

PREPARATION AND ANALYSIS OF BIODIESEL-CONVENTIONAL DIESEL BLENDS DERIVED FROM WASTE-COOKING OIL

Lincoln Blouin*, Anna Scofield*, Kendall Ahern*, Karis Desotell*, Samuel Cook*, Cooper Stroka*, Timm Knoerzer†

United States Air Force Academy, Department of Chemistry, United States Air Force Academy, CO 80840

Abstract

The production of biofuel-petrol blends from waste cooking oil (WCO) is a viable method for generating a sustainable, green chemistry approach to energy production. In this case, the cadet dining hall at the US Air Force Academy provides a substantial and cheap feedstock for the ready production of biodiesel. Herein, we describe our efforts at using that feedstock to synthesize a clean source of biodiesel and the blending of the resultant purified biodiesel with standard No. 2 petroleum diesel in various proportions – B0-B100. Various parameters were assessed including density, refractive index, viscometry, high heating value, and cloud point in order to ascertain the viability of use for the various blends in base-related, diesel-engine vehicular use. Of the various proportioned blends tested, B10 and B20 were identified as excellent alternative fuel configurations based upon their resultant analytical results.

†Corresponding author: timm.knoerzer@afacademy.af.edu

* Undergraduate researchers and co-authors

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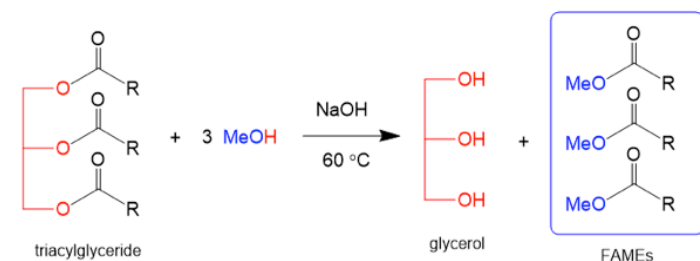
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INTRODUCTION

The development of alternative fuel sources remains an important societal goal especially considering the current expense of petroleum diesel and the growing interest in green approaches to energy production. For example, in July 2023, the average price of diesel in Colorado hovered around \$4.00/gallon, considerably lower than the previously high value of \$5.84/gallon reported in June 20, 2022, but still exceeding the 2021 cost of \$3.48/gallon.^{1,2} Furthermore, with the on-going political instability internationally, the increased level of inflation, and issues related to the environment, the inconsistent price of diesel is expected to persist. Therefore, the cost considerations of diesel fuel are likely to continue to drive organizational decision-making especially as it pertains to operating costs.

One such option that has been exploited over the past several decades to address such energy issues is the use of biodiesel as a partial or even complete replacement for diesel fuel. Biodiesel, a mixture of fatty-acid methyl esters (FAMES), is a primary option to many industrial developers due to its ready synthesis via trans-esterification of triacylglycerides obtained from vegetable oils (**Scheme 1**).

The interest in biodiesel is driven by particular advantages that have been effectively reviewed in the scientific literature.^{3,4}



Scheme 1. Transesterification of triacylglyceride to synthesized FAMES (biodiesel)

First of all, the transesterification is a facile and efficient synthetic methodology, which can be accomplished with a variety of reaction conditions, most notably acidic versus basic conditions. In addition, many different feedstock sources of the triacylglyceride oil are available including both plant and animal fat sources. Commonly, vegetable oils- such as canola, soybean, corn, and sunflower oils are utilized due to their low cost and ready access. Beyond the synthetic advantages, the resultant performance properties of biodiesel also possess certain advantages. For instance, biodiesel generated from a variety of feedstock sources can be readily proportioned with other conventional petroleum diesel to generate a fuel blend, designated by BX abbreviation wherein the X factor indicates the relative percentage of biodiesel. Moreover, the lubricity, oxidation, and environmentally-friendly emission profiles of biodiesel are widely considered attractive advantages in comparison to other conventional fuel options.^{3,4} Indeed, biodiesel is a safer and more transportable fuel in comparison with petroleum diesel.^{3,4} Finally, given the strong infrastructure and raw material resources available domestically, the broader use of biodiesel as a fuel source could lead to furthering US energy security as well. Also, because biodiesel can be made with organic matter, there is inherently wide access to biodiesel production throughout the world. This worldwide availability has created a broad scientific interest, which is reflected in the 4586 research outputs from 481 organizations in 56 countries across the world between 2010 and 2021 on the topic of biodiesel production.⁵ In fact, a recent report indicated that the two most critical factors that have influenced the intense research activity in biodiesel are availability of feedstock and sustainability interests.⁶ Therefore, continued efforts to explore the use of biodiesel remain significant.

Although the advantages are clear for use of biodiesel, there are some disadvantages that should also be considered as part of a complete assessment of applicability. The most significant drawback is the operational temperature range for biodiesel, especially as it pertains to use in cold temperature conditions (for example, <0 °C).^{7,8} A second common disadvantage is the broad use in all

types of diesel engines. In fact, some diesel engines are not biodiesel compatible.^{7,8} Finally, the use of biodiesel in engines is often accompanied by degradation in the fuel hoses as well as in fuel tank corrosion.^{3,7,8} In addition to performance, there are also potential problems that arise in the biodiesel production process. For example, the synthesis of biodiesel requires solvents and reagents that lead to cost increases and may not be readily accessible for a particular community looking to generate biodiesel. Moreover, if a waste oil is selected as the feedstock, pre-treatment processes are required prior to actual conversion to biodiesel, which can actually be quite costly.⁹ Finally, there are economic, political, and ecological issues that arise when biodiesel is produced from agriculturally-derived vegetable oils.^{10,11}

To address any concerns related to effective biodiesel implementation, developmental methods have turned toward the use of *biodiesel-conventional diesel blends*. In fact, the US Department of Energy indicates that certain biodiesel blends can be readily used in standard diesel engines without the need for engine modification.¹² A variety of blends have been investigated primarily because of the complete miscibility of biodiesel-diesel mixtures with the most widely exploited being B20, ostensibly due to its attractive balance among cost and performance factors.¹³ In addition, B20 exhibits only a modest decrease in performance with a mere 1-2% loss of energy output per gallon versus petroleum diesel.¹³ This potential disadvantage can be offset by the fact that biodiesel undergoes more complete combustion upon burning, ultimately leading to a cleaner burning fuel with positive environmental benefits.^{13,14}

On the negative side, blends may exhibit the same unfavorable gelling factors that are seen with biofuel applications. In fact, the cloud point values of blends tend to be only modestly different from the petroleum diesel values.¹⁵ This effect may lead to clogged filters and ultimately to damaging seals and gaskets. In addition, the acidic nature combined with increased water content, due to biodiesel composition, may lead to fuel tank corrosion over time.¹⁶ Finally, the implementation of lower fuel ratios, such as B5 or B10, likely provides only marginal sustainability benefits in comparison with use of pure diesel fuel.

With these considerations, our group initiated a course-based undergraduate research project wherein we explored the use of waste cooking oil as a readily available feedstock for the in-house production of biodiesel. In the context of this work, we identified a clear opportunity to develop a green chemistry approach that aligns nicely with the *12 Principles of Green Chemistry* and which allowed us to strategically incorporate the use of (1) a renewable feedstock, (2) catalysis conditions, and (3) waste-reduction strategies.¹⁷ The Air Force Academy is a substantially large military base that is responsible for the education of nearly 4000 cadets annually. In order to properly serve those students, a network of vehicles are used on the installation to transport cadets, service the facilities, and to operate key equipment. It is estimated that approximately 10,000 gallons of diesel fuel are consumed annually to effectively support base operations of the buses alone.¹⁸ Clearly, the cost burden has increased recently due to rising fuel prices and fuel availability and, therefore, a distinct need has emerged in terms of finding a method to provide fuel resources at a reasonable cost. Biodiesel is an attractive alternative option due to the

readily accessible source of raw material available for conversion to biofuel at the Air Force Academy, which provides a renewable resource with an integrated potential cost-saving option. Currently, the cadet dining hall (Mitchell Hall) uses and ultimately releases an estimated 800 gallons of waste cooking oil (WCO) per 3-month period.¹⁹ The open loop of cooking oil use limits the efficiency and green potential that exists when the oil is properly re-purposed. Therefore, in order to close the loop, we envisioned the possibility of using the used waste cooking oil as a “third-generation” biodiesel feedstock. Indeed, prior work has suggested that the majority (75-80%) of cost investment into biofuel production lies with the feedstock cost.²⁰ The intentional recycling of an immediately available feedstock with low cost likely provides a crucial dimension to yield a fuel product with low cost. Upon production of biodiesel from WCO, an environmentally-sensitive fuel resource could be developed that is consistent with previous findings.²¹ Herein, we describe the production and evaluation of a series of WCO-derived biodiesel-petroleum diesel blends as potential diesel fuel replacements for a large military base.

METHODS

General

A 500 mL portion of waste cooking oil (WCO) was obtained from the Mitchell Hall Dining Hall at the US Air Force Academy. The WCO sample was evaluated for free fatty acid content before and after a pre-treatment regimen that was used to prepare the crude WCO for conversion to biodiesel via a base-catalyzed transesterification process. The details for pre-treatment, FFA content analysis, and transesterification are provided below. Following transesterification, the biodiesel was blended in several proportions – B0, B5, B10, B20, B30, B40, B100 – with standard No. 2 petroleum diesel and stored in opaque receptacles until being subjected to analysis.

Fuel combustion analysis was performed using an IKA 200C bomb calorimeter, FTIR analysis was conducted using a Thermo Scientific IS10 FTIR spectrometer equipped with a single bounce ATR sampler, and GCMS analysis was accomplished using an Agilent Technologies 7890A GC interfaced with an Agilent Technologies 5975C inert XL MSD. The GC column consisted of a Zebron ZB-5HT Inferno capillary column with 400 °C max temperature limit of the following dimensions: 30 m x 0.25 mm x 0.25 μm. Cloud point values were determined using a TA Instruments Q20 Differential Scanning Calorimeter with multi-cell autosampler. Laboratory grade solvents were used and instruments were properly calibrated and referenced as required to ensure reproducibility.

FFA Determination

Individual samples of pre-treatment WCO, post-treatment WCO, and post-transesterification fuel blend (4-5 g) were dissolved in 30 mL of absolute ethanol and 1-2 drops of phenolphthalein was added. The solution was moderately stirred and titrated using standardized 0.0982 M NaOH solution to a persistent pale pink endpoint. The volume of titrant needed to reach the endpoint was used in the following **equation 1** to calculate the acid value.

$$\text{ACID VALUE} = \frac{(\text{Volume of titrant in L}) \times (0.0982 \text{ M}) \times (39.997 \text{ g/mol})}{\text{Mass of sample (g)}} \quad (\text{Eq. 1})$$

The acid value was then converted to percent of free fatty acid (%FFA) according to the following **equation 2**.

$$\% \text{ FFA} = \frac{\text{ACID VALUE}}{2} \quad (\text{Eq. 2})$$

WCO Pre-treatment

FFAs were effectively converted to their corresponding FAMES using an acid-catalyzed esterification reaction in the presence of methanol congruent to a previously reported method (*Sustainable Cities and Society* 41 (2018) 220–226). WCO (50 mL) was introduced to a 250 mL round-bottom flask along with 10 mL methanol and 0.2% H₂SO₄ (aq). The mixture was stirred and heated at 50 °C for a total of 6 h. Upon completion, the resultant mixture was cooled, transferred to large volume centrifuge tubes, and centrifuged for 10 min. The methanol layer was removed and the treated WCO layer was collected and washed 3 times with water. Following overnight exposure to vacuum evaporation, the remaining treated WCO was evaluated for FFA content.

Transesterification of WCO to Biodiesel FAMES

Methanol (15 mL) was transferred into a 125 mL Erlenmeyer flask containing a magnetic stir bar. To this solution was added 0.375 g of pulverized NaOH (~0.8% catalyst). The contents of the flask were stirred for an additional 5-10 min ensuring proper dissolution of the NaOH catalyst. The appropriately pre-treated WCO (45 mL) was added slowly to the solution and then resulting mixture was stirred for 100 min at 55 °C.

While still warm, the mixture was poured into a separatory funnel and the layers were allowed to separate. Upon cooling and separation, the lower glycerin/by-product layer was drained into a 100 mL beaker. Any leftover glycerin was collected and re-purposed in our General Chemistry teaching laboratories for use in student experiments focused on the production of soap. The remaining top layer containing the desired biodiesel product was *carefully* washed with 10 mL of tap water. The bottom aqueous was discarded and the resulting biodiesel layer was transferred into a clean, dry beaker. Any traces of water were removed from the biodiesel by adding 0.5 g of anhydrous sodium sulfate. Na₂SO₄ was removed by filtration.

FTIR

A background spectrum was acquired from a blank ATR surface and saved. A single drop of the FAME biodiesel sample prepared from treated WCO was introduced to the ATR surface. A total of 16 scans were acquired and then the background was subtracted to provide the resultant FTIR spectrum.

GCMS

A 3 uL aliquot of the fuel blend sample (measure by micropipette) was transferred to a GCMS vial and the volume was brought to a total of 2 mL using dichloromethane. The sample was injected into a HP5-MS column with dimensions of 30 m x 0.25 mm x 0.25 mm. Samples (2 uL) were injected with a 2.00 min solvent delay at an initial temperature of 65 °C held constant for 2 min. The temperature was ramped at 20 °C per min to 200 °C and then ramped at 25 °C per min to final temperature of 325 °C with a hold time of 1.00 min. The injector temperature was held at 275 °C and the source temperature was set to 200 °C. The sample was injected

using 100:1 split mode after 3 pre-injection solvent cycles.

Density

A 1000 uL single channel variable volume autopipette was used to deliver precisely 0.500 mL of sample to a pre-weighed vial. The mass was recorded for the 0.500 mL sample and the process was repeated 2 more times to achieve an average density value.

Viscometry

Viscometry values were determined by use of a Gilmont falling ball viscometer. A size #3 tube was employed along with a size #3 glass float. The sample was introduced into the viscometer tube until completely full followed by addition of the ball. The insert was slowly fitted into the open end of the tube being sure not to introduce any air bubbles. The insert was secured with a plastic nut and the cap was screwed on to the top of the insert. The tube was inverted and timing were recorded from when the ball passed through the first two-line designation to the last two-line designation on the tube. This process was repeated for a total of 10 iterations and the results averaged to provide the time for each sample in seconds. Viscosity in centipoises (cP) were calculated using **equation 3**,

$$k = \frac{\mu}{(p_f - p) \cdot t} \quad (\text{Eq. 3})$$

where k is the viscometer constant ($K = 35$ for the size #3 tube), μ is the viscosity in cP, p_f is the density of the ball (2.3 g/mL for the glass ball), p is the density of liquid (determined above) and t is the time of descent (min).²²

The conversion from Cp to centistokes (cSt) for kinematic viscosity was performed using **equation 4**.

$$v = \frac{\eta}{\rho} \quad (\text{Eq. 4})$$

where v = kinematic viscosity (cSt), η = dynamic viscosity (cP), and ρ = density (kg/m³).²³

Refractive Index

An Abbe analog refractometer was used to measure the refractive index of the values biodiesel blends. The sampling surface was thoroughly cleaned prior to introduction of each sample. A small 5 uL sample was introduced to the matted surface and the device was closed to compress the liquid between two prisms. The surface was illuminated and the refractive index value was optimized by viewing through the instrument eyepiece. Adjustments were made to provide a sharp white/black bisection without shadows. At this point, a measurement could be made to 0.0001 precision.

Cloud Point Determination

Cloud point analysis was performed using 15 mg samples of each fuel blend using a DSC Q20 differential scanning calorimeter. The samples were held isothermally for 1 min at 20 °C and then cooled from 20 °C to -70 °C at a rate of 10 °C per min and equilibrated isothermally for 1 min at -70 °C. The samples were then heated to 20 °C at a rate of 10 °C per min and held at the final temperature for 1 min to complete the cooling-heating cycle. Instant Explorer software was used to visualize the results and determine the cloud point of each fuel blend sample.

Bomb Calorimetry (High Heating Value)

An IKA 200C calorimeter was used in manual isoperibol mode which had been calibrated by combustion of a benzoic acid standard in triplicate. The stainless steel decomposition vessel was thoroughly cleaned and prepared for acquisition. A cotton combustion fuse was tied to the ignitor wire and placed in contact with a pre-weighed sample (0.4-0.5 g) contained in a sample crucible held below the ignitor wire by a metal crucible holder. High purity water (1.00 mL) was pipetted into the bottom of the stainless steel vessel prior to assembly. The vessel was then assembled being sure to gain a good seal via the o-ring on the securing nut. The apparatus was charged with high purity oxygen to a level of 30 bar. The ignition head was then attached and the entire assembly was placed into the calorimeter resting correctly on the three holding pegs. The calorimeter was filled with water and the cover was closed. The run was commenced with 7 temperature readings for the fore period (1 reading per min) at which point the sample was ignited. Temperature readings were continued until the 20 min mark at which point the run was completed and one additional temperature reading was taken. The bomb was degassed and the remaining liquid in the bottom of the pressure vessel was titrated using standardized 0.0982 M NaOH and phenolphthalein as indicator. The temperature readings were transcribed to an Excel document (see Supporting Information) for data processing taking into account any temperature drift in the fore and after periods surrounding ignition as well as to account for contributions from the ignition fuse, the formation of HNO_3 from residual N_2 in the chamber, as well as for the calorimeter constant itself.

RESULTS AND DISCUSSION

Our investigative process began with the acquisition of a sample of the waste cooking oil (WCO) from the US Air Force Academy Mitchell Dining Hall. The WCO is used in large capacity oil fryers over a several week period and is therefore subject to hydrolytic processes leading undesirable free fatty acid (FFA) formation. In order to assess the acidic nature of the WCO and to determine the level of FFA in our sample, the raw oil was evaluated by NaOH titration following standard methods. Our results showed unacceptable levels of FFA, which averaged 1.58%, exceeding the acceptable limit for a good quality feedstock of 1%.²⁴ Therefore, a pre-treatment methodology was employed to process the WCO and render an oil of low acidity capable of ultimate trans-esterification conversion to biodiesel. This process involved the acid-catalyzed reaction of FFA with methanol to produce *in situ* formation of FAMES in addition to any remaining TAGs omnipresent in the WCO. Upon secondary assessment via the NaOH titration method, a substantial reduction in FFA composition was observed (0.55%), which now demonstrated an acidity below the 1% FFA limit for a feedstock material viable for conversion to biodiesel.²⁴

With an acceptable oil in hand, we embarked on the bulk trans-esterification of the pre-treated WCO in order to produce the high quality biodiesel for production of our target blends. A well-established base-catalyzed trans-esterification was used congruent with the chemistry outlined in **Scheme 1**. Following a careful work-up of the reaction mixture, we were able to isolate a clean biodiesel product in 70% yield. Further confirmation of a successful trans-esterification was achieved by FTIR and GCMS

structural elucidation methods. FTIR analysis (**Table 1**) showed strong evidentiary signals at 1741, 1195, and 1169 cm^{-1} , consistent with the desired methyl ester functionality, thus supporting the conversion of WCO to FAMES. To our delight, O-H stretching frequencies in the 3000-3500 cm^{-1} range were noticeably absent, which supported a high conversion to FAMES via the applied trans-esterification methodology.

Further confirmatory evidence was provided by GCMS analysis (**Table 2**), which showed a clean chromatogram comprised of 4 major peaks. The corresponding mass spectral data showed respective molecular ion peaks at 270, 294, 296, and 298 m/z , which are consistent with the following expected major constituents of pure vegetable oil-based biodiesel: methyl palmitate (270 m/z), methyl linoleate (294 m/z), methyl oleate (296 m/z), and methyl linolenate (298 m/z). In addition, the major constituent (methyl oleate, 296 m/z) was also consistent with conventional food service grade vegetable oil. Further support for the identification of each component as a FAME was drawn from the $[\text{M}^+ - 31]$ peaks in each corresponding mass spectrum suggestive of the loss of the terminal OMe group. The complete GCMS data set is accessible via the **Supplemental Information**.

With an acceptable FAME biodiesel product in hand, a wide ranging and inclusive series of blends were prepared to assess resultant fuel properties in the following ratios: B100, B40, B20, B30, B20, B10, and B0. The summary of the fuel property results for the various blends are provided in **Table 3**.

Initially, each of the blends were subject to a standard NaOH titration to determine a corresponding acid value. Each of the

Table 1. Major FTIR signals characteristic of the desired pure biodiesel product

Signal (cm^{-1})	Vibrational Assignment
3006.52	symmetric CH_2 and asymmetric CH_2 & CH_3 stretching
2922.75	symmetric CH_2 and asymmetric CH_2 & CH_3 stretching
2853.05	symmetric CH_2 and asymmetric CH_2 & CH_3 stretching
1741.50	C=O stretching
1458.83	CH_3 asymmetric bending
1435.21	CH_3 asymmetric bending
1195.20	O- CH_3 stretching
1169.21	O- CH_3 stretching
722.35	Methylene (CH_2) rocking

Table 2. Gas chromatographic results showing major components of the isolated biodiesel sample produced from WCO.

GC Peak Retention Time (min)	Mass Spectral MI Peak (m/z)	$[\text{M}^+ - 31]$ Peak (m/z)	Corresponding Molecular Formula	Assigned FAME
9.218	270	239	$\text{C}_{17}\text{H}_{34}\text{O}_2$	methyl palmitate
10.370	294	263	$\text{C}_{19}\text{H}_{34}\text{O}_2$	methyl linoleate
10.407	296	264/265	$\text{C}_{19}\text{H}_{36}\text{O}_2$	methyl oleate
10.541	298	267	$\text{C}_{19}\text{H}_{38}\text{O}_2$	methyl linolenate

Table 3. Summary of fuel characteristics for blends of biodiesel made from WCO and commercial diesel fuel.^a

Blend types	Acid Value (mg NaOH/g sample)	Refractive Index ^a	Density ^a (kg m^{-3})	Dynamic Viscosity (cP or mm^2s^{-1})	Kinematic Viscosity ^a (cSt)	Bomb calorimetry (kJ/g)	Cloud Point ($^{\circ}\text{C}$)
B100	0.330	1.4569	872	7.302	8.374	-39.74	-7.16
B40	0.309	1.4589	852	4.170	4.894	-43.08	-16.55
B30	0.273	1.4601	842	4.155	4.935	-43.73	-17.58
B20	0.227	1.4608	839	3.620	4.315	-44.64	-18.28
B10	0.173	1.4616	832	3.447	4.143	-45.97	-19.79
B5	0.136	1.4622	828	3.425	4.137	-46.49	-22.72
B0	0.116	1.4621	825	3.163	3.834	-46.96	-25.24

(a) Measurements for density, refractive index, and viscosity conducted at 21.5 $^{\circ}\text{C}$.

values were compared to the maximum ASTM D7467 value of 0.50 mg KOH/g sample for B100 and 0.30 mg KOH/g sample for B6-B20.²⁵ Satisfyingly, the B100 sample exhibited a reasonable value of 0.330 mg NaOH/g sample suggesting that the synthesized biodiesel was effectively freed of undesirable FFA by-products. Not surprisingly, the acid value decreased as the percentage of biodiesel in the blend also decreased with all blends demonstrating acid values at or below the ASTM D7467 B6-B20 standard (**Figure 1**). The empirical acid value for B20 observed here was slightly elevated but generally in line with the expected value of 0.20 mg KOH/g sample seen in the literature.²⁶ The acidic nature is attributed to the free fatty acid content that arises in the prepared biodiesel and is expected to be the stronger contributor to acidity versus conventional diesel fuel. Therefore, the blends with lower percentages of FAME predictably revealed more desirable characteristics and in our estimation, the B5-B20 blends all exhibited acidic properties within a desirable range for practical use by providing low potential for adverse engine corrosion and fuel deposit characteristics of the fuel.

In order to further explore the physical characteristics of the fuel blends, both density and refractive index values were determined, which are summarized in **Table 3**. As seen in **Table 3**, refractive index showed an expected steady increase in value from B100 to B0 with the range at 21.5 °C (294.5 K) correlating well with literature precedence.²⁷ These values are useful for future project development as refractive index values can be used as a fast and reliable quality control method in the transesterification process.²⁷ In addition, these values can also be used to estimate density and viscosity values in this same quality control process.²⁷ In terms of density values, the series from B100 to B0 showed the expected decrease in mass per unit volume. However, the empirical values obtained here appear to be slightly lower than calculated (predicted) literature values at a similar temperature value,²⁸ but substantially below the maximum ASTM standard value of 859 kg/m³ as seen in **Figure 2**. With these results, it appears that we have achieved fuel blends with refractive index and density values acceptable for fuel development purposes, especially as it pertains to the B5-B30 blends.

Another key factor to assess in order to identify a fuel blend with characteristics for optimal performance is the fuel viscosity. Viscosity measurements were determined by the falling-ball method and are summarized in **Table 3**, both in terms of kinematic viscosity and dynamic viscosity. Either value is useful as they express

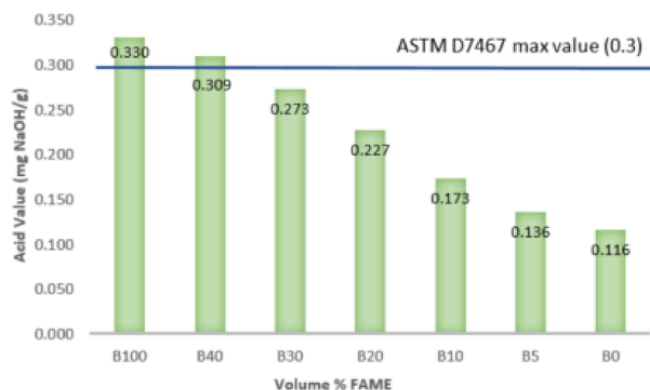


Figure 1. Acid value as function of % FAME in various biodiesel-conventional diesel blends.

the ability of a fluid to flow against a frictional force. Dynamic viscosity is also known as the absolute viscosity and is absent any influence of the density of the fluid of flow rate. Kinematic viscosity integrates fluid density into the flow rate determination and is the more commonly reported value in fuel-based reports. Regardless, either value can be used to illustrate the flow property of the fluid at various temperatures, which is important due to determining the capacity of the fuel or fuel-blend to atomize liquid droplets effectively.³⁰ Failure to properly generate fuel droplet quality will result in weaker engine performance, generally in terms of poorer combustion reactions within the engine itself.²⁹ The ASTM standard with regard to observed kinematic viscosity measurements for our fuel blends is indicated as the maximum allowed value in **Figure 3**.³⁰ The values reported are for measurements made at 21.5 °C, however the following equation (**Eq. 5**) can be used to convert

$$\ln \eta = A + B/T + C/T^2 \quad (\text{Eq. 5})$$

the kinematic viscosity measurement at a non-standard temperature to one for the standardized 40 °C measurement seen in the literature.³¹ A, B, and C are constants that apply to a particular fluid, in this case these are values for the B20 fuel blend, along with temperature values expressed in K.³¹ Using this equation, the B20 value decreases from 4.32 cSt at 21.5 °C to 1.80 cSt at 40 °C. A congruent application of this formula to the other fuels assessed in this study would result in adjusted kinematic velocity values for all of the fuel blends well below the ASTM standard maximum value

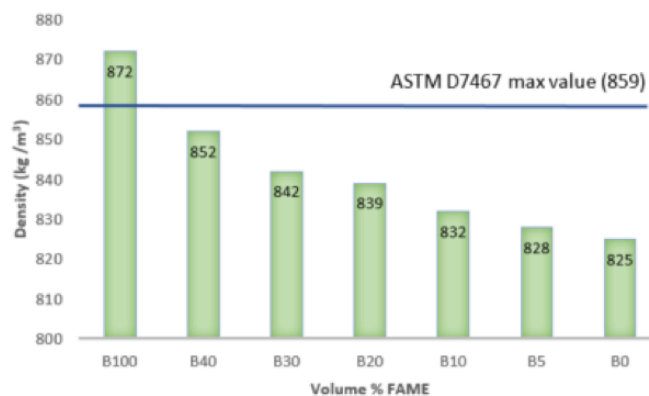


Figure 2. Density as function of % FAME in various biodiesel-conventional diesel blends.

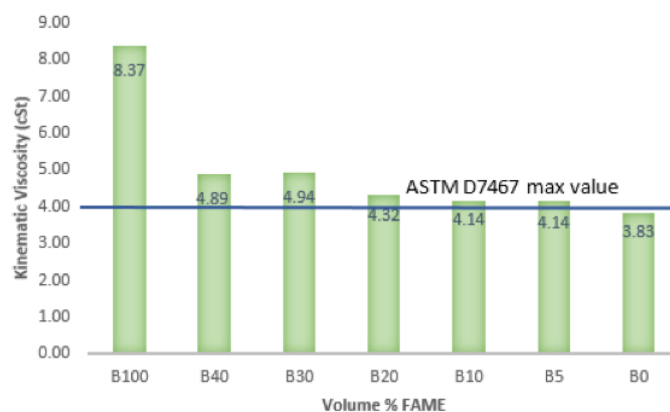


Figure 3. Kinematic viscosity as function of % FAME in various biodiesel-conventional diesel blends. NOTE: the values shown here were determined at 21.5 °C, while the standard is for viscosity performance at 40 °C.

of 4.1 cSt. Confidently, the viscosity profiles for the fuel blends from B0-B40 would meet the ASTM standard and allow for a fuel blend possessing the required atomization and fuel flow properties needed for optimal engine performance. In addition, these values appear to be in agreement with previous work investigating temperature-dependent viscosity behavior.³²

With the fundamental fuel attributes confirmed, we now turned our attention to the evaluation of two key fuel performance characteristics that are important for identifying optimal blends for practical use in the Colorado climate. The first of these is the determination of the high heating value that could be readily obtained via bomb calorimetry analysis, the results of which are shown in **Table 3** and **Figure 4**. The European minimal high heating value (HHV) standard is included simply to calibrate the energy output of the blends studied here and our results show that the blends generated exceed the minimal energy requirement for practical use. However, the trend in data also show the expected desirable HHV for pure diesel (46.96 MJ/kg) and the less desirable HHV for pure biodiesel at 39.75 MJ/kg. HHV is an important factor because fuel combustion efficiency and ultimate engine performance is directly correlated to calorific value. Therefore, fuel blends with higher HHV values more closely approaching the B0 (pure diesel) sample are determined to be more attractive configurations to achieve engine performance goals. As such, the B5 and B10 blends which showed HHV values of 46.49 MJ/kg and 45.97 MJ/kg, respectively reveal calorific profiles that would be acceptable for use in powering large vehicles such as buses, which are common cadet transport vehicles on base. The B20 at 44.64 MJ/kg (Figure 4) still achieves an acceptable calorific value with only a 5% reduction in energetic output versus pure diesel at 46.96 MJ/kg. It is reasonable to conclude that any fuel that maintains energetic output >95% of pure diesel would likely remain effective and can be effectively used in a standard diesel engine. In addition, B20 is a common formulation used extensively in the marketplace and is a commonly studied fuel blend.³³ It is also important to consider the density and viscosity measurements as well in terms of estimating the use potential of a particular biodiesel blend. For example, it is well established that lower heating value indeed will lead to a reduction in power, but density and viscosity differentials of the various proportioned blends also contribute.³⁴ As the density and viscosity of the blend increase, the flow rate of the fuel through the system decreases. Additionally, fuel-air mixing is likewise reduced which leads to a concomitant decrease in effective combustion reactions.

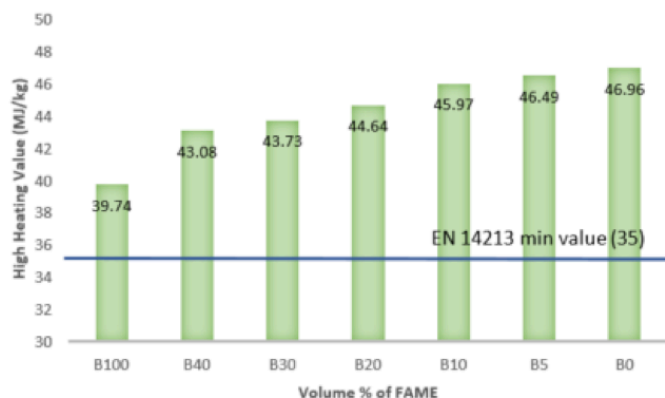


Figure 4. High heating value as function of % FAME in various biodiesel-conventional diesel blends.

Therefore, considering the three-fold effect of HHV, density, and viscosity (**Table 3**), it appears that the B5 and B10 blends achieve performance values that would result in effective use in the Colorado climate and in the types of vehicles used on base. B20 possesses marginal performance characteristics that would render it as a summer seasonal use fuel only. These results are consistent with previous findings and are congruent with the blends nominally used in unmodified, standard diesel engines.³³⁻³⁶

The second performance characteristic evaluated in this study was cloud point determination which is summarized in Table 3 and Figure 5. Cloud point is a key determinant for assessing the cold weather performance capacity of a fuel. In this case, the cloud point was obtained by DSC by analyzing the key phase change onset point in the thermogram (Figure S7). The cloud point by definition is where the first indication of solid material appears in the liquid sample.³⁷ Although still viable as a fuel, any further cooling of the sample below the cloud point could lead to the pour point wherein the flow properties of the fuel are halted.³⁷ Therefore, the cloud point here represents the most reasonable temperature limit for effective fuel use in an operational vehicle. As expected, there was an observable increase in the cloud point temperature as the percentage of biodiesel in the blend was increased. In addition, the B100 cloud point value of -7.16 °C would render a fuel mixture unlikely to be used in cold weather climate such as existing in Colorado during the winter months. However, to our delight, all of the remaining fuel blends showed cloud point values (< -16.55 °C, or -2.21 °F) that would lead to positive implementation throughout the majority of the year regardless of cold weather factors. Moreover, B0-B20 exhibited cloud point values that would allow for use down to 0 °F (any value < -17.78 °C). In Colorado Springs, January and February represent the months most likely to demonstrate a low temperature at or below 0 °F (-17.88 °C).³⁸ A review the temperature data from the past 5 years via weatherspark.com showed a total of 16 days below 0 °F.³⁸ There were 61 total days over the past 5 years in which the recorded low was between 0-10 °F. As such, we can estimate that 3.2 days per year would show low temperatures below 0 °F and 12.2 days would show low temperatures between 0-10 °F. Therefore, there would be 15-16 days per year in which B0 would be the optimal choice for fuel use in diesel vehicles on base. For the remaining days, ostensibly 349-350 days, any of the fuel blends B5-B30 would be acceptable for use in base vehicles.



Figure 5. Cloud point as function of % FAME in various biodiesel-conventional diesel blends.

In summary, we have presented here a facile and validated method for the repurposed use of waste cooking oil from the campus dining hall for the production of several viable biodiesel-petroleum diesel blends. Our findings demonstrate that implementation in base diesel engine vehicles can be effectively accomplished using B5-B30 blends. Ideally, we recommend the use of either B10 or B20 primarily due to them being a well-established and well-studied fuel blend that can be readily used in unmodified diesel engines. There are excellent HHV and cloud point factors that would allow for ready use throughout the year in the climate of Colorado and for producing acceptable energetic output, especially as it pertains to powering campus buses. In addition, the lower percentage of biodiesel in the blends would protect against undesirable fuel line degradation and fuel tank corrosion that could be experienced with higher proportions of biodiesel. B20 blends also have the potential economic advantage by reducing the overall fuel cost due to our ability to generate biodiesel with extremely low cost via our in-house biodiesel synthesis system and the ready no-cost access to the WCO feedstock. Expected costs would be incurred for acquisition of raw materials such as NaOH and methanol. Therefore, if we have a 10,000 gallon/year diesel fuel need, then with implementation of B20, we would need to produce 2000 gallons/year of biodiesel. Considering that the biodiesel synthesis showed a 70% yield and accounting for any loss, this means that we would need nearly 3000 gallons of WCO as feedstock. Currently, approximately 3200 gallons of WCO is available per year for repurposing. Thus, in order to effectively process the WCO into functional biodiesel using our 45-gallon lab-scale reactor, 1100 gallons of methanol with an approximate cost of \$5700 and 200 lb of NaOH with an approximate cost of \$260 are required and can be readily obtained in bulk quantities.^{38,39} Total cost for raw materials is estimated at \$5960/year. The current cost for 2000 gallons of No. 2 diesel is \$7200. Therefore, the approach described here can be considered essentially an economic trade-off, but our method has the advantage of providing a cost-reasonable alternative with considerable sustainability benefits. In terms of sustainability, the key attractive factor here are the gains shown by an assessed green chemistry metric. For instance, the E-factor (environmental factor) was calculated for our process in which the actual amount of waste generated was compared to the desired products obtained. These values were determined according to the formula shown in **equation 6**. Herein, the waste mass (numerator) was comprised of

$$\text{E-factor} = \frac{\text{total mass of waste (g)}}{\text{total mass of products (g)}} \quad (\text{Eq. 6})$$

unused MeOH along with catalysts used and drying agents. The mass of products (denominator) included the yielded biodiesel and glycerol products, both of which are purposefully used in subsequent applications. The E-factor for the trans-esterification process alone was determined to be 0.30 and if the pre-treatment process is included alongside trans-esterification, the E-factor value rises to 0.52. In terms of the empirical values attained here, our results are elevated relative to biodiesel synthesis literature values,⁴¹ but clearly toward the low end of environmental metrics suggesting that our process achieves excellent waste reduction capacity.⁴² Finally, we evaluated a secondary green chemistry metric to further support the sustainability benefits of the reported project. Here, the reaction mass efficiency or RME was calculated using **equation 7**. The numerator was comprised of the sum of mass of both biodiesel

$$\text{RME} = \frac{\text{mass of products}}{\text{mass of reactants}} \times 100 \quad (\text{Eq. 7})$$

and glycerol products whereas the denominator contained masses for MeOH and WCO. Our calculation returned a value of 60%, which corroborates a related finding reported in the literature for an analogous conversion strategy and is consistent with conversions involving esterification reactions.⁴¹ Taken together, the RME and E-factors strongly support that the methodology reported here is characterized by positive green chemistry attributes leading to an attractive approach for alternative fuels development possibilities. Further efforts in our group are focused on incorporation of additives that could extend the practical temperature range of use for biodiesel-petroleum diesel blends as well as modifications in methodology that could lead to even further improvements in the green chemical approach to fuels production.

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SUPPORTING INFORMATION

Available upon request timm.knoerzer@afacademy.af.edu for the following:

1. GCMS data for the trans-esterified WCO (FAMES)
2. FTIR for the trans-esterified WCO (FAMES)
3. DSC cloud point data for the various fuel blends
4. Raw bomb calorimetry data sets used to determine high heating values for the following blends
 - a. B0
 - b. B5
 - c. B10
 - d. B20
 - e. B30
 - f. B40
 - g. B100

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