol was contacted with 1−5 g of CaO catalyst for 1 h at room temperature and was centrifuged to remove the solid catalyst.

The results of Figure 11 further suggest that the contribution of homogeneous catalysis in the batch reactor was not very significant, since the FAME yield was still below 22% within 2.5 h reaction time under all these circumstances. In contrast, a much higher yield of above 90% could be achieved in the same batch reactor under similar reaction conditions over 3.5 g CaO catalyst (Figure 6). Moreover, the results of Figure 11 might not be entirely due to homogeneous catalysis because some quantity of calcium methoxide dissolved in methanol during the CaO catalyst activation at room temperature could appear as solid during reaction at 60 °C, given a somewhat significant decrease of CaO solubility in methanol with temperature increase (being around 0.03−0.04 g/L at 60 °C).[61]

When it comes to the transesterification reaction in the CCCS, the contribution of homogeneous catalysis is expected to be even less significant, due to relatively short residence time in the annular zone (approximately in a range of 13.9−33.4 min) and relatively large amount of CaO in use (catalyst weight being 6.6−66.2 g when compared with the weight of the oil present in the annular zone being roughly estimated up to 250 g).[61] Thus, the prepared CaO catalyst functioned mainly as a heterogeneous one in the current work.

It should be mentioned that as the reaction progressed in the presence of CaO catalyst, the leached species could further include calcium diglyceroxide formed via the reaction of CaO with the byproduct glycerol.[57,60−64] Calcium diglyceroxide was found to be a more soluble compound than CaO.[61] However, the homogeneous and heterogeneous catalysis nature of calcium diglyceroxide still needs to be clarified. For example, the results of Kouzu et al.[64] relating to the soybean oil transesterification suggested that calcium glyceroxide only sent out homogeneous catalysis and only acted as a precursor of the solid base catalyst, whereas in some other work calcium glyceroxide was considered as an active solid catalyst phase in biodiesel production.[60−62]

3.7. Physicochemical Properties of the Produced Biodiesel. The produced FAME is known as biodiesel when it meets the fuel standards for alternative pure and/or diesel-biodiesel blended fuel in diesel engines. Therefore, a sample of biodiesel produced in the CCCS under the optimal conditions (cf. section 3.4.3) was collected and purified with washing method using reverse osmosis water. Some important properties of thus purified biodiesel were measured based on the ASTM D6751 standard. The measured properties met the standard except the calclium content (cf. Table S2 in the Supporting Information). De Sousa et al.[62] and Kouzu et al.[65] investigated the transesterification of soybean oil and waste cooking oil, respectively, over CaO catalysts obtained from different sources. The calcium content of the prepared biodiesel in their work was reported mostly around 200 ppm, which was considered mainly due to the leaching of calcium diglyceroxide into biodiesel. Calcium leaching into biodiesel in the present study was found to be much less (at 60 ppm level), which could be due to the relatively short residence time in the annular zone of the CCCS. However, in order to have a compliant calcium content, an improvement in the biodiesel purification method is needed, e.g., by removing the calcium species from biodiesel via cation-exchange resin.[65]

3.8. Comparison of Biodiesel Production in the CCCS Using Various Catalyst Systems. A comparison has been made between the performance of the sunflower oil transesterification over the prepared CaO catalyst of the current study and that from the previous work of our group employing either homogeneous sodium methoxide or immobilized enzyme catalyst in the CCCS device (cf. Table S3 in the Supporting Information).[35,37] A FAME yield of above 70%

could be achieved by optimizing the operating conditions in the CCCS device for each catalyst system. The volumetric production rate of FAME appears to be the highest (at 2470 $kg_{FAME}/(m^3{}_{reactor}\cdot h)$) when utilizing sodium methoxide as the homogeneous catalyst. This shows that sodium methoxide could provide a much faster reaction rate than the solid CaO or enzyme catalyst, thus allowing operation of the CCCS at much larger flow rate (or shorter residence time) for an enhanced biodiesel production rate. The prepared CaO catalyst could reach a volumetric production rate of 638 kg FAME/(m^3reactor·h) under the identified optimal conditions. Although this productivity is somewhat lower than the homogeneous catalysis case, it is at least 1 order of magnitude higher than the immobilized enzyme catalysis case. This shows the prepared CaO catalyst, when combined with operation in the CCCS, is a promising heterogeneous catalyst for enhanced biodiesel production in terms of both high biodiesel yield and acceptable biodiesel production rate.

4. CONCLUSIONS

In the present study, CaO solid catalyst has been derived from chicken eggshells as an environmentally friendly waste resource and incorporated into the CCCS for an effective biodiesel synthesis and in situ product separation. XRD and TGA analyses proved that upon calcination of the chicken eggshells above a temperature of 800 °C, CaO species were the major component.

The catalytic activity of the prepared CaO catalyst has been tested in the CCCS in the transesterification of sunflower oil (containing 5 wt % THF as a cosolvent) with methanol at 60 °C. The oil flow rate was varied from 8 to 16 mL/min, the alcohol to oil molar ratio from 6 to 12, the weight of catalyst (loaded in the annular zone) from 6.6 to 66.2 g. The influence of reaction parameters on the FAME yield was well modeled by RSM. An optimized FAME yield of 83.2% with a volumetric production rate of 638 kg $_{FAME}/(m^3{}_{reactor}\cdot h)$ could be achieved at an oil flow rate of 9 mL/min, an alcohol to oil molar ratio of 11:1, and a weight hourly space time (defined as the mass of catalyst over the oil mass flow rate) of 0.050 h.

The prepared CaO catalyst could be reused in the CCCS for at least four cycles. The contribution of homogeneous catalysis due to catalyst leaching was considered not significant. The properties of FAME produced in the CCCS met the ASTM D6751 standard except the calcium content, requiring an improved biodiesel purification method. Although the biodiesel production rate in the CCCS using the prepared CaO catalyst is somewhat lower than that obtained in the case with homogeneous base catalyst, it is at least 1 order of magnitude higher than the case with immobilized enzyme catalyst.

Thus, the above findings reveal that CaO catalyst derived from the chicken eggshells represents a promising heterogeneous catalyst for continuous biodiesel production in the CCCS.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b02678.

> Geometry of the CCCS used in this work, produced biodiesel properties in comparison with the ASTM D6751 standard, performance comparison of biodiesel production via the transesterification of sunflower oil with methanol in the CCCS over various catalyst systems (PDF)

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Notes

The authors declare no competing financial interest.

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