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THE EFFECTS OF CATALYST, FREE FATTY ACIDS, AND WATER ON TRANSESTERIFICATION OF BEEF TALLOW

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ABSTRACT. *Transesterification of beef tallow and methanol is affected by many factors. Catalyst, free fatty acids, and water in beef tallow, and reaction time were investigated. Sodium hydroxide (NaOH) was a more effective catalyst than sodium methoxide (NaMeO). NaOH and NaMeO reached their maximum activities at 0.3% and 0.5%, w/w of beef tallow, respectively. The presence of water had more negative effect on transesterification than did the presence of free fatty acids (FFA). For best results, the water content of beef tallow should be kept not beyond 0.06%, w/w. FFA content of beef tallow should be kept below 0.5%, w/w. The transesterification of beef tallow was very slow in the first minute. The production of beef tallow methyl esters (BTME) was complete after about 15 min. There were still some mono- and diglycerides in the BTME phase after the reaction was finished. **Keywords.** Biodiesel, Transesterification, Beef tallow.*

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, and has low emission profiles compared to petroleum diesel (Krawczyk, 1996). Fatty acid methyl esters (FAME) can be used as biodiesel fuel or can be used as an additive or extender to diesel fuel. Transesterification or alcoholysis (i.e., methanolysis) is commonly used to convert triglycerides to FAME. Transesterification of vegetable oils has been studied extensively (Bradshaw and Meuly, 1944; Freedman et al., 1984; Freedman et al., 1986; Kildiran et al., 1996; Schwab et al., 1987).

Transesterification is influenced mainly by catalyst, molar ratio of alcohol to triglycerides, mixing, free fatty acids, water content and reaction time. Generally, molar ratios of methanol to triglyceride used have been in the range of 5.25-6:1. Bradshaw and Meuly (1944) reported that a molar ratio greater than 5.25:1 affected the separation of FAME and glycerol phases. Freedman et al. (1984) suggested that, for maximum yield of FAME, a molar ratio of 6:1 should be used. He also noted that molar ratios greater than 6:1 did not increase the yields of FAME, complicated the recovery of FAME and glycerol, and increased the cost of alcohol recovery.

There are two kinds of catalyst, alkali and acid. Alkali catalysts were more effective (Freedman et al., 1984). NaMeO was more effective than NaOH because a small amount of water was produced upon mixing NaOH and MeOH (Liu, 1994). Wright et al. (1944) noted that the glycerides should have an acid value less than 1, and all materials should be substantially anhydrous. More NaOH was required to neutralize the free fatty acids (FFA) if the acid value was greater than 1. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency.

Beef tallow was used as a raw material of transesterification to make biodiesel, because the price of edible beef tallow was driven down by the market. The objective of this study was to investigate the effects of catalyst, FFA and water on the transesterification of beef tallow. The changes of FAME, mono-, di- and triglycerides with reaction times also were studied.

MATERIALS AND METHODS

MATERIALS

Rendered, edible beef tallow (water and FFA contents of $0.06 \pm 0.01\%$ and $0.29 \pm 0.01\%$, respectively) was received gratis from Excel Corp. (Schuyler, Nebr.). Anhydrous methanol (S/P) was purchased from Baxter Diagnostics, Inc. (Deerfield, Ill.). Sodium methoxide (GR) was purchased from Mallinckrodt Chemical, Inc. (Paris, Ky.). Sodium hydroxide (GR pellets), was purchased from EM Science (Gibbstown, N.J.). Glacial acetic acid, Reagent A.C.S., was purchased from Fisher Scientific (Fair Lawn, N.J.). The free fatty acid used in the experiment was technical grade oleic acid (Pfaltz & Bauer, Inc., Waterbury, Conn.).

TRANSESTERIFICATION

Beef tallow was melted and weighed into a 1000 mL three-neck distillation flask using a molar ratio of 6:1 of methanol to beef tallow. The flask was assembled with a condenser, an adjustable speed mechanical stirrer, and a thermometer (fig. 1). The beef tallow was heated to 65°C

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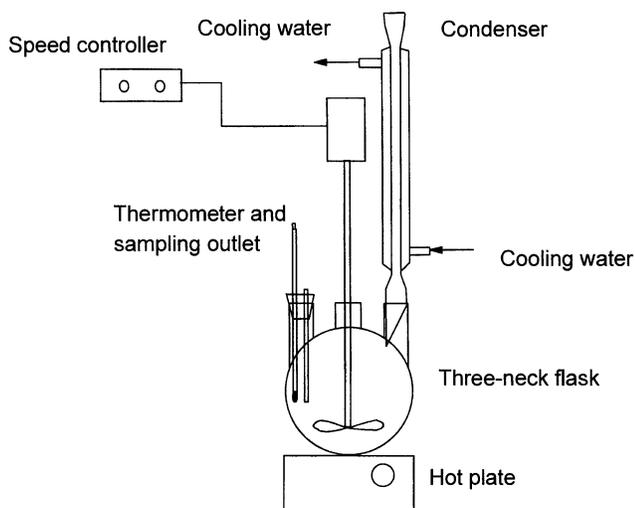
Figure 1–Transesterification batch reactor apparatus.

Hewlett Packard 3396 A Integrator. The capillary column was an Alltech Econo-cap SE-30 column (Deerfield, Ill.), with a length of 30 m, a film thickness of 0.25 μ, and an ID of 0.32 mm. A flame ionization detector was used. The injector and detector temperatures were 350°C. A split mode injector was used with split ratio of 200:1. The oven temperature was programmed from 160 to 350°C at 30°C/min and then was held at 350°C for 25 min. Nitrogen was used as the carrier gas with a flow rate of 200 ml/min and a back pressure of 20 kPa. The run time was 30 min. The 1 μL samples were injected manually.

The response of beef tallow methyl esters (BTME) was used to quantitatively analyze the production of BTME. The response was defined as the sum of the GC peak area of BTME divided by the GC peak area of an internal standard (tricaprin). This procedure eliminated operator error and gave good reproducibility. The response was proportional to the yield of BTME and is referred to as apparent BTME yield in figures 2 through 5.

on a hot plate. In the mean time, NaOH or NaMeO, 0.3 to 0.5% w/w beef tallow, was dissolved in the prescribed amount of methanol. The solution was added to the flask. This mixture was heated to its boiling point (62-65°C) to start the reaction. After 20 to 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. Samples were drawn from the reaction flask for analysis. The sampling position is shown in figure 1.

CATALYST EXPERIMENT

Based on preliminary experiments, both NaOH and NaMeO were used in this experiment. Five levels of each catalyst, 0.1, 0.3, 0.5, 0.7, and 0.9%, w/w of beef tallow, were investigated. There were three replications for each treatment. The other reaction conditions were the same as described in the transesterification section.

THE FFA AND WATER CONTENTS EXPERIMENTS

This was a completely randomized experimental design (CRD) with three replications. The treatment design was 4 × 4 factorial arrangement of treatments (FAT). There were two factors, FFA and water. Based on preliminary experiments, the amounts of FFA added were 0.0, 0.2, 0.4, and 0.6%, w/w of beef tallow. The amounts of water added were 0.0, 0.3, 0.5, and 0.9%, w/w of beef tallow. Transesterifications were conducted as described previously.

REACTION TIME EXPERIMENT

Samples were taken at the beginning of the reaction (0 min) and after 1, 2, 3, 5, 7, 9, 13, 15, 20, 30, 45, and 60 min of reaction. There were two replications. The transesterifications were conducted as described previously.

GAS CHROMATOGRAPHY ANALYSES

Gas chromatography was used to evaluate the conversion efficiencies of the various transesterifications. Analyses were performed using Hewlett Packard 5890 Series II Gas Chromatograph (Avondale, Pa.), and a

RESULTS AND DISCUSSION

EFFECT OF CATALYSTS

The catalyst is an important factor in the transesterification of beef tallow. Alkali catalysts are most commonly used, especially NaOH and NaMeO. Both were used in this experiment.

Figure 2 shows the results of the transesterification of beef tallow with NaOH and NaMeO. When the amount of catalyst was at 0.1% of beef tallow, the yields of BTME were lowest for both catalysts. At 0.3%, however, the yield of BTME reached the maximum value for NaOH, decreased slightly at 0.5%, and then remained relatively constant at higher NaOH contents. The 0.3% level of NaOH was significantly better than the other levels. The transesterification of beef tallow with NaMeO followed a similar trend. The 0.5% level of NaMeO gave the maximum yield. However, the 0.5% level of NaMeO was not significantly different from 0.3% and 0.7%.

Comparing the two catalysts, NaOH was significantly better than NaMeO. This was different from previous reports (Freedman et al., 1984; Hartman, 1956). Part of the difference may be attributable to the differences in the reaction systems used. NaOH was chosen to catalyze the transesterification in the rest of the experiments, because it
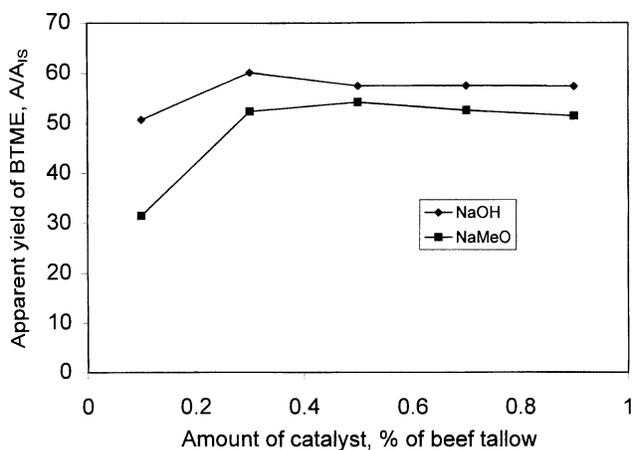

Figure 2–The effect of catalysts on transesterification of beef tallow.

was effective and cheaper. The amount of catalyst used depends upon the qualities of the beef tallow and methanol. If more free fatty acids and water exist in the reactants, more NaOH is needed to neutralize the free fatty acids and react with triglycerides to produce soap. The beef tallow used had a water content of 0.06 ± 0.01% and a free fatty acid content of 0.29 ± 0.01%. The methanol used was anhydrous grade. For such a system, 0.3% NaOH was enough to catalyze the reaction.

EFFECT OF FFA AND WATER

FFA and water contents of beef tallow were important factors in the transesterification. Figure 3 shows the results of the experiment. Table 1 shows the SAS analysis output. The interaction between FFA and water content treatments was significant. This means that when FFA and water were present in the reaction system at the same time, they had a synergistic negative effect on the reaction. The main effects of FFA or water did not reflect the real reaction.

The single effects of FFA content and water contents should be noted. Without adding FFA and water, the
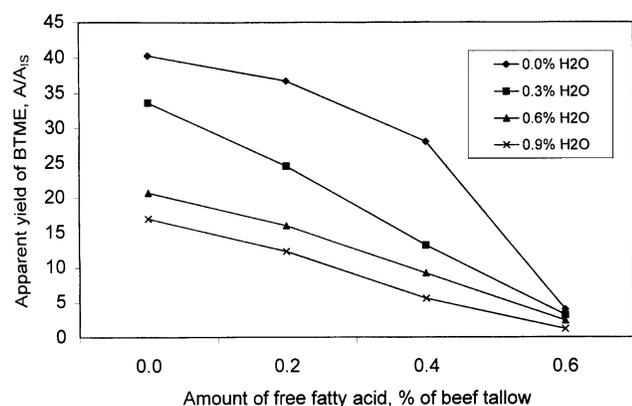

Figure 3–The effects of free fatty acid and water on transesterification of beef tallow.

Table 1. Analysis of variance of the effects of free fatty acids and water on transesterification of beef tallow

Source	df	EMS	F - value	P - Value
Free fatty acids (F)	3	$\sigma^2 + 12\kappa_F^2$	9398.61	0.0001
Water (W)	3	$\sigma^2 + 12\kappa_W^2$	3871.94	0.0001
F × W	9	$\sigma^2 + 3\kappa_{FW}^2$	461.80	0.0001
Error	32	σ^2		
Total	47			

Notes:
1. Model: $Y_{ij} = \mu + F_i + W_j + (F \times W)_{ij} + e_{ij}$
   i - 0.0 , 0.2 , 0.4 , and 0.6% (w/w)
   j - 0.0 , 0.3 , 0.6 , and 0.9% (w/w)
   Y_{ij} - dependent variable, the apparent yield of BTME.
   μ - the overall mean of the apparent yield.
   F_i - the effect of ith level on response.
   W_j - the effect of jth level on response.
   $(F \times W)_{ij}$ - the effect of level i and level j on the response.
   e_{ij} - the error term of level i and level j.
2. Assumption:
   $e_{ij} \sim$ iid $N(0, \sigma^2)$.
3. $\alpha = 0.05$.
4. df = degree of freedom.

apparent yield of BTME was highest. When 0.6% of FFA was added, the apparent yield of BTME reached the lowest, less than 5, with any level of water added. The products were solid at room temperature, similar to the original beef tallow. When 0.9% water was added, without addition of FFA, the apparent yield was about 17. The apparent yield decreased with the increase of the amount of FFA added, and reached the lowest point with 0.6% FFA.

For transesterification with NaOH, any addition of water beyond the 0.06% inherent in the tallow will significantly reduce the ester yield. Additionally, FFA level added to the beef tallow needs to be kept below 0.2%. Because the original FFA content in the beef tallow was 0.29%, the FFA content needs to be kept below 0.5%. If low quality beef tallow and cooking oils are used to make biodiesel fuel, they must be refined by saponification using a NaOH solution to remove free fatty acids because of their high FFA contents. The refined beef tallow and cooking oils then can be transesterified to make biodiesel fuel. Otherwise, the acid catalyzed process (Freedman et al., 1984), a high pressure process known as the Henkel process (Kreutzer, 1984), or the Lion Corporation's ES process (Ogoshi and Miyawaki, 1985) can be used. Acid catalysts are well known for their slow rates and lower conversions. The Henkel's process uses 9000 kPa pressure and 240°C, so that FFA can be converted to fatty esters with alkali catalysts. In the ES process, FFA in oils and fats are esterified before the oils and fats are transesterified with alkali. The FFA are converted into methyl esters by passing the acid containing oils or fats through a packed column of a special catalyst resin. The later two processes require low water content oils and fats.

EFFECT OF REACTION TIME

Figure 4 shows the changes in apparent yield of BTME with reaction time. The reaction was very slow during the first minute. From 1 to 5 min, the apparent yield of BTME surged from 1 to 38. Then the production of BTME slowed down and reached the maximum value at about 15 min. There was very little additional BTME produced after 15 min.

The initial delay was due to the mixing and dispersion of methanol into beef tallow. Since the reaction only happened on the interface of methanol and beef tallow, the more the surface area, the faster the reaction. The reaction yielded diglycerides, monoglycerides and BTME. Di- and
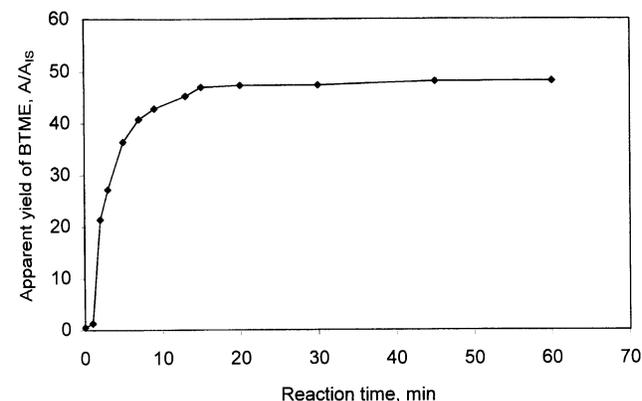

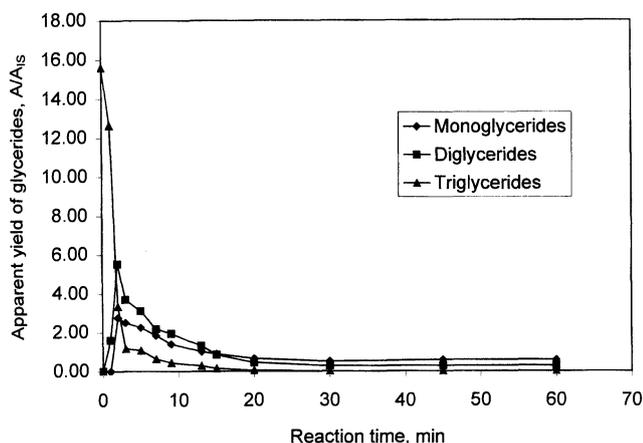Figure 4–The changes of BTME production with reaction time.

Figure 5–The changes of glycerides with reaction time.

monoglycerides are good emulsifiers, which with the mixing made the two immiscible phases become a stable emulsion. Then the reaction proceeded very quickly to its end point.

The transesterification was adaptable to a continuous process, because of its fast reaction rate. Using a batch process will frequently require repeating some operations, such as adding reactants and separating glycerol in a short time. Obviously, this increases the operating cost. A continuous process could increase recovery rates of BTME and glycerol due to the elimination of wastes in the batch reactor.

The changes of glycerides (mono-, di-, and triglycerides) with reaction time is shown in figure 5. After 1 min, the apparent yield of triglycerides decreased from 15.60 to 12.64, that of diglycerides increased from 0 to 1.60, and that of monoglycerides, remained at zero. After 2 min, the apparent yield of triglycerides decreased to 3.34, those of di- and monoglycerides were at their maximums of 5.53 and 2.76, respectively. After that, the apparent yields of tri-, di- and monoglycerides decreased with increases in reaction time. After 30 min, there were no triglycerides detected and the di-, and monoglycerides were present in the reaction system at 0.28 and 0.51, respectively.

In the reaction, triglycerides reacted with methanol to first produce diglycerides, BTME and no monoglycerides. Then more triglycerides reacted, and more di- and monoglycerides and BTME were produced. Eventually, tri-, di- and monoglycerides decreased to their lowest levels and BTME increased to its highest level. This pattern was similar to that reported for transesterification of soybean oil and butyl alcohol (1:30 molar ratio) with 1% of H_2SO_4, except that the latter required a longer reaction time (Freedman et al., 1986). The pattern, however, was different from that of transesterification of sunflower oil and ethanol (1:6 of molar ratio) with alkali catalyst (Freedman et al., 1984) and peanut oil and ethanol (3:1, w/w) with NaOH (Feuge and Gros, 1949).

There were more monoglycerides than diglycerides in the BTME phase. The mono- and diglycerides will form crystals in the BTME, even at room temperature. To improve the low temperature properties of biodiesel fuel, first these mono- and diglycerides should be removed. Then, if possible, some saturated fatty acid methyl esters should be removed. The preliminary results showed that after the removal of mono- and diglycerides crystals by winterization and filtration, the cloud point of the BTME was 9°C and pour point was 6°C.

CONCLUSIONS

Transesterification of beef tallow and methanol is affected by many factors. Catalyst, FFA and water in beef tallow, and reaction time were investigated in this article. Because the catalyst activity of NaOH was greater than that of NaMeO and because it was cheaper, it was chosen to catalyze the transesterifications. Both FFA and water in beef tallow inhibited its transesterification. The presence of water had a more negative effect on the transesterification than FFA. There was a synergistic effect when both FFA and water were present in the reaction system. Reaction time replaced the effect of mixing when the two reactants became homogenous in a very short time. Within the range of reaction conditions used, given enough time, high yields of BTME were obtained.

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