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# Biodiesel Fuel from Animal Fat. Ancillary Studies on Transesterification of Beef Tallow

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**Abstract**
Transesterification of beef tallow was investigated. The solubility of ethanol in beef tallow was much higher than that of methanol. At 100 °C the solubility of methanol was 19% (w/w). The solubility of ethanol in beef tallow reached 100% (w/w) at about 68 °C. For the distribution of methanol between beef tallow methyl esters (BTME) and glycerol, the percentage of total methanol in the glycerol phase was higher than that in the fatty acid methyl ester (FAME) phase in a simulated system at room temperature. At 65-80 °C, however, the percentage of total methanol in FAME (60% (w/w)) was higher than that in glycerol (40% (w/w)) in a 90:10 (w/w) blend of FAME and glycerol. This coincided with the methanol distribution in the transesterified product. The process for making beef tallow methyl esters should recover methanol using vacuum distillation, separate the ester and glycerol phases, and then wash the beef tallow methyl esters with warm water. At neutral pH, the separation of ester and glycerol and water washing was easier because it reduced emulsion formation.

## Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources, vegetable oils and animal fats. It is biodegradable and nontoxic and has low emission profiles.[1] Fatty acid methyl esters (FAME) can be used neat as biodiesel fuel or can be used as an additive or extender to diesel fuel. Transesterification or alcoholysis (i.e., methanolysis) is used to convert triglycerides to FAME. Transesterification of vegetable oils has been studied extensively.[2-6] However, transesterification of beef tallow has not been studied as extensively as vegetable oils for making FAME.

Obstacles to commercialization of biodiesel are the prices of raw materials and the operating costs.[1,7,8] The overall process includes transesterification, recovery of unreacted methanol, separation of glycerol and FAME, recovery of glycerol as a high-grade co-product, and purification of FAME. Hassett and Hasan[9] presented a process for producing FAME and Kreutzer[10] presented a flow diagram for manufacturing methyl esters. This paper reports basic studies conducted on beef tallow to determine an efficient production scheme, which also would be applicable to other transesterification processes. The solubilities of methanol and ethanol in beef tallow and the distribution of methanol between beef tallow methyl ester (BTME) and glycerol phases were investigated to optimize the process and lower the operating costs.

## Experimental Section

**Materials.** Edible beef tallow was received gratis from Excel Corp. (Schuyler, NE). Anhydrous methanol (S/P) and anhydrous ethanol (S/P) were purchased from Baxter Diagnostics, Inc. (Deerfield, IL). White glycerol (USP grade) was purchased through Chemical Stores, University of Nebraska (Lincoln, NE). Sodium methoxide (OR) was purchased from Mallinckrodt Chemical, Inc. (Paris, KY). Sodium hydroxide (GR pellets) was purchased from EM Science (Gibbstown, NJ). Acetic acid glacial (Reagent A.C.S.) was purchased from Fisher Scientific (Fair Lawn, NJ).

**Solubility Measurement.** The temperature of the water bath was set to the desired temperature. A 15 g sample of beef tallow was weighed into a 40 mL clear borosilicate vial with a 3 mm Septa liner (VWR Scientific, West Chester, PA). Then, 1 g of methanol or ethanol was added. After that, additional alcohol was added drop by drop, not more than 0.10 g at a time. The vial was capped and put into the water bath for 20 min, after which the vial was removed from the water bath and shaken vigorously. The vial was returned to the water bath for another 30 min. If the mixture became a single phase (clear), meaning the methanol or ethanol was dissolved in the beef tallow, the vial was cooled. A few more drops of the alcohol were added, and the vial was again capped and put back into the water bath at the same temperature. This was repeated until the beef tallow was saturated with alcohol. The amount of alcohol dissolved at this point was used to calculate the maximum solubility of the alcohol at that temperature. The temperature of the water bath was raised sequentially to higher levels, and the procedure was repeated to obtain the solubility curves over the temperature range of 45–100 °C.

**Distribution of Methanol.** There were two parts to this experiment. One was the simulation of the distribution of methanol in both BTME and glycerol at room temperature. Another was mea-
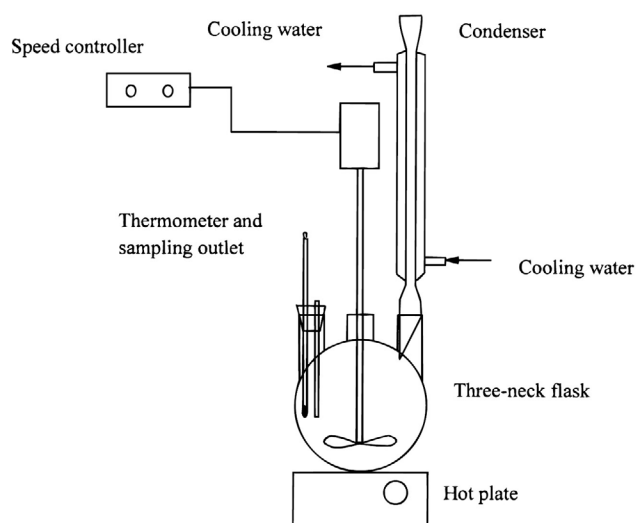
**Figure 1.** Transesterification batch reactor apparatus.



**Figure 2.** Solubility of methanol in beef tallow.

suring the distribution of methanol in the products of the transesterification of beef tallow.

Ratios of methyl esters to glycerol from 100:0 to 0:100 (w/w) at 10 unit intervals were used to examine the distribution of methanol between the phases at 25 °C. The amounts of BTME and glycerol were 35 and 15 g, respectively. A 125-mL Pyrex separatory funnel was used to separate the two phases. The separatory funnel was weighed and the methyl esters, glycerol, and methanol were added separately and weighed. The funnel was stoppered and shaken for 5 s to mix it completely. Then it was allowed to settle for 2 h. The two phases were separated. The fractions were weighed. The differences in the weights of BTME and glycerol phases were taken to be the amounts of methanol dissolved in each phase. This amount of methanol was divided by the total amount of methanol to obtain the distribution of methanol in that phase.

The transesterification products were cooled to room temperature. The ester and glycerol phases were separated by separatory funnel and weighed. They were distilled under vacuum, supplied by a water pump, at the boiling point of the solution, which ranged from 30 to 80 °C. The weights were recorded, and the distribution of methanol in each phase was calculated.

**Transesterification.** Beef tallow was melted and weighed into a 1000-mL three-neck distillation flask. The flask was assembled with a condenser, an adjustable speed mechanical stirrer, and a thermometer (Figure 1). The beef tallow was heated to 65 °C on a hot plate. In the meantime, 0.3–0.5% of NaOH or NaMeO, on the weight basis of beef tallow, was dissolved in methanol, and the mixture added to the tallow in a 6:1 molar ratio. The overall mixture was heated to its boiling point (62–65 °C) to start the reaction. After 20–45 min the reaction was stopped by adding acetic acid to neutralize the catalyst. The heating and stirring were stopped. The flask was removed from the hot plate, and the products of the reaction were settled. The two phases, glycerol and BTME, were distilled under vacuum and then separated in a separatory funnel. Glycerol was purified using an existing industrial method.[11] Because of the high content of glycerol (>90%), the crude glycerol did not need to be concentrated as it does in a soap or fat splitting process. Glycerol was purified by filtration, deodorized under high vacuum by blowing steam into it, and bleached with activated carbon.
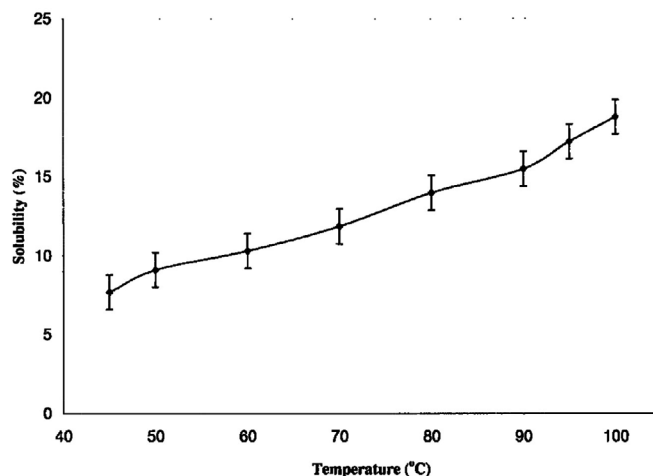
**Purification of BTME.** The purification of the BTME included washing with water, removing the water, and winterizing the esters. An equal amount of warm water (50-70 °C) was used to wash the BTME twice. The washed BTME was distilled under vacuum, over the temperature range of 30–80 °C, and then held at 80 °C for 10 min to remove residual water. The BTME was winterized at 20 °C for 24 h to separate the monoglycerides and diglycerides.

## Results and Discussion

The solubilities of methanol and ethanol in beef tallow at different temperatures were studied. Methanol was less soluble in beef tallow than was ethanol. At 45 °C, the solubility of methanol was about 8% (w/w). With an increase in temperature, the solubility increased at the rate of 2–3% (w/w) per 10 °C and reached 19% (w/ w) at 100 C. At the generally recommended transesterification reaction temperature of 65-80 C, the solubility was 11–13% (w/w).

Because methanol, which has one hydroxy group, is polar and beef tallow, a triglyceride, is nonpolar, methanol does not dissolve readily in beef tallow at low temperatures and can be only partially dissolved in beef tallow even at higher temperatures. Figure 2 shows the solubility of methanol in beef tallow at different temperatures.

Ethanol was highly soluble in beef tallow. At 45 °C, its solubility was about 24% (w/w). Above 60 °C, the solubility of ethanol increased rapidly. At 68 °C, the solubility of ethanol in beef tallow was 100% (w/w). Ethanol has one more carbon in its hydrophobic chain than does methanol, so it is less polar than methanol and more soluble in beef tallow. Figure 3 shows the solubility of ethanol in beef tallow at different temperatures. The results are similar to the solubility of ethanol in peanut oil.[12]

For the transesterification of beef tallow with methanol, stirring was necessary to mix the two phases well and to increase the reaction areas between the two phases. During the progress of the reaction, some intermediates, such as monoglycerides and diglycerides, were formed and acted as emulsifiers. Then the two immiscible liquids formed a relatively stable emulsion system. From that time on, the stirring can be stopped to allow the glycerol and ester phases to separate, while the transesterification process is still going on. Because of the removal of glycerol from the reaction system, the
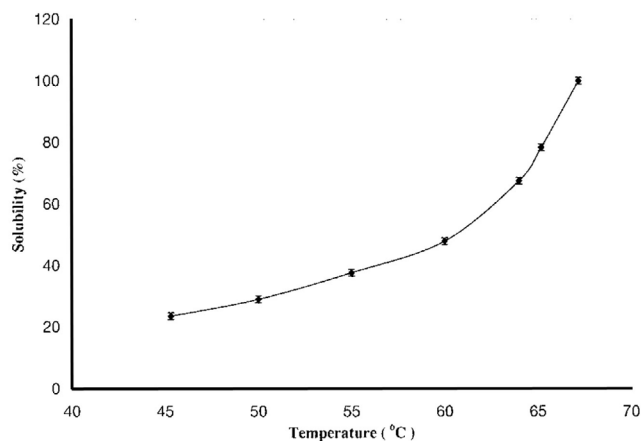
**Figure 3.** Solubility of ethanol in beef tallow.



**Figure 4.** Transesterification of beef tallow with methanol.

equilibrium of the transesterification reaction goes to the products side and increases the reaction rate and the yield of beef tallow esters. The experimental results showed that the BTME yield of this process was not significantly different from that obtained with continuous stirring during the reaction ($p < 0.1494$).

Because ethanol dissolved completely in beef tallow at reaction temperature, stirring was not necessary during the transesterification reaction. Avoiding stirring not only reduces the power consumption but also increases the yield of methyl esters. Since the glycerol produced is denser, it separates from the reaction system, shifting the equilibrium to the products side.

After the transesterification reaction, the use of acetic acid is recommended to neutralize the alkali and stop the reaction. In addition, neutralization makes the water washing easier. Without acid neutralization, an emulsion is formed during water washing, making the separation of the oil and water phases more difficult. This results in either a longer separation time or loss of some of the methyl esters, both of which increase the production cost. The neutralization procedure also can make the separation of BTME and glycerol phases easier. When the catalyst is neutralized, glycerol immediately separates from the BTME phase.

In the transesterification, excess methanol is used to shift the reaction equilibrium to the products side and produce more methyl esters. The stoichiometry of the transesterification of beef tallow requires three molecules of methanol to react with one molecule of triglyceride of beef tallow (Figure 4). Usually, the reaction uses a molar ratio of 6:1 methanol/triglyceride. After the reaction is finished, about half of the methanol is unreacted. It is necessary to know how the methanol is distributed between the ester and glycerol phases in order to set up an efficient separation process. In the reaction products, the ratio of methyl esters to glycerol is about 90:10, and the ratio of unreacted methanol to glycerol is about 51:49. These ratios are important for transesterification.

In this study, pure beef tallow methyl esters (BTME), glycerol, and methanol were used. The experiment was conducted at 25 °C. Methanol was dissolved in pure BTME or glycerol (100% w/w) at room temperature. However, when methanol was mixed with BTME and glycerol, it was distributed differently between them. Table 1 shows that the distribution of methanol between BTME and glycerol changed with the ratio of these two components. With the increase of the ratio of BTME to glycerol, the percentage of total methanol
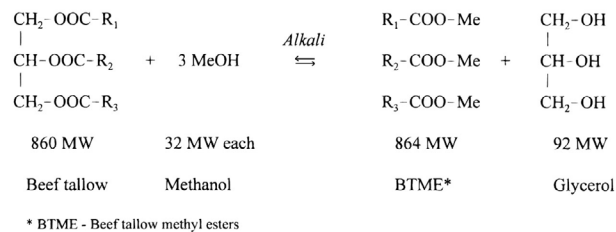
in glycerol decreased and that in BTME increased. At a 90:10 (w/w) ratio of BTME to glycerol, 40% (w/w) of the methanol dissolved in the BTME phase and 60% (w/w) of the methanol dissolved in the glycerol phase. At a 50:50 ratio of BTME to glycerol, 9% (w/w) of the methanol dissolved in the BTME phase and 91% (w/w) of the methanol dissolved in the glycerol phase. As the ratio increased, the mass fractions of methanol in BTME and glycerol increased from 0.03 to 0.12 and 0.25 to 0.65, respectively. The corresponding mole fractions of methanol in BTME and glycerol increased from 0.24 to 0.55 and 0.49 to 0.85, respectively. The differences between the mole fractions of methanol in BTME and glycerol were almost constant at about 0.21. The mole distribution coefficients of methanol between the two phases were in a range of 0.45–0.67.

Methanol and glycerol are polar molecules, while BTME is a nonpolar molecule. When they were mixed, methanol preferentially dissolved in glycerol and only a small amount dissolved in BTME. Because the glycerol was not saturated with methanol, a decrease in the amount of glycerol in the mixture resulted in an increase in the mass or mole fraction of methanol in the glycerol. Because there was less glycerol to compete with the BTME for the methanol, more methanol went into the BTME phase, which made the mass or mole fraction of methanol in BTME increase slightly.

In transesterification of the beef tallow with methanol, 90% (w/w) BTME and 10% (w/w) glycerol were produced. The unreacted methanol was almost the same amount as that of the glycerol produced. The results of the experiments showed that about 60% of the unreacted methanol was in the BTME phase and 40% was in the glycerol phase.

To determine what makes the difference, an experiment was conducted using 90:10 (w/w) methyl esters to glycerol. The amounts of methanol and glycerol used were the same. This was to simulate the system of transesterification products, except that pure BTME, glycerol, and methanol were used. This mixture was heated to the reaction temperature, refluxed for 10 min, cooled to room temperature, and separated. Distillation under vacuum showed 60% of the methanol was in the BTME and 40% of the methanol was in the glycerol. It appeared that temperature was the main factor in determining the distribution of methanol in the two phases.

At the recommended transesterification reaction temperature (65–80 °C), methanol molecules become very active and some of them go into the BTME phase. Because of their polarity some glycerol molecules also go into the BTME phase. This causes even more methanol to go into the BTME phase. This will repeat until the limit of methanol in BTME is reached. When the mixture cools to room temperature, the molecules do not go back into the glycerol phase immediately. Even though some glycerol molecules go back into the glycerol phase after setting for several hours, methanol does not go with it. It was concluded that although methanol

**Table 1.** Distribution of Methanol between BTME and Glycerol

| ratio of BTME to glycerol | MeOH (g) | | MeOH (%) | | mass | | | mole | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | BTME | glycerol | BTME | glycerol | $M_B$ | $M_G$ | $m$ | $X_B$ | $X_G$ | $x$ |
| 0:100 | 0.00 | 15.21 | 0.00 | 100.00 | | 0.23 | | | 0.47 | |
| 10:90 | 0.18 ± 0.03 | 14.94 ± 0.38 | 1.19 | 98.81 | 0.03 | 0.25 | 0.14 | 0.24 | 0.49 | 0.50 |
| 20:80 | 0.37 ± 0.04 | 14.73 ± 0.35 | 2.45 | 97.55 | 0.04 | 0.27 | 0.13 | 0.25 | 0.51 | 0.48 |
| 30:70 | 0.56 ± 0.06 | 14.54 ± 0.35 | 3.71 | 96.29 | 0.04 | 0.29 | 0.12 | 0.25 | 0.54 | 0.46 |
| 40:60 | 0.87 ± 0.05 | 14.25 ± 0.34 | 5.75 | 94.25 | 0.04 | 0.32 | 0.13 | 0.28 | 0.58 | 0.49 |
| 50:50 | 1.38 ± 0.08 | 13.78 ± 0.34 | 9.10 | 90.90 | 0.05 | 0.35 | 0.15 | 0.33 | 0.61 | 0.54 |
| 60:40 | 2.13 ± 0.11 | 13.00 ± 0.28 | 14.08 | 85.92 | 0.07 | 0.39 | 0.17 | 0.39 | 0.65 | 0.60 |
| 70:30 | 2.94 ± 0.12 | 12.15 ± 0.27 | 19.48 | 80.52 | 0.08 | 0.45 | 0.17 | 0.43 | 0.70 | 0.61 |
| 80:20 | 4.02 ± 0.12 | 11.11 ± 0.25 | 26.57 | 73.43 | 0.09 | 0.52 | 0.17 | 0.47 | 0.76 | 0.62 |
| 90:10 | 6.03 ± 0.15 | 9.16 ± 0.21 | 39.70 | 60.30 | 0.12 | 0.65 | 0.18 | 0.54 | 0.84 | 0.65 |
| 100:0 | 15.16 | 0.00 | 100.00 | 0.00 | 0.23 | | | 0.73 | | |

The experiment was conducted at room temperature (25 °C).
$M_B$, $X_B$, mass and mole fraction of MeOH in BTME, respectively.
$M_G$, $X_G$, mass and mole fraction of MeOH in glycerol, respectively.
$m$, $x$, mass and mole distribution coefficient, respectively.

can dissolve in pure BTME or glycerol, its polarity was closer to glycerol than to BTME.

The neutralized transesterification products were then distilled under vacuum over a temperature range of 30–75 °C. As the methanol was distilled off, the boiling point of the mixture increased. About half of the methanol added to the reaction system should be recovered in this way. After this operation, the glycerol can be efficiently separated from the methyl ester phase by gravitational settling. If the glycerol is separated before the methanol is removed, there are two disadvantages. One is there is a certain amount of glycerol remaining in the BTME, lowering the recovery rate of glycerol. The other is that an additional distillation operation is needed to recover the methanol, which increases the operating cost.

The salt produced from the acid neutralization was removed as a precipitate with the glycerol phase. The specific gravity of the salt was slightly lower than that of glycerol, so it was on top of the glycerol phase. The salt can be removed from glycerol subsequently by filtration or centrifugation.

The BTME was washed with an equivalent volume of warm water by weight. Washing two times was enough to remove the impurities from the BTME. The washed BTME was distilled under vacuum at 30–80 °C. If necessary, they were held at 80 °C for 10 min to remove trace moisture. The BTME yield using this method was 97–99%.

The process, as shown in Figure 5, summarizes the discussions above. This process can lower energy consumption and is more efficient. Because of the very low solubility of methanol in beef tallow, the transesterification of beef tallow and methanol required mixing to initiate the reaction. Once the reaction was started, mixing was no longer necessary. The distribution of unreacted methanol in BTME and glycerol determined the sequence of downstream operations. Recovery of methanol before separation of BTME from glycerol makes the process more efficient. Neutralization of the catalyst made the phase separation and water washing easier. Another way to lower the production cost is to recover the glycerol as a high-grade coproduct.

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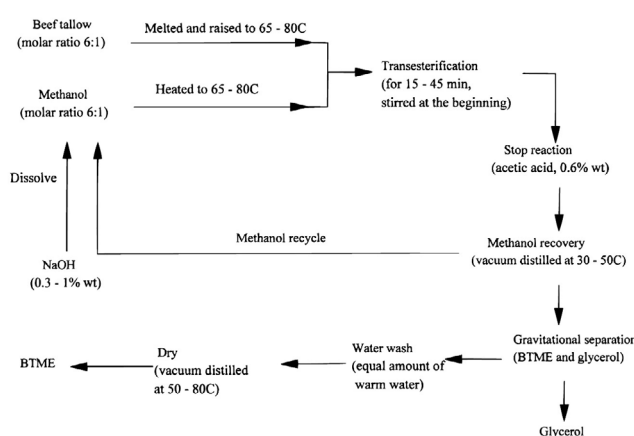
**Figure 5.** Flow sheet of transesterification of beef tallow.

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