Continuous Production of Palm Methyl Esters

D. Darnoko[1] and Munir Cheryan*

University of Illinois, Department of Food Science and Human Nutrition, Agricultural Bioprocess Laboratory, Urbana, Illinois 61801

ABSTRACT: A system for continuous transesterification of palm oil was developed using a continuous stirred-tank reactor (CSTR) and pumps for continuous delivery of oil and catalyst and for continuous removal of product. Potassium hydroxide was used as the catalyst, the methanol-to-oil molar ratio was 6:1, and reaction temperature was 60°C. The yield of methyl esters increased from 58.8% of theoretical yield at a residence time of 40 min to 97.3% at a residence time of 60 min. However, higher residence times decreased the production rate. During long-term continuous operation, the CSTR displayed steady state conditions in terms of product profile and methyl ester concentration. This process has good potential in the manufacture of biodiesel.

Paper no. J9575 in *JAOCS 77*, 1269–1272 (December 2000).

KEY WORDS: Biodiesel, continuous process, methyl esters, palm oil, transesterification.

The most common method for producing biodiesel is the one-step or two-step batch transesterification process. Batch processes suffer several disadvantages compared to continuous processes: batch processes require larger reactor volumes, thus requiring higher capital investment; they are inherently less efficient than continuous processes owing to their start-up and shutdown nature; there are batch-to-batch variations in the quality of the products; and labor costs are higher with batch processes. There have been some attempts to develop continuous transesterification processes. Krisnangkura and Simamahamnop (1) reported that the reaction time for continuous transmethylation of palm oil could be reduced to a few minutes by using an organic solvent such as toluene to enhance mixing of the reactants and improve the reaction rate. However, solvent consumption was relatively high, which would increase production costs. The Stratco Company (Kansas City, KS) has developed a continuous process that apparently significantly reduces the size of some of the equipment (2). However, no technical data is available in the literature. Kreutzer (3) described a continuous process for the production of methyl esters from vegetable oil as a preliminary process for fatty alcohol production, but the process used high temperatures and pressures that might not be suitable for biodiesel production. Kusy (4) suggested a scheme for continuous ethanolysis of vegetable oil, but no actual process details were reported. Noureddini *et al.* (5) used a motionless high-shear mixer for continuous conversion of vegetable oil into methyl esters and achieved a methyl ester yield in excess of 98% of the theoretical yield.

The objective of this work was to develop a process for the continuous transesterification of palm oil. Oil palm is one of the most efficient oil-bearing plants, and the production cost of palm oil in the major producing countries, Malaysia and Indonesia, is lower than any other vegetable oil (6). This provides an opportunity for the palm oil industries to increase their economic returns by developing value-added products such as methyl esters which have value not only as biodiesel but also as feedstocks for the production of oleochemicals such as fatty alcohols, fatty alkanolamides, isopropyl esters and sucrose polyesters. This study focused on determining the optimal residence time for maximum production of methyl esters from palm oil.

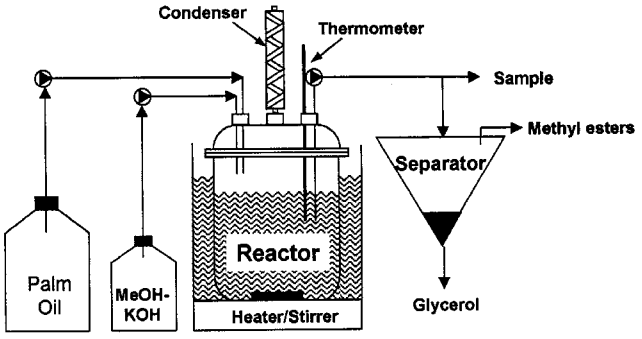
EXPERIMENTAL PROCEDURES

Refined, bleached, and deodorized (RBD) palm oil was obtained from Archer-Daniels-Midland (Decatur, IL). Reference standards such as tripalmitin, triolein, diolein, monoolein, methyl oleate, methyl palmitate, and glycerol of >99% purity were purchased from Nu-Chek-Prep, Inc. (Elysian, MN) and Sigma Chemical Co. (St. Louis, MO). Methanol and potassium hydroxide were of analytical grade.

Scheme 1 is a diagram of the experimental setup, which consisted of a 1-L reactor equipped with a condenser, reservoirs for the feed (oil) and the catalyst (1% w/w KOH dissolved in the methanol); three pumps for the oil, catalyst, and product streams; and a separating funnel for separating methyl esters from glycerol. The temperature of all experiments was fixed at 60°C based on previous work in our laboratory (7). Heating was provided by a thermostatically controlled water bath that was capable of maintaining the temperature within ±0.2°C. Initially the reactor was charged with 500 g palm oil and heated to 60°C with stirring. After the temperature had reached 60°C, the catalyst and methanol were added and the reaction was allowed to proceed in a batch mode for one residence time. The feed pumps and product pump were then simultaneously started. The two feed pumps delivered oil and catalyst to the reactor at a combined flow rate, F, such that residence time (θ) = V/F, where V is

[1]Present address: Indonesian Oil Palm Research Institute, Jl. Brigjen Katamso 51, Medan 20001, Indonesia.

*To whom correspondence should be addressed at University of Illinois, Department of Food Science and Human Nutrition, Agricultural Bioprocess Laboratory, Urbana, IL 61801. E-mail: mcheryan@uiuc.edu



SCHEME 1

the volume of the reaction mixture. The product pump removed methyl esters and co-products out of the reactor. The timing was started at the moment the pumps were started.

Catalyst (KOH) concentration was 1% w/w of the weight of the oil, and the molar ratio of methanol/oil was 6:1 for all experiments, based on previous optimization studies (7). The weight of 1 mol oil was determined from the calculated average molecular weight of palm oil based on the known fatty acid composition of the oil.

Samples (about 1 g or less) were taken from the outlet and analyzed for concentrations of triglycerides, diglycerides, monoglycerides, methyl esters, and glycerol using gel permeation chromatography (8). Typically, sampling was done every half volume replacement. All experiments were run for at least 5 vol replacements to ensure steady state had been achieved, i.e., the product volume was five times the volume of the reaction mixture. Data presented are averages of at least two replicate determinations.

A residence time distribution study was performed to characterize the state of mixing in the reactor. Palm methyl esters containing a tracer (β-carotene) were used as the feed. Initially the reactor was charged with pure palm methyl esters containing no detectable amount of carotene. The feed, catalyst, and product pumps were then started. The total reactor volume was kept constant by maintaining the same flow rate for the feed and the product to give a residence time of 60 min. Samples were taken at the product line periodically and diluted with hexane; their absorbances were determined at 446 nm, which was the optimal wavelength for β-carotene (9). An ideal continuous stirred tank reactor (CSTR) will show a residence time distribution described by the following equation (10):

$$F(t) = 1 - e^{-t/\theta} \qquad [1]$$

where $\theta = V/F$ = residence time (min), t = time of operation (min), V = volume of the reaction mixture (L), and F = flow rate (L/h).

RESULTS AND DISCUSSION

Figure 1 shows the residence time distribution of the continuous reactor. It generally followed the CSTR mixing pattern, although

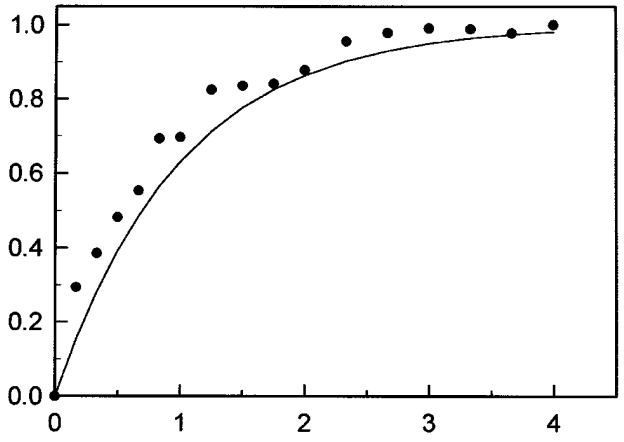


FIG. 1. Residence time distribution of the continuous stirred-tank reactor. Solid line is ideal behavior according to Equation 1, points are experimental data.

there was a slight shift to lower times compared to the ideal condition. This could be because we did not completely account for the total volume of the system, e.g., the tubing, and perhaps also due to evaporation of methanol. After four residence times, there was no significant difference between concentration of the tracer in the feed and in the product. All reactions in this study were run for at least five residence times or volume replacements to ensure steady state conditions had been achieved.

Reactor performance. Figure 2 shows the concentration of reaction products during continuous transesterification of palm oil at 60°C and a residence time of 40 min. The concentration of methyl esters was 82.7% w/w at the beginning of the continuous run (because the reactor had been operated as a batch reactor for the previous 40 min). However, the methyl ester concentration decreased continuously after startup, reaching only 58.8% w/w after 5 vol replacements. The triglyceride concentration simultaneously increased and reached 26.4% w/w after 5 vol replacements. This indicates that a residence time of 40 min is too short to complete the reaction and in effect, there was a dilution of the reaction products by incoming feed. This in turn caused a buildup of intermediate products that reduced the reaction rate.

Increasing the residence time to 50 min resulted in a better conversion rate and the average methyl esters concentration was 78.26% w/w [not shown here, see Darnoko (9)]. Further improvement was achieved with a residence time of 60 min (Fig. 3). The average concentrations of esters and triglyceride under these conditions were 85.6 and 2.08% w/w, respectively. However, at a residence time of 70 min, a decrease in concentration of methyl esters was observed (Fig. 4). Thus, the optimal temperature for maximal concentration of methyl esters is 60 min (Fig. 5). The lower conversion rate at the 70-min residence time could be due to a shift of the reaction equilibrium to the left at higher residence time, e.g., free glycerol would react with methyl esters to form glycerides.

Long-term stability. The stability of the continuous reac-

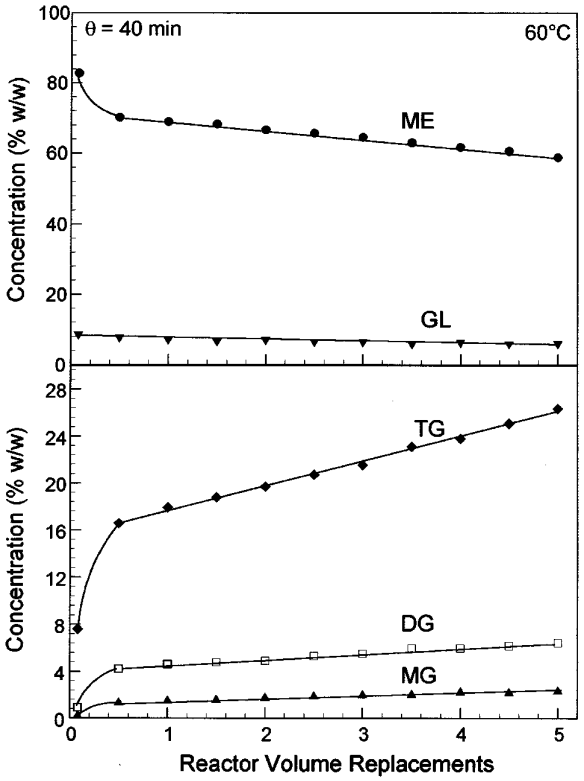


FIG. 2. Continuous production of palm methyl esters at a residence time of 40 min. Oil/methanol molar ratio = 6, catalyst = 1% w/w KOH, temperature = 60°C. ME, methyl esters; GL, glycerol; TG, triglycerides; DG, diglycerides; MG, monoglycerides.

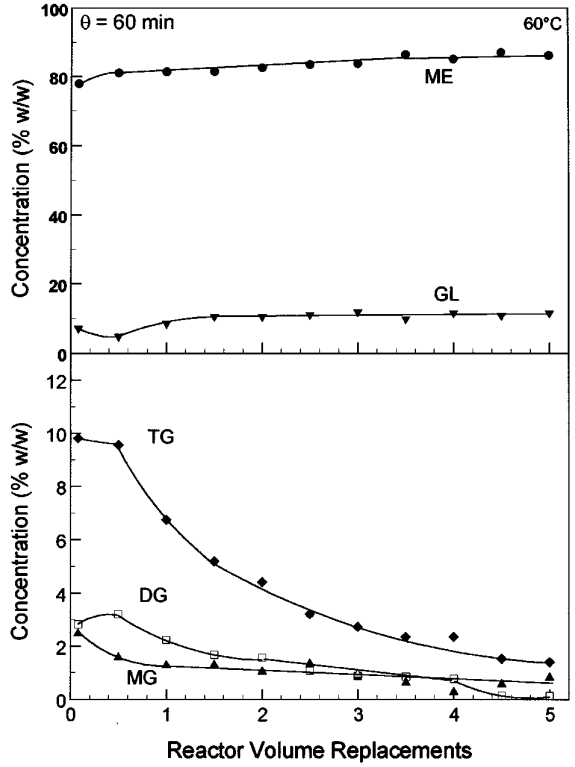


FIG. 3. Continuous production of palm methyl esters at a residence time of 60 min. See Figure 2 for reaction conditions and abbreviations.

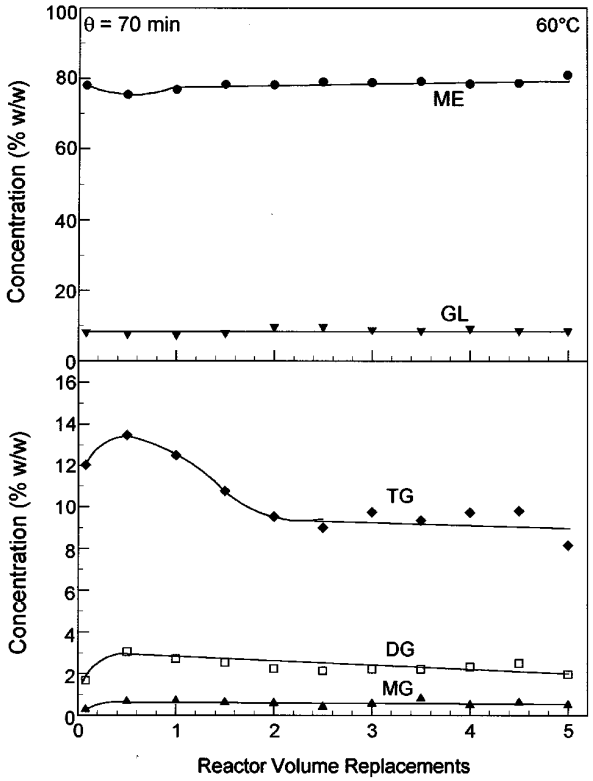


FIG. 4. Continuous production of palm methyl esters at a residence time of 70 min. See Figure 2 for reaction conditions and abbreviations.

tion was evaluated by operating the reactor under optimal conditions for 20 vol replacements at a residence time of 60 min. As shown in Figure 6, a steady output was observed during this run with minimal variability of the conversion rate. The average yield of methyl esters was 89.5% w/w of the maximum theoretical yield, with a relative standard deviation of 2.61%. This is in contrast to the study by Krisnangkura and Simamahamnop (1) who reported yields for continuous transmethylation of palm oil in a reactor coil of 50% w/w or less using the same methanol/oil molar ratio of 6:1. Their low con-

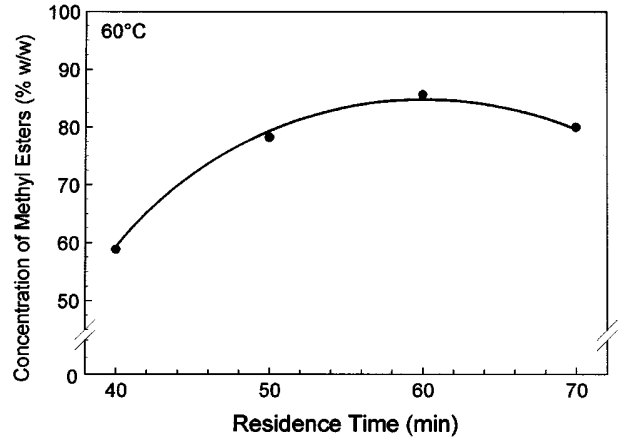


FIG. 5. Effect of reactor residence time on concentration of methyl esters. See Figure 2 for reaction conditions and abbreviations.

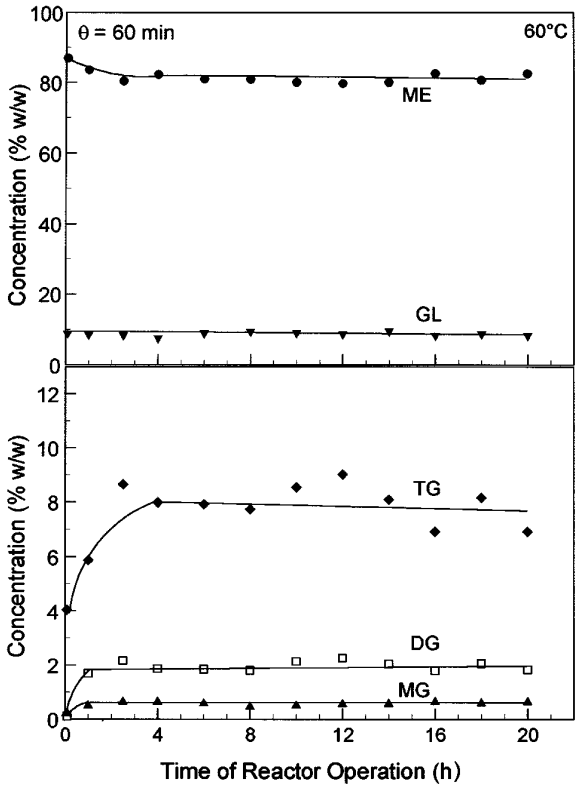


FIG. 6. Long-term operation of the continuous transesterification reactor at a residence time of 60 min. See Figure 2 for reaction conditions and abbreviations.

version could be due to poor mixing conditions in their reactor. Good mixing is critical in transesterification reactions since methanol and oil are not miscible. Noureddini and Zhu (11) reported that mixing Reynolds numbers should be greater than 10,000 in order to reduce the lag time at the beginning of transesterification reactions.

High conversions are important for biodiesel applications since residual triglyceride, diglyceride, monoglyceride, and glycerol can cause serious problems in diesel engines. According to the European Union standards for alternative diesel fuels (12), the minimum acceptable purity of biodiesel is 96.5%. After separation of the glycerol, the simple continuous transesterification process described in this work could produce crude biodiesel with a methyl esters content of 95% or more. After refining, the purity can be increased to exceed the standard, e.g., even simple water washing should be able to reduce the concentration of the monoglycerides. Other advantages of a continuous process are the reduction in reactor volume and consequent reduction in capital cost, easier process control and less variation in product quality.

ACKNOWLEDGMENTS

This study was partly supported by the Illinois Agricultural Experiment Station, University of Illinois. The authors acknowledge Indonesian Oil Palm Research Institute for the leave and scholarship provided to D. Darnoko.

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[Received March 29, 2000; accepted August 27, 2000]