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Utilizing the 3/27 Conversion Test to Measure the Effects of Temperature on the Base-Catalyzed Transesterification of Waste Vegetable Oils into Fatty Acid Methyl Esters

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Abstract

Fatty Acid Methyl Esters (FAME), used as components of biodiesel, are commonly manufactured using a base-catalyzed transesterification process. In this process, triglycerides are converted into FAME and glycerol by reacting with methanol and sodium hydroxide. Multiple factors can affect the reaction efficiency of the transesterification process, including temperature.

Many home-processors of biodiesel fuel encourage the *3/27 Conversion Test* as an indicator of acceptable reaction efficiency. This test recognizes the miscibility of FAME and methanol to provide a qualitative result of the transesterification process. The 3/27 Conversion Test can be used to determine if a processing variable affected the composition of the reaction product.

Materials and processes used in this study were chosen from research of similar processing as well as from previous successful experiments. The processor used in the study is a version of an *Appleseed*, which is a commonly utilized design by individuals making biodiesel for personal use in approximate batch sizes to those tested in this study.

For purposes of this study, nine-25 gallon batches of waste vegetable oil were transesterified into FAME. While all other factors of process and materials were kept continuous, pre-processing feedstock temperature was varied in three stages. Three batches were processed at 110°F, three at 130°F, and three at 150°F. After starting the reaction, samples from the processor were collected at 15-minute intervals. After 60 minutes of processing, four samples for each batch were collected.

All samples were tested for completion using the 3/27 Conversion Test. Results were recorded for each temperature and interval. After analyzing the data, no proof was discovered which showed that increasing pre-reaction feedstock oil temperature between 110°F and 150°F increased the likelihood of reacted FAME to pass a 3/27 Conversion Test.

Keywords: Transesterification, biodiesel processing, 3/27 Conversion Test, Fatty Acid Methyl Esters (FAME), Waste Vegetable Oil (WVO), Appleseed processor, feedstock temperature

Notice

The information contained in this study refers solely to the effects of changing temperature on the transesterification process of waste vegetable oils. This article is not intended as a guide to manufacture motor vehicle fuel. Nor does it recommend the usage of transesterified waste vegetable oil as a motor vehicle fuel.

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Transesterification

Fatty Acid Methyl Esters (FAME), when referred to as *biodiesel*, is a manufactured liquid product for use specifically as a type of diesel fuel. Vegetable oils are triglyceride molecules consisting of three long chain fatty acids that are ester bonded to a single glycerol molecule (Meher, et al., 2006). According to Freedman et al. (1986), "In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol." The overall transesterification process is a sequence of three separate reactions: conversion of a triglyceride into a diglyceride and a FAME, diglyceride into a monoglyceride and a FAME, and finally a monoglyceride into a glycerol and a FAME.

According to Schuchardt, et al. (1998), several variables influence the course of the transesterification process. These factors include type of catalyst (acid or base), molar ratio of alcohol to vegetable oil, reaction temperature, purity of components, and free fatty acid (FFA) content of the feedstock. Industrial processes favor base-catalyzed over acid-catalyzed transesterification due to improved speed of reaction and lower corrosivity. Alkaline catalysts used in these processes include alkoxides, hydroxides, and carbonates.

Stoichiometric conversion of triglycerides to FAME requires 3 mol of the alcohol and 1 mol of a triglyceride, a 3:1 molar ratio. However, an excess of alcohol is normally used to increase yields and to allow phase separation from the glycerol formed. Balat and Balat (2008) reported sharply improved FAME yields with a molar ratio of 6:1, but only moderate improvements with increasing ratios until reaching a maximum of a 30:1. In studies using heated palm oil feedstock, Gabriel, et al. (2015) were able to obtain a completion rate of 95% using a molar ratio of only 4:1.

A variety of alcohols have been explored for transesterification, including methanol, ethanol, propanol, and butanol. According to Musa (2016), "Methanol is particularly preferred because…its reaction with triglycerides is quick and it can be easily dissolved in NaOH." In addition to being more reactive than ethanol, methanol is relatively inexpensive, and does not form an azeotrope with water, leading to easier recovery and recycling.

Waste vegetable oil (WVO) is a common term used to describe vegetable oils which have previously been used to fry foods. WVO is collected from restaurants and similar facilities after use and disposal. FFA's are present in waste vegetable oil, due to carbon chains breaking away from glycerol molecules during the frying process. During a base-catalyzed transesterification, these FFA's are saponified in the presence of water to form soap. Low FFA content feedstocks are routinely transesterified using a base catalyst, creating only a minimal amount of soap.

Higher FFA feedstocks are usually transesterified with an acid catalyst or a two-step acid esterification/base transesterification process. FFA content of feedstock oil is measured through a titration process. The result is a titration number used to calculate the proper amount of catalyst to complete the reaction.

Reaction temperature has been shown to notably affect the efficiency of the transesterification process. According to Clifford (n.d.), “The reaction typically takes place at between 40-65°C. As the reaction temperature goes higher, the rate of reaction will increase.” Experiments to optimize biodiesel production by Leung and Guo (2006) were performed with reaction temperatures ranging from 30-70°C. Their conclusions stated higher reaction temperatures had a positive influence on increasing the rate of transesterification and shortening the reaction time. Using a waste vegetable oil feedstock, they were able to achieve a complete reaction at 60°C in only 15 minutes. Multiple recipes for FAME processing were researched online and the published temperature range was 48-65°C (Blair, 2005; Pelly, 2000; Rick Da Tech, n.d.).

3/27 Conversion Testing

To test for completion of the transesterification process, samples can be sent out for analysis, but this will add cost to the research. Another option, according to Biodiesel Community (2017), is the *3/27 Conversion Test*.

Introduced by Jan Warnquist in 2006 as an alternative to gas chromatograph testing, the 3/27 Conversion Test correlates very closely regarding the conversion of triglycerides into FAME. Biodiesel Community recommends the 3/27 Conversion Test as a way of determining if a change to the conversion process creates a change in the results. If performed properly, and FAME passes the 3/27 Conversion Test, the FAME is likely to pass ASTM standards for total glycerides.

The test relies on the fact that FAME dissolves completely in methanol, but diglycerides and triglycerides do not. To perform a 3/27 Conversion Test, mix 9 parts of methanol with 1 part of FAME in a container, mix thoroughly, then allow to settle. Components must be approximately 70°F for best results. If oily material settles to the bottom of the container, the test result is a fail (Figure 1). If no fallout occurs, the test is a pass (Figure 2). This test is considered a qualitative test only, as no correlation between fallout volume and percent conversion has been established.

The 3/27 Conversion Test is widely recognized by the home biodiesel manufacturing community and endorsed by prominent biodiesel advocate Graydon Blair (2013).

Figure 1

3/27 Conversion Test Fail

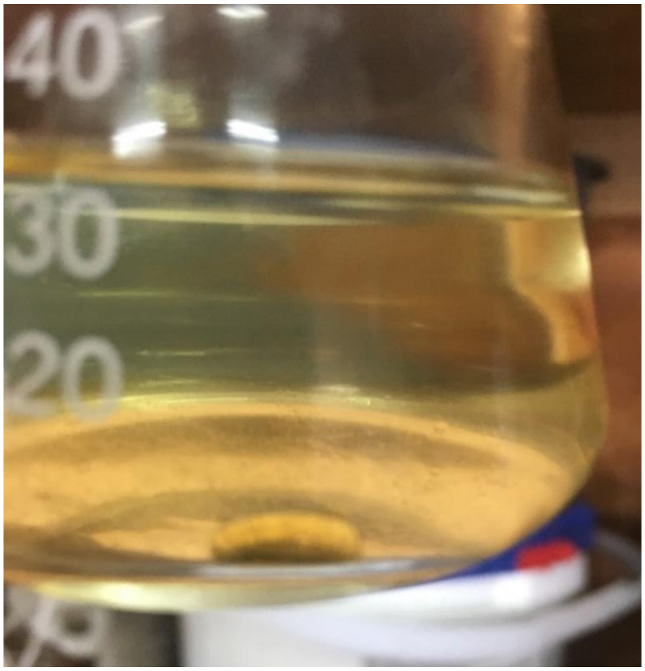
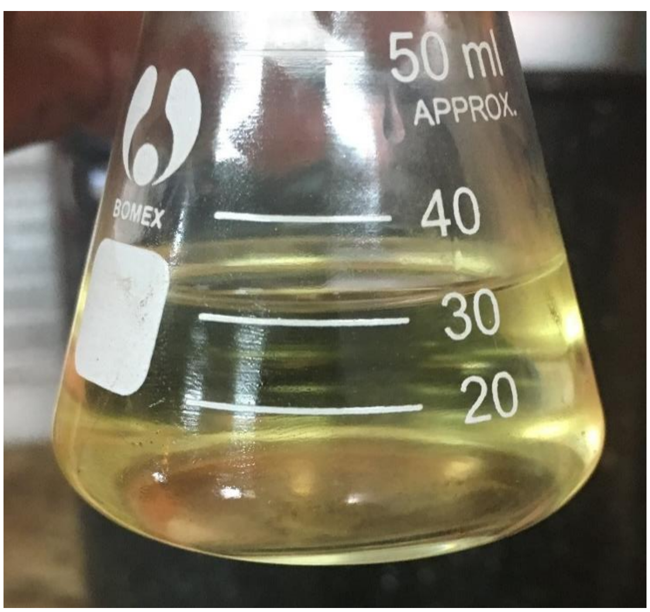


Figure 2

3/27 Conversion Test Pass



Materials and Methods

The feedstock used in this study was WVO obtained from multiple restaurants in the original 35 lb. containers. Labels show ingredients of liquid and partially hydrogenated soybean oil. Labels include manufacture dates from 2011-2013. Titration testing verified the feedstock was of low FFA content, suitable for base-transesterification.

Methanol used in the transesterification process was obtained from a local fuel supplier in a 55-gallon barrel. The product was labeled *Methyl Alcohol (Racing Fuel)* and identified by the UN# 1230. All transesterification performed in this study was completed using methanol from this one barrel. The barrel was unused and kept sealed before the study began.

Methanol used in the conversion tests was *Heet Gas-Line Antifreeze & Water Remover*. It was obtained from an automotive supply store in 12 oz. bottles. The MSDS document identified this product as 99% methanol with no proprietary additives. No discernible differences in the methanol used in transesterification and completion testing are implied.

All lye used in this study was *Rooto Crystals of Household 100% Lye Drain Opener*. This product was packaged in individual one lb. containers and was purchased in a 12-container case. It is manufactured by Rooto Corporation, Howell, MI.

The isopropanol used in the study was *Mac's Thermo-Aid.* It was obtained from an automotive supply store in 12 oz bottles. The label identified this product as 99.9% isopropyl alcohol. This product was used in the titration testing procedures as well as for rinsing beakers and pipettes.

Turmeric powder was used as a titration indicator mixed in solution with isopropanol. The turmeric used in the study was *McCormick Ground Turmeric* and was obtained at a local grocery store in a 0.95 oz container.

Processor

The processor used in this study was assembled from components and hardware obtained from common retail sources. The design of the processor was a version of the *Appleseed* (Alovert, 2007), which is a commonly utilized design by individuals making biodiesel for personal use. One common design aspect of the Appleseed is the use of a water heater assembly as the main heating and processing unit.

The processor was assembled with a 25 gallon primary holding tank, 50 gallon heater/processing tank, 55 gallon settling tank, 55 gallon washing tank, and a 55 gallon drying tank. Two separate electric pumps were used to move product within the processor. Iron piping and brass ball valves connected the various tanks and pumps (Figure 3). The potential capacity of the processor was 50 gallons; however, batch size in this study was limited to 25 gallons.

Figure 3

Appleseed style processor used in the study

Experimental Method

A total of nine transesterification reactions were performed on a consistent sample of WVO feedstock. Each reaction was performed following the comparable process detailed below, with a variable of feedstock oil temperature. Three batches were made with a feedstock temperature of 150°F(65.6°C), three batches at 130°F(54.4°C), and three batches at 110°F(43.3°C). After the methoxide induction was complete, samples were taken at 15-minute intervals and tested for completion using the 3/27 Conversion Test. In each case, the reaction was stopped after one hour, and the reacted product was transferred to the settling tank. Results from the 3/27 Conversion Tests were used to determine if changes in feedstock reaction temperature affected transesterification efficiency.

Process

In order to have a consistent feedstock, the oil to complete all batches was transferred into a 275 gallon IBC tote. An amount of feedstock oil in excess of 250 gallons was admitted into the tote and thoroughly mixed with a drill-mounted paint mixer for approximately 10 minutes. The mixing was an effort to homogenize the oil and to perform a more accurate titration of the entire sample.

Titration measurements were made on multiple samples of the feedstock oil to determine the FFA content of the sample and the proper amount of lye catalyst required to transesterify the feedstock oil. Titration procedures were performed using processes from *Titrating with Turmeric* (Essen & Chug, 2005), and *Titrating Oil to Make Biodiesel* (Blair, n.d.). The initial titration was performed multiple times and 2.3 mL of titrating solution was required to neutralize the FFA content of each sample. This reading was noted for future reference.

Blair (2005) and Pelly (2000) both agree to use an amount of methanol equal to 20% of the volume of oil in the reaction. Reacting 25 gallons of WVO then required five gallons of methanol. Using 32.04 g/mol for methanol and 879.4 g/mol for WVO, this was an approximate 4.7:1 molar ratio of methanol to oil. As was suggested earlier, using methanol in excess of the stoichiometric ratio of 3:1 was recommended for a successful transesterification (Balat & Balat, 2008).

To begin each batch, 25 gallons of feedstock oil was transferred into the processor and circulated for a minimum of ten minutes. The oil was again titrated to verify proper catalyst amount and adjusted accordingly.

The titration number of each batch was added to a base amount of 5.5 grams to determine the total grams per liter of oil. Using a 25-gallon batch size converted to 94.6353 liters, the base amount of catalyst in each batch was 520.5 grams. Multiplying each batch's titration number by 94.6353 provided the required additional catalyst to neutralize FFA's. The measure of lye was added to the methanol and thoroughly incorporated by manual stirring.

After titration, the oil was heated by turning on the processor heating element while the oil circulated. Oil temperature was tested at periodic intervals using an analog dial thermometer. When the oil temperature reached the proper temperature for each batch, the heating element was shut off. At this time the prepared methoxide was inducted. Methoxide induction was completed within 11 minutes for each batch. Methoxide induction time was recorded for each batch.

After methoxide induction was complete for each batch, a 15-minute timer was started. At 15-minute intervals, a sample of transesterifying product was taken. After 60 minutes of processing, four samples were taken. The finished product was then transferred to the settling tank, ending the processing stage for that batch. Samples were allowed a minimum of 15 minutes to settle into raw FAME floating on a layer of glycerol byproduct (Figure 4).

Figure 4

Set of four raw FAME samples

A 3/27 Conversion Test was performed on the raw FAME from every sample of each batch. Component temperatures were adjusted to approximately 70°F before conversion testing. In each test, 27mL of methanol was placed into a glass beaker. Three mL of FAME from the sample was added. The mixture was swirled to dissolve the FAME, then allowed to settle. Any unreacted oil falling to the bottom of the container was registered as a *fail*. If no fallout was observed, the test was registered as a *pass*. Variations in sample clarity as well as qualitative results were observed and documented.

After processing each batch of FAME, the product was settled, separated, washed, and dried. No data from the process after transesterification is discussed in this study.

Results

Batches 1-3 were performed at a pre-reaction oil temperature of 150°F. Batch 1 titrated at 2.3 mL and was reacted with a total catalyst dose of 738 grams. Batch 2 titrated at 2.2 mL and was reacted with 728.7 grams of catalyst. Batch 3 titrated at 2.4 mL and was reacted with 747.6 grams of catalyst. Methoxide induction for batches 1 & 2 was steady with each having an elapsed time of 6 minutes. Methoxide induction for batch 3 was completed in an elapsed time of 10 minutes. Conversion test results for batches 1-3 are shown in Table 1.

Table 1

3/27 Conversion Test Results at 150°F

150°F	15 min. sample	30 min. sample	45 min. sample	60 min. sample
Batch 1	Fail-Cloudy	Pass-Clear	Pass-Clear	Pass-Clear
Batch 2	Fail-Cloudy	Fail -Cloudy	Pass-Clear	Pass-Clear
Batch 3	Fail-Cloudy	Fail-Cloudy	Pass-Cloudy	Pass-Clear

Batches 4-6 were performed at a pre-reaction oil temperature of 130°F. Batches 4 & 6 titrated at 2.3 mL and were reacted with a total catalyst dose of 738 grams. Batch 5 titrated at 2.0 mL and was reacted with a total catalyst dose of 710 grams. Methoxide induction for batches 4-6 was steady with an elapsed time of 8-11 minutes. Conversion test results for batches 4-6 are shown in Table 2.

Table 2

3/27 Conversion Test Results at 130°F

130°F	15 min. sample	30 min. sample	45 min. sample	60 min. sample
Batch 4	Fail-Cloudy	Pass-Cloudy	Pass-Clear	Pass-Clear
Batch 5	Fail-Cloudy	Pass -Clear	Pass-Clear	Pass-Clear
Batch 6	Fail-Cloudy	Pass-Cloudy	Pass-Clear	Pass-Clear

Batches 7-9 were performed at a pre-reaction oil temperature of 110°F. Batches 7-9 all titrated at 2.4 mL and were reacted with a total catalyst dose of 747.6 grams. Methoxide induction for batch 7 occurred rather quickly, but steady, with an elapsed time of 2 minutes. Methoxide induction for batches 7 & 8 was steady with an elapsed time of 8-10 minutes. Conversion test results for batches 7-9 are shown in Table 3.

Table 3

3/27 Conversion Test Results at 110°F

110°F	15 min. sample	30 min. sample	45 min. sample	60 min. sample
Batch 7	Fail-Cloudy-Poor separation	Fail-Clear	Pass-Clear	Pass-Clear
Batch 8	Fail-Slightly cloudy	Fail-Slightly cloudy	Pass-Slightly cloudy	Pass-Clear
Batch 9	Fail-Clear	Pass-Cloudy	Pass-Cloudy	Pass-Clear

Discussion

After all batches of FAME were processed, the data was collected and results were analyzed. The data was expected to discover if variation in pre-reaction temperature had any discernable effect on the 3/27 Conversion Test results of each batch.

In each of the 9 batches, none of the samples taken at the 15-minute mark passed the 3/27 Conversion Test. This result suggests that at all temperatures tested, 15 minutes was simply too short of a reaction time to fully transesterify the WVO into FAME. This data suggests the possibility of eliminating the sample taken at 15-minutes and extending all future transesterification reaction first samples to the 30-minute mark.

Looking at samples taken at the 30-minute mark, results show no definitive correlation between increasing pre-reaction temperature and passing the 3/27 Conversion Test. At 150°F, one sample clearly passed and the other two samples failed with a cloudy appearance. At 130°F, all three samples passed the 3/27 Conversion Test. At 110°F, one sample passed and two samples failed. All three samples reacted at 110°F had a cloudy appearance. Slight variations in methoxide induction rate and catalyst amounts could explain the difference in these conversion test results. However, as both higher temperatures and lower temperatures included failed tests, variation in temperature cannot be responsible for these test results.

All samples taken at the 45-minute mark for each temperature range passed the 3/27 Conversion Test. Samples taken at both 150°F and 110°F exhibited some cloudy results and some clear results, however all tests passed. All samples taken at 130°F passed with a clear test result. As in the 30-minute samples, variation in induction rate and catalyst amounts could be cause to the cloudy test result, but cannot be responsible on variation in temperature.

All samples taken at the 60-minute mark for all batches passed the conversion tests with a clear result. No variation was found among any samples across the tested temperature ranges. With no variation in result, no effect from variable temperature ranges was able to be verified at the 60-minute mark.

The most successful transesterification reactions were obtained at a temperature of 130°F. At this temperature, nine conversion tests passed and three failed. Increasing reaction temperatures to 150°F did not result in improved test results. At 150°F, seven conversion tests passed and five tests failed. Since increasing feedstock temperature also increases input costs, transesterification at this higher temperature is not recommended. At 110°F, seven conversion tests passed and five failed. More passed conversion tests at this temperature exhibited a cloudy appearance, which could indicate higher levels of monoglycerides in the FAME. Though decreasing reaction temperature will decrease input costs, the improvement in conversion results at 130°F provides reason to recommend reacting future batches at 130°F.

To summarize the results from the study, no proof was discovered which showed that increasing pre-reaction feedstock oil temperature between 110°F and 150°F increased the likelihood of reacted FAME to pass a 3/27 Conversion Test.

Additional Notes

During the study, two batches were made which were not included in the results. One of the batches reacted at 150°F had a vinyl hose failure during methoxide induction. Induction was erratic, then stopped altogether. The final 3 quarts of methoxide were poured into the reactor to keep induction time from exceeding 10 minutes. Subsequently, all samples of this batch failed to pass a 3/27 Conversion Test. Due to the variable of the methoxide inductor, this batch was not included in the study. Additionally, one of the batches reacted at 130°F was performed using different WVO feedstock than all other batches of the study. This batch titrated at 1.7 mL and was reacted with 681.4 grams of catalyst. All four samples of this batch passed the 3/27 Conversion Test. Due to inconsistency of feedstock, this batch was also not included in this study.

These results could point to the need for future research testing variation in methoxide induction rates and lower titrating feedstocks to affect completion test results and further efficiency improvements in the transesterification process.

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