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ORIGINAL PAPER

Glycerolysis of Fatty Acid Methyl Esters: 2. Simulation and Experiments in Continuous Reactors

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Abstract The glycerolysis of methyl ester was investigated in flow reactors. This reaction represents a liquid two-phase reaction with changing reaction rates in a batch reactor. A semi-empirical model tested earlier with batch reactor data was used to simulate different continuous processes for this reaction. Among the processes simulated, a single continuous-flow stirred tank reactor (CSTR) without recycling was considered most appropriate for experimental implementation, although simulations showed that a faster reaction rate is possible with the application of a CSTR followed by a tubular reactor with certain associated residence times. The CSTR simulations were verified experimentally. A good agreement was found between the experimental data and simulation results.

Keywords Diglycerides · Fatty acid methyl esters · Glycerolysis · Liquid–liquid reaction · Monoglycerides · Transesterification · Continuous production

Introduction

Mono- and diglycerides represent the most important class of food emulsifiers [1]. Other important uses of mono- and diglycerides have been discussed by Meffert [2]. These chemicals are mostly manufactured by batch processes. Batch reactors have some inherent disadvantages compared to continuous reactors; for example, lower productivity, higher operating costs and varying product quality. Moreover, with the increasing number of applications and demand for these chemicals, better process alternatives with higher productivity and better product quality are required. Monoglycerides are mostly produced by fat glycerolysis. A good amount of information on monoglyceride production by fat glycerolysis is available in the form of publications and patents [3], but, to our knowledge, information on models or correlations for process design and scale-up is still lacking. Monoglycerides intended for certain end-uses can be produced by the glycerolysis of fatty acid methyl esters (FAME). Biodiesel production is a similar process but one which employs the reverse of the reaction used for FAME glycerolysis. Attempts have been made to investigate processes that can be used for the continuous production of monoglycerides by fat glycerolysis and biodiesel experimentally [4–6]. However, the inadequacy of mathematical models or correlations makes it difficult to scale-up or transfer knowledge gained in this way to other processes. Some investigators have used commercial process simulators [7] to develop processes for biodiesel production. However, information on experiments based on these simulations is not available. Dittmar et al. [8, 9] proposed a continuous method of biodiesel production based on their simulations and experiments. In their work, Dittmar et al. modeled fat methanolysis as a homogeneous first-order irreversible reaction, and they proposed a cascade of three CSTRs (continuous flow stirred tank reactors) for that reaction.

The objective of this work was to find a suitable kinetic model to simulate the process of FAME

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glycerolysis and to develop a process for producing monoglycerides continuously.

In the first part (this issue) of this series of papers, a kinetic model was verified with batch reactor data. In this part, some selected continuous processes were simulated with this kinetic model, and one of the continuous processes was verified experimentally. All of the simulations in the present work were performed with Aspen Custom Modeler (version 11.1).

Experimental Procedure

The glycerolysis of FAME was carried out in stirred tank reactor, working in batch and continuous modes. The process implemented experimentally was chosen based on simulations. Therefore, the results from the simulations are presented first, followed by a description of the experimental procedure and results.

Kinetics Modeling and Simulation

The reaction steps were modeled as follows:

$$\text{FAME} + \text{Glycerol (G)} \underset{k_{1R}}{\overset{k_1}{\rightleftarrows}} \text{Monoglycerides (MG)} + \text{Methanol (MeOH)} \tag{1a}$$

$$2\ \text{Monoglycerides} \underset{k_{2R}}{\overset{k_2}{\rightleftarrows}} \text{Diglycerides (DG)} + \text{Glycerol} \tag{1b}$$

$$\text{FAME} + \text{Diglycerides} \underset{k_{3R}}{\overset{k_3}{\rightleftarrows}} \text{Triglycerides (TG)} + \text{Methanol} \tag{1c}$$

In an ideal CSTR, the component mass balance can be written as follows:

$$\frac{dC_i}{dt} = r_i + \frac{v_0}{V}(C_i^{\text{feed}} - C_i), \tag{2}$$

where C_i represents the concentration of component i in the ester phase in the reactor, V is the total volume of liquid in the reactor, v_0 is the volumetric feed flow rate, and r_i represents the production rate from the reaction for component i. For the components in the present reaction, the rate terms are given by

$$r_{ME} = -k_1 C_G C_{FAME} + k_{1R} C_{MG} C_{MeOH} - k_3 C_{DG} C_{FAME} + k_{3R} C_{TG} C_{MeOH} \tag{3}$$

$$r_{MG} = k_1 C_G C_{FAME} - k_{1R} C_{MG} C_{MeOH} - 2k_2 C_{MG}^2 + 2k_{2R} C_{DG} C_G \tag{4}$$

$$r_{DG} = k_2 C_{MG}^2 - k_{2R} C_{DG} C_G - k_3 C_{DG} C_{FAME} + k_{3R} C_{TG} C_{MeOH} \tag{5}$$

$$r_{TG} = k_3 C_{DG} C_{FAME} - k_{3R} C_{TG} C_{MeOH}. \tag{6}$$

The glycerol and methanol concentrations in the liquid ester phase are governed by phase equilibrium rather than chemical kinetics [10]. These were modeled empirically as follows:

$$C_{MeOH} = \text{Constant} \tag{7}$$

$$C_G = A \bullet X + B. \tag{8}$$

The values of all the parameters were calculated using experimental data from batch reactor and are given in part one of this series. Likewise, A, B and X are as described in part one.

In an ideal plug flow tubular reactor (PFTR), the component mass balance can be written as follows:

$$\tau = \frac{V}{v_0} = -\int_{C_i^{\text{feed}}}^{C_i^{\text{exit}}} \frac{dC_i}{-r_i'} \tag{9}$$

which is identical to a batch reactor with reaction time τ. In this equation, the r_i are given by Eqs. 3–6. Figure 1 shows the conversion and monoglyceride selectivity obtained from simulations of CSTRs and PFTRs with different nominal residence times. Here monoglyceride selectivity is defined as the number of moles of monoglyceride produced per mole of FAME reacted.

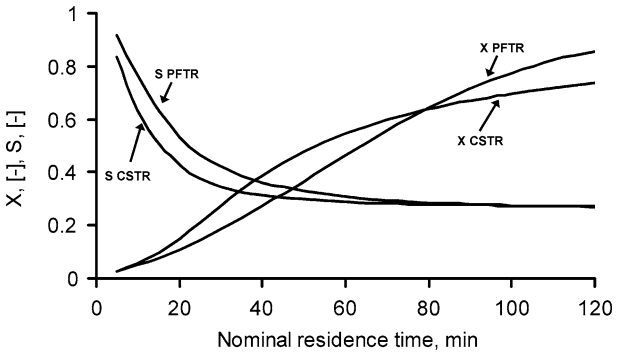

Fig. 1 Comparison of FAME conversion (X) and monoglyceride selectivity (S) in ideal CSTR and PFTR as obtained through simulation (for reactions at T = 135°C, P = 1 bar with methanol removal)

In Fig. 1, it can be seen that the residence time required for intermediate conversion is longer for a tubular reactor than for a CSTR. This happens because the reaction rate is faster at intermediate conversions than at lower conversions (see part one of this series). In comparison to a CSTR, a PFTR gives no significant improvement in monoglyceride selectivity. There would also be other problems with a tubular reactor. Here we are assuming the reaction to be homogeneous (in the ester phase), which requires that mass transfer is not rate-limiting, an assumption which is valid only when the phases are well mixed, i.e., the dispersed phase drop sizes are small (<400 μm) [11]. In the absence of stirring, the phases tend to separate and the reaction would slow down due to mass transfer limitations. Hence a normal pipe will not suffice for this reaction. Static mixers producing high shear and good plug flow behavior would possibly solve this problem, but then the pipe required would be quite long (several tens of meters) for such a reaction. A German patent [12] mentions the use of a 6-m-long static mixer for base-catalyzed fat glycerolysis, with a nominal residence time of 0.5–5 min at temperatures of around 280 °C.

Figure 1 also indicates that a cascade of CSTRs would not bring any significant improvement in conversion or selectivity, as that would approach plug flow behavior. A comparison of the monoglyceride yield obtained in a single CSTR with that from a cascade of two CSTRs is shown in Fig. 2. Here, yield is defined as the product of ester conversion and MG selectivity. A comparison of the conversion profiles in Fig. 1 also suggests that faster conversions would be obtained in a reactor combination with a CSTR followed by a PFTR. Figure 3 shows the simulated conversion profile obtained by such a combination, which would be the most time-efficient for higher conversions. However, the residence times required in the tubular reactor are still very long and the acceleration in conversion is not very good. Therefore, despite being more efficient, this is probably not a practical option.

The conversion–time curve in a batch reactor shows autocatalytic behavior, so recycling a part of the product stream was expected to give higher reactor efficiency. A US patent [13] on fat glycerolysis mentions returning a part of the product stream containing monoglyceride back into the reactor. A US patent [14] on FAME glycerolysis also mentions recycling monoglyceride to the inlet of the reactor to increase the reaction velocity. For the reaction investigated here, simulations showed that no advantages were obtained in terms of monoglyceride yield by considering a recycle stream.

In all of the simulations described here, it was assumed that methanol is effectively removed from the liquid reaction mixture. Hence for C_{MeOH} (Eq. 7), a constant value of 0.01 mol/kg was used based on our previous experiments (part one of this series). Methanol could be removed from the reaction mixture by applying vacuum, by passing an inert gas through the liquid, or by other means. A constant value of 0.4 for parameter A (Eq. 8) was used in all simulations.

Based on the results from these simulations, a single CSTR without a recycle stream was chosen for experimental verification. An experimental unit with a CSTR was installed in our laboratory and experiments were performed to verify the simulation results.

Materials

Glycerol (>99%, Sigma, Munich, Germany) and methyl oleate (>75%, Lancaster, Frankfurt am Main, Germany) were used as reactants. Sodium methoxide (30 wt% in methanol, Fluka, Munich, Germany) was used as catalyst. Details of the additional material used for analysis are given in part one of this series.

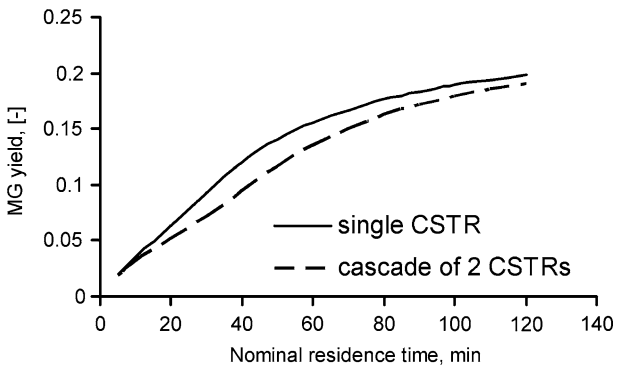

Fig. 2 Comparison of the monoglyceride yield from a single CSTR with that from a cascade of two CSTRs

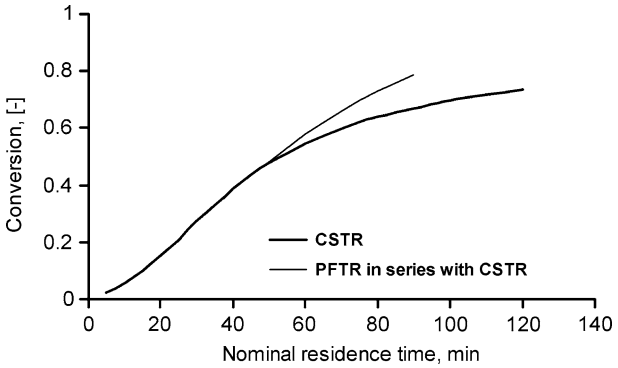

Fig. 3 FAME conversion in a cascade of a CSTR and then a PFTR

Experimental Set-up and Procedure

The experimental set-up is shown in Fig. 4. The main parts of the set-up were: feed reservoirs, diaphragm pumps (CGM ProMinent A2001 with teflon diaphragm; Pittsburgh, PA, USA), reactor and oil thermostat (not shown in the figure) to heat the reactor. The catalyst was mixed with glycerol to yield 1 wt% of total reactant. Two feed reservoirs, one containing methyl ester and one containing glycerol and catalyst, were preheated to 75 °C. This was done to reduce the viscosity of glycerol for pumping. Preheating the feed also facilitated temperature control in the reactor in continuous operation. The pumps were calibrated with respective fluids at reaction conditions and were preset to give the desired flow rate during the reaction. The reaction was carried out at 135 °C. The temperature was measured with a PT-100 probe. Heating was provided by a thermostatically controlled (±0.1 °C) oil bath.

The reaction was run initially in batch mode for about 1.5–2 times the desired residence time to reach an intermediate conversion. The liquid volume in the reactor was 300 ml (200 ml ester + 100 ml glycerol). The feed and the product outlet pumps were switched on simultaneously to start the continuous mode. The temperature dropped by about 3–5 °C upon starting the pumps. The temperature was soon restored to the set point and it was maintained within ±1.5 °C thereafter. The reactor contents were pumped out at a constant rate. The product stream was cooled by heat exchange with cold water, as the temperature limit of the fluid for the pumps was 50 °C. The outlet fluid was collected in a measuring cylinder and the volumes of both phases were monitored every 20 min to ensure that both of them had a constant residence time in the reactor. Since the equilibrium conversion obtained in batch reactor without methanol removal is very low, all of the experiments were carried out with methanol stripping by nitrogen. The nominal residence time was chosen based on trial simulations to get the desired value of conversion. The reaction was run in continuous mode for a minimum of five residence times. This was roughly the time needed to reach steady state if the continuous mode is started at zero conversion. When running in continuous mode, some decline in the residence time (up to ~10%) is expected, as the reactant volume decreased over time due to sample withdrawal and liquid evaporation. At the end of the continuous mode, the pumps were switched off simultaneously, and the reaction was allowed to continue for some time in batch mode, which would be similar to connecting an ideal plug flow reactor to a CSTR in series. During the reaction run, samples were taken directly from the liquid phase in the reactor at different times. The sampling and data analysis methods used are explained in part one of this series of papers.

Results and Discussion

Figure 5a,b show a comparison between the ester conversion and monoglyceride selectivity profiles obtained by experiment and simulation. The comparison is shown for a complete experimental run, including the batch modes before and after the continuous mode. The run represented in Fig. 5 was run for 75 min in batch mode, then from 75 to 275 min in continuous mode, and after that it was run for 35 min in batch mode. The nominal residence time based on reactant volume and feed pumping rate was 40 min. The experimental and simulated data agree well. The

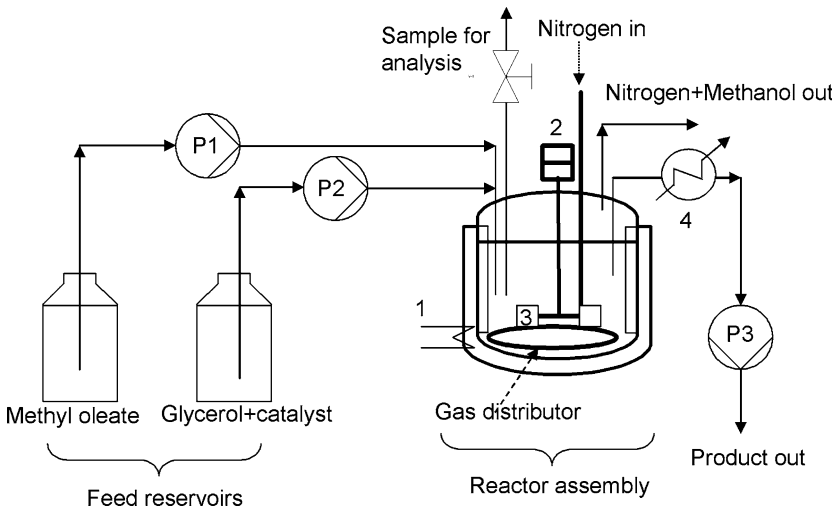

Fig. 4 Experimental set-up. (*P1*, *P2*, *P3* pumps, *1* oil heating, *2* motor, *3*: six-blade turbine stirrer, *4* heat exchanger)

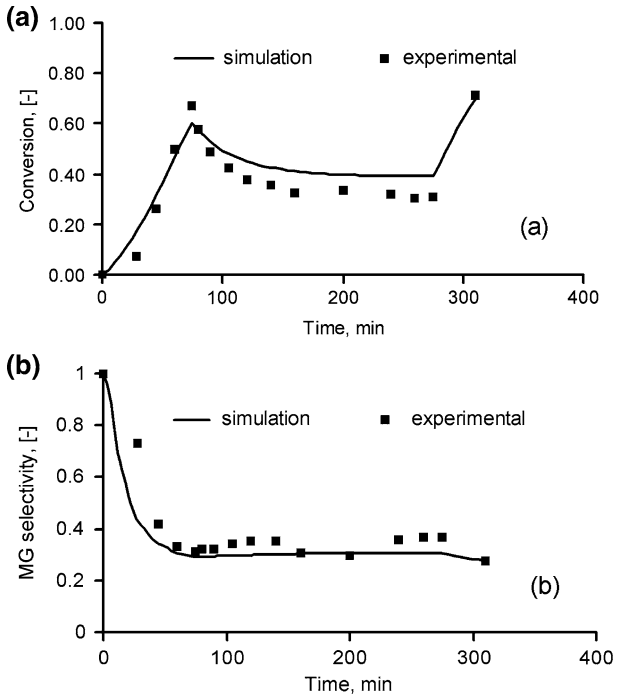

Fig. 5a–b Simulation and experimentally determined data for a reaction run. 0–75 min: batch mode, 75–275 min: continuous mode, 275–310 min: batch mode. Nominal residence time in continuous mode was 40 min. **a** Variation in FAME conversion over an experimental run. **b** Variation in monoglyceride selectivity

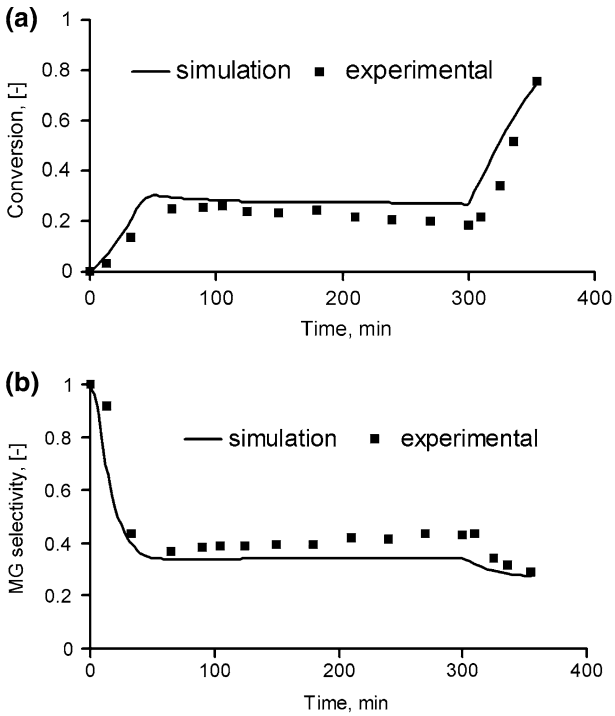

Fig. 6a–b Simulation and experimentally determined data for an experimental run. 0–45 min: batch mode, 45–300 min: continuous mode, 300–355 min: batch mode. Nominal residence time in continuous mode was 30 min. **a** Variation in FAME conversion over an experimental run. **b** Variation in monoglyceride selectivity

predicted conversion and selectivity data are mostly within 12% of the measured values. For continuous operation, higher steady state conversions are predicted by simulation. Figure 6a,b represents the conversion and selectivity data for a similar experiment where the nominal residence time for continuous operation was 30 min. The initial batch run duration was 45 min; the continuous mode was run for 300 min (i.e., for 8.5 reactor volume replacements), and then finally the reactor was operated in batch mode for another 55 min. The simulations in this case also show good agreement with experimental data, although the calculated conversions are slightly higher again. In this case, the run was switched from batch to continuous mode at a conversion value near to the steady state conversion; therefore, a very small transition period was observed in this run. From the experiments, lower values of conversion were obtained after 200 min, which could be due to the reduction in the volume of liquid inside the reactor due to sample withdrawal and methanol stripping. Since the liquid streams were pumped at a constant rate, this leads to a drop in the residence time. In this reaction, the monoglyceride selectivity follows the opposite trend to the conversion (Fig. 1). Hence deviations with the opposite sign are seen in the selectivity data in Fig. 6b.

Faster reactions rates are expected at higher temperatures due to the effect of temperature on the reaction rate and on the glycerol and methanol concentrations. Also, higher monoglyceride selectivity is expected at higher glycerol concentrations. Although simulations show this trend, in the absence of information on glycerol solubility at higher temperatures under actual reaction conditions, it is not possible to predict the reaction behavior with a known degree of accuracy at present. The model used here can be applied to the preliminary design and selection of processes for FAME glycerolysis.

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