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Glycerolysis of Fats and Methyl Esters

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ABSTRACT: The glycerolysis of methyl esters and triglycerides with crude glycerol, a coproduct from the transesterification of triglycerides, was studied. Three procedures were followed for this conversion. The first procedure was a one-step glycerolysis with methyl esters. The second procedure was a two-step process. This procedure involved an initial partial glycerolysis with methyl esters, followed by fat glycerolysis. The third procedure was a simultaneous glycerolysis with methyl esters and triglycerides. In the glycerolysis with methyl esters, the removal of methanol is vital to the production of mono- and diglycerides. Methanol was removed either by drawing vacuum on the reactor or by stripping methanol out by means of an inert carrier gas (nitrogen). Different molar ratios of methyl esters to glycerol were tested in the first two processes. At low concentration of methyl esters, total conversion of methyl esters to mono- and diglycerides was achieved. As the concentration of methyl esters was increased, the conversion of methyl esters to mono- and diglycerides was decreased. Furthermore, the ratio of mono- to diglycerides was also higher at lower concentrations of methyl esters. The conversion of triglycerides in the two-step process with crude glycerol was similar to a one-step fat glycerolysis with pure glycerol. The composition of different components and the ratio of mono- to diglycerides were also comparable.

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KEY WORDS: Biodiesel, diglycerides, fatty acid methyl esters, glycerol, glycerolysis, monoglycerides, transesterification, triglycerides.

Glycerolysis of fats and oils produces industrially important mono- (MG) and diglycerides (DG). Fatty acid MG and their derivatives have many applications as surfactants and emulsifiers in a wide range of foods, cosmetics, and pharmaceutical products (1,2). MG are commercially manufactured by the glycerolysis reaction in which fats and oils undergo a transesterification reaction with glycerol. This is a physicochemical process and requires high temperatures (210–260°C) and the use of an inorganic catalyst, such as sodium, potassium, or calcium hydroxide (3–6). Glycerolysis of fats and oils with glycerol has been intensively patented as widening industrial uses were found for MG in the 1940s and 1950s. Sonntag (3) has a complete collection of these patents in his review.

During the last decade, enzymatic synthesis of MG by various lipase catalysts has received a lot of attention due to lower energy requirements and selectivity of the catalyst (7–10). Although enzymatic synthesis of MG offers perhaps the greatest potential for future production of MG, current industrial processes are based on the physicochemical glycerolysis of fats and oils.

Fatty acid glycerides have also been prepared by direct esterification of fatty acids or their alkyl esters with glycerol. The chemical reactions involved are reversible and result in formation of MG, DG, and possibly triglycerides (TG). Water or alcohol is also formed in the reaction. Masuyama and coworkers (11) transesterified methyl esters (ME) of various vegetable oils with glycerol and potassium hydroxide catalyst and reported 50–55% conversion to MG. Takeda *et al.* (12) used both fatty acids and their alkyl esters in a two-step reaction to prepare MG. The fatty acid or alkyl ester was first reacted with glycerol in the presence of an alkaline catalyst. The second step, which involved further addition of catalyst and an organic solvent, had a significant increase in the yield of MG. Use of organic solvents in the production of fatty acid MG from the glycerolysis of fatty acids with glycerol has also been reported in other studies (13,14). In both studies, zinc compounds were used as the catalyst.

Glycerol. Natural glycerol is the process coproduct in the conversion of fats and oils to fatty acids (fat splitting) or fatty acid esters (transesterification). Crude glycerol from fat splitting is a 15–20% solution of glycerol in water. The transesterification process results in a 75–90% solution of glycerol in alcohol, depending on the initial ratio of the alcohol to the fat or oil and the catalyst concentration. The coproducts from both processes are further purified to different purities. Several grades of refined and crude glycerol with such names as sweetwater, soap-lye crude, saponification crude, alcoholysis crude, high-gravity, dynamite, and UPS are marketed (15).

Over the last few years, fatty acid methyl esters have assumed importance as research intensifies on the utilization of vegetable oils and animal fat derivatives as liquid fuels (better known as biodiesel). Fatty acid methyl esters are the product of the oils' transesterification reaction. Crude glycerol from the transesterification process contains methanol, ME, impurities from the raw material, and an insignificant amount of glycerides. Because of the presence of fatty acid esters in the crude glycerol, utilization of crude glycerol in the fat glyc-

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erolysis process would require its removal prior to or after the process. The alternative to its removal is its possible conversion to MG and DG.

The objective of this article was to explore utilization of crude glycerol from the transesterification process in the production of MG and DG. Three different physiochemical treatments were considered. The first approach was a one-step glycerolysis with ME. The second approach was a two-step glycerolysis: an initial glycerolysis with ME, followed by a second glycerolysis with TG. The third procedure was a simultaneous glycerolysis with ME and TG. The concentrations of the glycerolysis products were monitored in the experiments, and the feasibility of the utilization of crude glycerol in the glycerolysis process was studied. Throughout this manuscript, these three procedures will be referred to as Procedure A, B, and C for the first, second and, third procedures, respectively

EXPERIMENTAL PROCEDURES

Materials. Pure glycerol (99.8%) was obtained from Fisher Scientific Company (Fair Lawn, NJ). Soybean oil, which was refined and bleached, was provided by Archer Daniels Midland Company (Lincoln, NE). The free fatty acid content of the oil was determined to be 0.09% according to AOCS method #Ca 5a-40 (Ref. 16). Sodium hydroxide (98.4%) and phosphoric acid (85%) were both obtained from Fisher Scientific Company. The standards for ME were from Sigma Chemical Company (St. Louis, MO).

Crude ME and glycerol were prepared in a one-step batch transesterification process (17). A 10:1 molar ratio of alcohol to soybean oil was used in this process. Sodium hydroxide (0.10 wt% based on the vegetable oil) was the catalyst. The reaction was carried out for 1 h under total reflux. Upon gravity settling, the reaction products separated into an upper layer of crude ME and a lower layer of crude glycerol. Excess methanol was removed from both product layers under vacuum distillation. No additional purification or neutralization was carried out. The amount of sodium hydroxide was measured in both product layers by titration. The titration results show 3.29 g of NaOH per 1000 g of methanol-free glycerol and 0.281 g of NaOH per 1000 g of methanol-free ME. Table 1 shows the composition of the ME and glycerol as analyzed in our laboratory.

TABLE 1
Crude Methyl Esters and Crude Glycerol Composition

Compounds	Crude methyl esters[a] (wt%)	Crude glycerol (wt%)
Glycerol	<0.5	90.0
Methyl linolenate	7.9	0.8
Methyl linoleate	54.1	5.4
Methyl oleate	25.3	2.5
Methyl palmitate	8.6	0.9
Methyl stearate	3.9	0.4

[a]The concentration of methyl esters is based on the distribution in crude methyl esters.

Equipment. A bench-top mini reactor (model number 4562; Parr Instrument Company, Moline, IL) was used for the glycerolysis reactions. The reactor assembly was constructed from type 316 stainless steel with a 450-mL bomb. The reactor was equipped with a magnetic stirrer, a four-blade, downward-thrust impeller, and a 1/12-hp, variable-speed motor with a pulley arrangement to turn the stirrer at speeds from 0 to 800 rpm. A heating mantle and internal cooling loop provided the heating and cooling requirements. A Parr 4843 controller was used for controlling as well as mouitoring the reaction temperature and the impeller speed. The reactor was equipped with a take-off condenser, which was attached to the head assembly. A nitrogen cylinder provided the purge gas for the process. The purge gas was introduced into the bottom of the reactor bomb and was also used for stripping methanol during the reaction. An air/vacuum/pressure pump, made by Fisher Scientific Company, provided the vacuum inside the reactor bomb up to 600 mm Hg of vacuum.

A metering pump (E plus series; Pulsafeeder Company, Rochester, NY) was attached to the head assembly of the reactor to provide for the injection of material into the bomb. The flow chart for the experimental set-up is presented in Figure 1.

Procedure A—glycerolysis of ME. In the presence of an alkaline catalyst, glycerol (G) and ME of fatty acids form methanol (MeOH), and a mixture of MG and DG. Theoretically, TG may also form in this reaction, but none was detected in the reaction products. The reactions involved are reversible, and simultaneous removal of methanol from the reaction environment will shift the equilibrium toward the glycerides. The reaction steps are:

$$ME + G \rightleftharpoons MG + MeOH \quad [1]$$

$$ME + MG \rightleftharpoons DG + MeOH \quad [2]$$

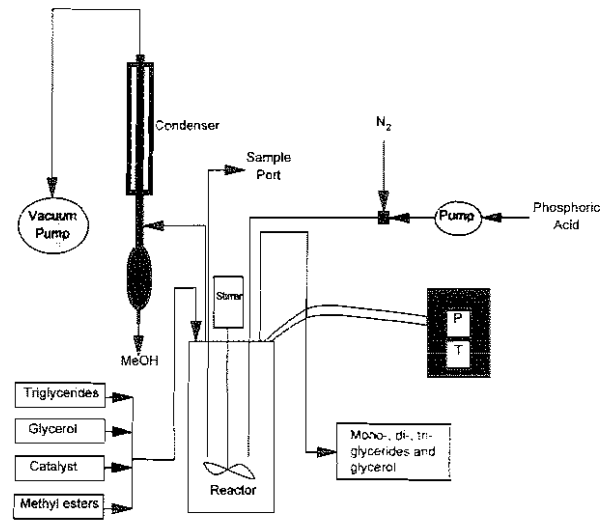

FIG. 1. Flow diagram for the experimental set-up.

$$ME + DG \rightleftharpoons TG + MeOH \quad [3]$$

Both methanol-free crude glycerol and pure glycerol were used in the glycerolysis with ME. The amount of ME charged into the reactor relative to glycerol varied from 25 to 100% molar equivalents when pure glycerol was used, which made the actual molar ratio of ME to pure glycerol vary from 0.25:1.0 to 1.0:1.0. For crude glycerol, the amount of ME used in the reaction varied from about 3.5 to 115% molar equivalents of glycerol, including the ME initially present in the crude glycerol (about 10 wt%). This made the actual molar ratio of ME to glycerol vary from about 0.035:1.0 to 1.15:1.0 when crude glycerol was used. The 0.035:1.0 ratio was for the situation when no additional ME were added to the crude glycerol. The lower range of ME to glycerol (0.035:1.0, 0.145:1.0, and 0.313:1.0) was used to examine the elimination of ME as a preliminary step for the overall glycerolysis, whereas the larger concentrations (0.59:1.0, 0.87:1.0, and 1.15:1.0) were used to examine ME glycerolysis as an alternative to fat glycerolysis.

The amount of sodium hydroxide in the crude glycerol and ME was quantitated by titration and was presented earlier. Based on the total mass of the mixture, the amount of sodium hydroxide was 0.30 to 0.10 wt% when the molar ratios of ME to crude glycerol varied from 0.035:1.0 to 1.15:1.0. No additional sodium hydroxide was added in this case. For reactions with pure glycerol, sodium hydroxide was added to 0.10 wt% of the total mass of the reactants.

The reactor was initially charged with 46 g of pure/crude glycerol. A measured amount of ME was added to achieve a desired molar ratio. Then, the reactor was purged with nitrogen and heated to the desired temperature. The heating process took about 20 min. The desired temperature for the glycerolysis is the temperature at which methanol starts to form. The reaction temperature was consistently and significantly lower for crude glycerol reactions than for reactions with pure glycerol. The reaction temperature was maintained at 200–210°C for crude glycerol and 230–240°C for pure glycerol. The reaction was carried out for 30 min at this temperature, while methanol was continuously removed from the reactor. Methanol was condensed and collected in a separate container. At the end of the reaction period, the reactor was cooled to room temperature, and the reaction products were collected for further analysis.

In the glycerolysis of ME, the formation of methanol is indicative of glyceride (ester-bound) formation. Two procedures were employed for the removal of methanol. Methanol was removed either by drawing vacuum on the reactor or by stripping it out of the reactor by means of an inert carrier gas, such as nitrogen.

Procedure B—fat glycerolysis. Fat glycerolysis is the transesterification of glycerol with TG to MG and DG in the presence of an alkaline catalyst. Three stepwise and reversible reactions are believed to occur. MG are the main reaction product but DG and TG are also found in the final equilibrium state. The reaction steps are:

$$TG + G \rightleftharpoons DG + MG \quad [4]$$

$$DG + G \rightleftharpoons 2\,MG \quad [5]$$

$$TG + MG \rightleftharpoons 2\,DG \quad [6]$$

Methanol-free pure and crude glycerols were used in the glycerolysis reactions with TG. As was mentioned in Procedure A, the lower range of ME to crude glycerol (0.035:1.0, 0.145:1.0, and 0.313:1.0) was used to examine the elimination of ME in a preliminary step. Therefore, the reaction products from Procedure A under vacuum distillation, for which the initial molar ratios of the ME to crude glycerol changed from 0.035:1.0 to 0.313:1.0, were considered as the crude raw material for fat glycerolysis. Analysis shows that the reaction products from ME glycerolysis contained about 40, 32, and 22 g of glycerol when the initial molar ratio of ME to glycerol was 0.035:1.0, 0.145:1.0, and 0.313:1.0, respectively. Sufficient soybean oil was added to these reaction products to make the molar ratio of soybean oil to glycerol about 1.0:2.5. Sodium hydroxide was added to maintain its concentration at 0.18 wt%, based on the soybean oil. The reactor was purged with nitrogen and then heated to 245°C. The heating process took about 20 min. The reaction was continued at this temperature for 20 min. At the end of the heating and reaction period, 6 mL of phosphoric acid was injected into the reactor. The injection was done with a metering pump at 4.5 mL/min. Phosphoric acid was in excess of what is required to neutralize the catalyst. The reactor bomb was then cooled to 105°C in about 1 min with the aid of the internal cooling coils of the reactor and external ice-water bath. The glycerolysis experiments involving pure glycerol were performed according to a similar procedure, except that no initial glycerolysis with ME was involved. Pure glycerol was primarily used to establish a reference point.

Procedure C. In this procedure, we tried to carry out the two steps involved in Procedure B simultaneously. Only the crude glycerol with a molar ratio of glycerol to ME of 0.035:1.0 was considered in this experiment. Soybean oil was added to make the molar ratio of TG to glycerol 1.0:2.5. Additional sodium hydroxide was added to raise its concentrations to about 0.18 wt% based on the soybean oil. The reaction was placed under vacuum while the reaction temperature was raised to 245°C. Heating and distillation were simultaneously continued for 30 min. Postreaction neutralization and cooling were similar to Procedure B.

Analysis. A high-performance liquid chromatography (HPLC) pump, made by ISCO (Model No. 2350; Lincoln, NE), was used for analyzing the samples. A refractive index detector, made by Thermo Separation Products (Refracto Monitor IV; Riviera Beach, FL), was used for analyzing the separation. A Spherisorb OSD 2 column 250 × 4.6 mm with 80 Å pore size and 5 μm particle size was used for the separation. The mobile phase for the system was a 50:50 volume ratio of acetone and acetonitrile.

The batch from each glycerolysis experiment was allowed to settle overnight in a separatory funnel. The products from the glycerolysis reactions with ME formed two layers. The bottom layer consisted of most of the unreacted glycerol. The top layer contained the MG and DG, unreacted ME, and some of the unreacted glycerol. The top layer was separated for further analysis. The product from the glycerolysis reactions with TG formed a single layer and did not need to go through the separation stage.

The results from the HPLC analysis were integrated by HP Chemstation software. Standards for ME, MG, and DG were used to establish the calibration charts. With these calibration charts, all the integration results were corrected for the weight percentages of the individual components.

RESULTS AND DISCUSSION

The glycerolysis of TG (soybean oil) with pure glycerol at 245°C was performed to establish a reference point for our analysis. This process resulted in 54.3 wt% MG and 38.9 wt% DG. The reaction was 96.1% complete. The MG to DG weight ratio was 1.39.

Procedure A. Four sets of experimental results were collected for the glycerolysis of ME. Experiments were performed with pnre and crude glycerol, and for each, vacuum distillation and continuous purge with nitrogen were employed for the removal of methanol. The effect of the initial molar ratio of ME to glycerol on the product composition was examined. The ratio of MG to DG was also determined in the final product.

As was mentioned earlier, upon gravity settling, the glycerolysis of ME resulted in two liquid phases. Most of the unreacted glycerol was recovered in the bottom layer. No significant amount of MG and DG or unreacted ME was detected in this layer. Figures 2–5 summarize the experimental results for the glycerolysis experiments with ME. The analysis of the top layer for the weight percentages of MG and DG, unreacted ME, and glycerol is presented in these figures. The glycerolysis under vacuum distillation is presented in Figure 2. Figure 3 provides the same results under continuous purge with nitrogen. Figures 4 and 5 compare the glycerolysis results for crude and pure glycerol, respectively.

Inspection of Figures 2 and 3 did not reveal any significant change between the concentration of the product components for crude and pure glycerol. Similar trends were observed in all experiments for MG, DG, unreacted ME, and glycerol.

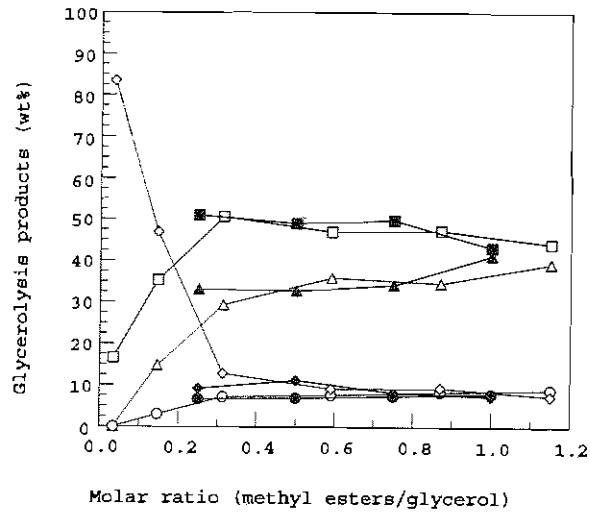

FIG. 3. The effect of variations in reactant concentration on the methyl esters glycerolysis products, subject to continuous purge with nitrogen: (□), monoglycerides; (△), diglycerides; (○), methyl esters; and (◇), glycerol. Solid and open symbols indicate pure and crude glycerol, respectively.

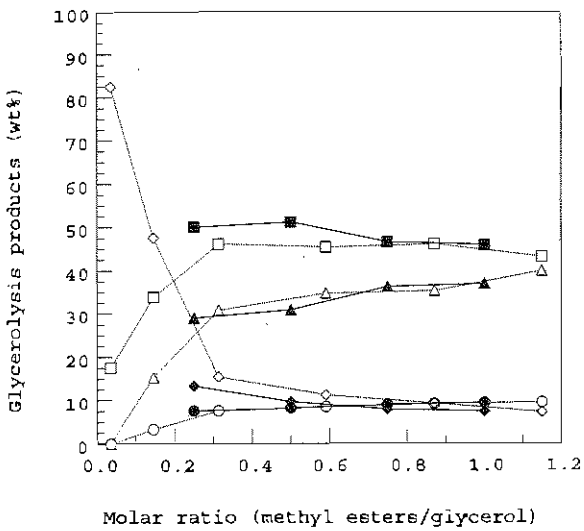

FIG. 2. The effect of variations in reactant concentration on methyl esters glycerolysis products, subject to vacuum distillation: (□), monoglycerides; (△), diglycerides; (○), methyl esters; and (◇), glycerol. Solid and open symbols indicate pure and crude glycerol, respectively.

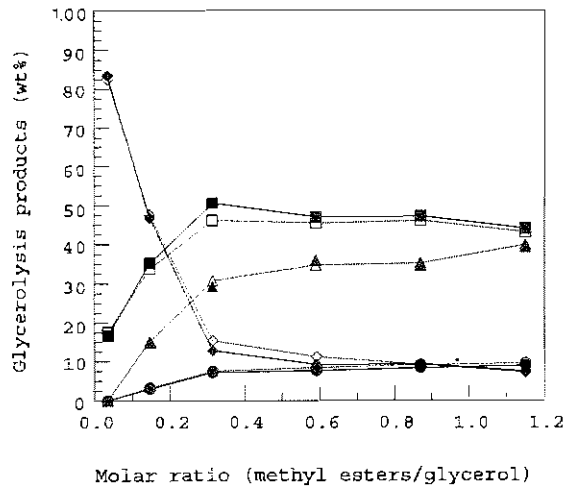

FIG. 4. The effect of variations in reactant concentration on the methyl esters glycerolysis products with crude glycerol: (□), monoglycerides; (△), diglycerides; (○), methyl esters; and (◇), glycerol. Solid and open symbols indicate vacuum distillation and continuous purge with nitrogen, respectively.

Figures 4 and 5 show that the reactions under constant nitrogen purge were slightly lower in the concentration of MG and DG than reactions under vacuum distillation. This may have been due to the reversibility of the glycerolysis reaction and the fact that vacuum is more effective in removing methanol from the reaction medium than continuous nitrogen purge. Consequently, equilibrium conditions at larger product concentrations are reached when vacuum distillation is used. However, because the reaction temperature was relatively high (200–240°C), the shift in equilibrium concentrations was not significant.

The technical MG are not pure monoesters, but a mixture of MG, DG, triglycerides, and glycerol. The percentage of MG is of particular importance in the mixture, because of its emulsification properties. Moreover, pure MG find many uses in the food industry. Therefore, for the purpose of comparing quality of the glycerolysis products, the ratio of MG to DG (RMD) was considered. This ratio will provide a convenient parameter for analysis and comparison of results.

The effect of the initial ME concentration on RMD was examined next. At the lower ratios of ME to glycerol, the product is more concentrated in MG. The product is primarily MG at 0.035:1.0 ratio. This is consistent with the collision theory and the probability of collision between functional groups. For all experiments (Figs. 2–5), when the molar ratio of ME to glycerol was increased, the RMD decreased. The RMD results are summarized in Figure 6 for all four sets of experiments. Compared to our reference point for fat glycerolysis with pure glycerol, which resulted in an RMD of 1.39, RMD values for the glycerolysis of ME were much higher at the lower ME concentrations. This characteristic makes RMD a reaction variable in ME glycerolysis, rather than a fixed parameter in fat glycerolysis.

Procedure B. The reaction products from glycerolysis of ME (Procedure A) were considered for further glycerolysis with TG. In the previous section, it was shown that glycerolysis under vacuum distillation results in a slightly higher product formation than reactions under continuous purge with nitrogen. Therefore, the product from Procedure A under vacuum distillation, for which the initial molar ratio of ME to glycerol varied from 0.035:1.0 to 0.313:1.0, was considered in these experiments. The reaction results are summarized in Figure 7. When an initial molar ratio of 0.035:1.0 was used in Procedure A, the composition of the final products from Procedure B was identical to one-step fat glycerolysis with pure glycerol, and no significant amounts of ME were detected in the final products. When larger concentrations of ME were used in the initial step (Procedure A), the concentration of MG was slightly lower in the products than for one-step fat glycerolysis with pure glycerol. For these experiments, the unreacted ME from Procedure A appeared unchanged in the final product. This was expected because the glycerolysis of ME is reversible and tends to reach and stay at equilibrium if at least one of the reaction products (preferably methanol) is not removed from the reaction medium. The calculated RMD was also comparable to one-step fat glycerolysis with pure glycerol.

Procedure C. The reaction results for one-step glycerolysis of crude glycerol with TG under vacuum distillation (Procedure C) are also shown in Figure 7 (shaded marks). The molar ratio of ME to glycerol in this experiment was 0.035:1.0. Compared to Procedure B, the reaction products from Procedure C were much lower in concentrations of MG and DG. The amount of unreacted ME was also higher than the results from Procedure B, which showed no unreacted ME in the product. This may be due to the higher solubility of ME in TG. With the transfer of ME to the glycerides layer, additional resistance for the diffusion of ME through the TG layer

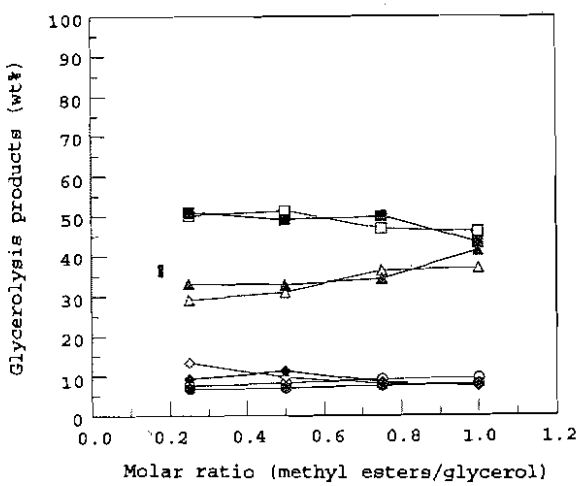

FIG. 5. The effect of variations in reactant concentration on the methyl esters glycerolysis products with pure glycerol: (□), monoglycerides; (△), diglycerides; (○), methyl esters; and (◇), glycerol. Solid and open symbols indicate vacuum distillation and continuous purge with nitrogen, respectively.

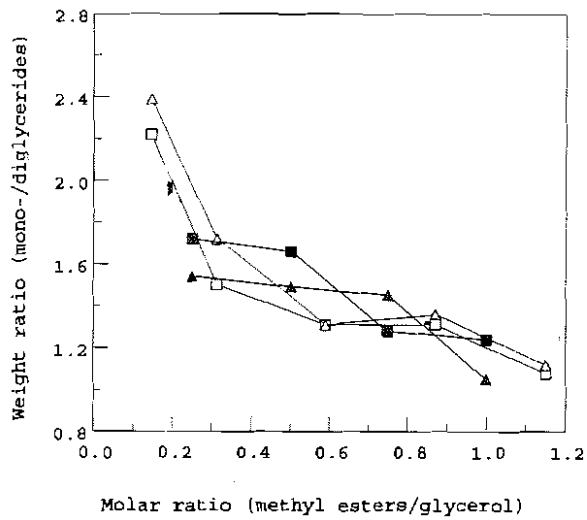

FIG. 6. The effect of variations in the reactants' concentrations on the ratio of mono- to diglycerides: (□), vacuum distillation; (△), continuous purge with nitrogen. Solid and open symbols indicate pure and crude glycerol, respectively.

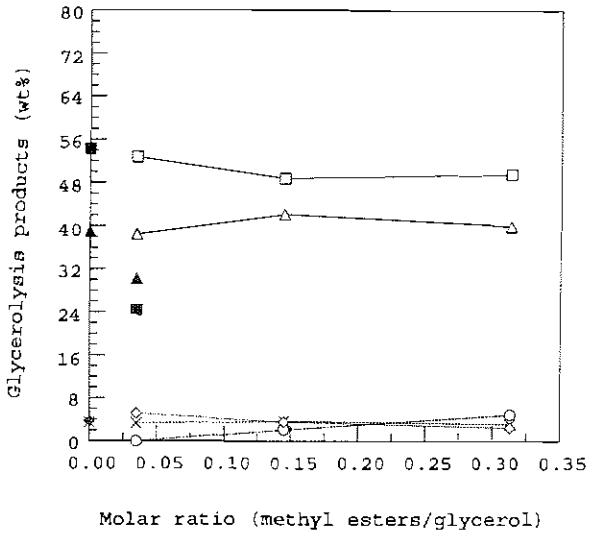

FIG. 7. Fat glycerolysis products for pure glycerol and partially reacted glycerol with methyl esters: (□), monoglycerides; (△), diglycerides; (○), methyl esters; (◇), glycerol and (×), triglycerides. Solid and open symbols indicate pure and crude glycerol, respectively. Shaded marks indicate the one-step glycerolysis of crude glycerol.

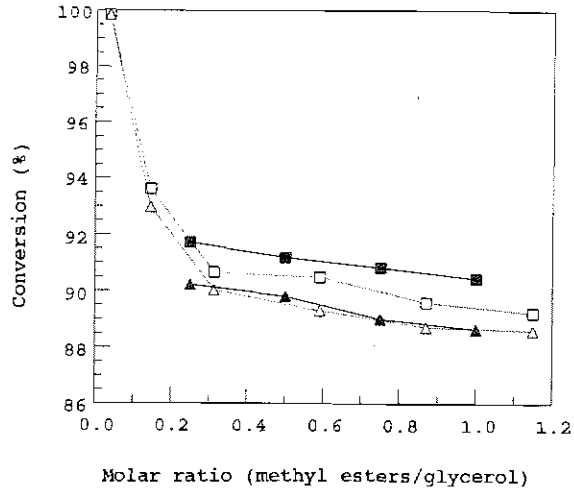

FIG. 8. The effect of variations in reactant concentration on the conversion of methyl esters: (□), vacuum distillation; (△), continuous purge with nitrogen. Solid and open symbols indicate pure and crude glycerol, respectively.

is created. This slows down the simultaneous glycerolysis of ME along with the fat glycerolysis.

Conversions. Conversions for the glycerolysis of ME (procedure A) were based on the initial amount of ME. Percentage conversion as a function of the molar ratio of ME to glycerol is presented in Figure 8. The overall conversion of ME was about 92%, at a 0.25:1.0 molar ratio of ME to glycerol, and showed a slight decrease as this ratio was increased. At lower concentrations of ME, conversion was higher. Conversion was about 94% at 0.145:1.0 and approached 100% at 0.035:1.0 molar ratio of ME to glycerol. In general, experimental conditions involving vacuum distillation resulted in a slightly higher conversion than experiments with continuous nitrogen purge, and pure glycerol resulted in slightly better conversion than crude glycerol.

Conversions for the glycerolysis of TG (Procedure B) were based on the amount of TG. In Procedure B, the products from Procedure A under vacuum distillation, for which the initial molar ratio of ME to glycerol varied from 0.035:1.0 to 0.313:1.0, were considered. Therefore, conversions of TG as a function of the initial ratio of ME to glycerol were considered. The results are presented in Figure 9. The conversion for a one-step reaction with pure glycerol is also included as a point on the y axis in this figure. This point indicates 0% for the initial concentration of ME. This figure shows that the initial presence of ME has no significant effect on fat glycerolysis when crude glycerol is used, provided that the ME are converted to MG and DG prior to fat glycerolysis.

In conclusion, glycerolysis of ME and TG was studied with crude glycerol, a coproduct from the transesterification of TG. Three procedures were examined. Procedure A was a one-step glycerolysis with ME. Procedure B was a two-step sequential glycerolysis, first with ME and then with TG. Procedure C was a two-step simultaneous glycerolysis with ME and TG.

Different molar ratios of ME to glycerol were examined in the glycerolysis of ME. At low concentrations of ME, complete conversion of ME to MG and DG was achieved. As the concentration of ME was increased, the conversion of ME to MG and DG decreased. The RMD was also higher at lower concentrations of ME. The conversion of TG in the two-step process (Procedure B) with crude glycerol was similar to a one-step fat glycerolysis with pure glycerol. The composition of different components and the RMD were also comparable.

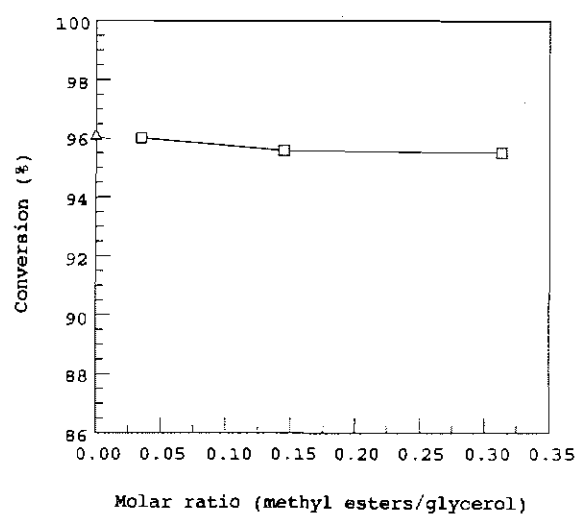

FIG. 9. The effect of the initial presence of methyl esters on the overall conversion in methyl esters and fat glycerolysis: (□), vacuum distillation; (△), pure glycerol.

Simultaneous glycerolysis with ME and TG (Procedure C) resulted in a significant reduction in the amount of MG and DG.

The experimental investigations are conclusive in that the glycerolysis of ME is an effective technique for the conversion of ME to MG and DG. When crude glycerol with a low concentration of ME is considered, glycerolysis of ME may be performed prior to fat glycerolysis or as a single step. Glycerolysis of ME occurs at considerably lower temperature, 200–210°C, compared to about 240–260°C for fat glycerolysis, which may result in significant thermal energy savings.

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