

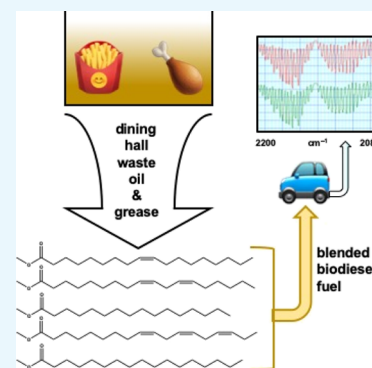
# Biodiesel Production from Locally Sourced Restaurant Waste Cooking Oil and Grease: Synthesis, Characterization, and Performance Evaluation

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## Supporting Information

**ABSTRACT:** Biodiesel was synthesized from locally sourced, on-campus, dining facility waste cooking oil and grease by base-catalyzed transesterification with methanol. The components and properties of the biodiesel were characterized by gas chromatography–mass spectrometry (GC–MS), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR (<sup>1</sup>H and <sup>13</sup>C)), inductively coupled plasma–mass spectrometry (ICP–MS), viscometer, and bomb calorimetry. Five major components of fatty acid methyl esters (FAMES) in the synthesized biodiesel were methyl oleate, methyl linoleate, methyl palmitate, methyl linolenate, and methyl stearate. The <sup>1</sup>H NMR spectra analysis strongly supports the GC–MS results for the percentage of each FAME in the biodiesel. Kinematic viscosity and heat of combustion of the biodiesel were measured, and their values were within optimal ranges recommended by the American Biodiesel Standard (ASTM D6751). The trace elemental composition of the biodiesel determined no significant environmental concerns. The biodiesel was blended with diesel and used to fuel a diesel generator. The combustion exhaust gas was analyzed by FT-IR, and results indicate that the fuel blend underwent complete combustion. Overall results indicate that the biodiesel–diesel fuel blend may be a sustainable, locally sourced alternative fuel for campus diesel utility vehicles.



## INTRODUCTION

The United Nations describes sustainability as “meeting the needs of the present without compromising the ability of future generations to meet their own needs.”<sup>1</sup> Sustainability is an overarching concept connecting governments, economies, and communities through developmental considerations in the environmental, economic, and societal realms. Indeed, many U.S. government agencies (Environmental Protection Agency, Department of Defense, General Services Agency, to name a few) have specific sustainability programs and policies. Likewise, many local communities, such as college campuses, emphasize sustainability through both policy and action. Our campus has a robust “sustainability committee” encouraging the campus community to become involved in local sustainability issues. To address sustainability through tangible action, our undergraduate chemistry student researchers embarked on a project to synthesize and characterize biodiesel produced from locally sourced waste cooking oil and grease produced at a popular campus dining facility. Subsequent use of the biodiesel blended with commercial diesel fuel in our diesel generator and analysis of exhaust products indicate that the biodiesel may be a sustainable, locally sourced alternate fuel source for campus operations, maintenance, and security

personnel who use diesel four-wheeled all-terrain utility vehicles throughout the campus.

Alternate energy sources have been sought because of the high price of petroleum products, decrease in fossil fuel reserves, and atmospheric pollution caused by petroleum-based fuels.<sup>2,3</sup> Biodiesel, derived from a renewable, domestic resource, and thereby relieving reliance on petroleum fuel imports, is an innovative solution to the rapidly evolving energy crisis.<sup>4</sup> Biodiesel fuels also emit lower levels of carbon monoxide, particulate matter, and unburned hydrocarbons compared to petroleum-based diesel.<sup>5</sup>

A common method for biodiesel production is transesterification, in which the triglyceride in the feedstock reacts with a monohydride alcohol to produce monoalkyl esters in the presence of a catalyst.<sup>6–8</sup> As cost-effective feedstocks are required, waste cooking oil, inexpensive compared to pure vegetable oil, draws attention as a promising alternative for the production of biodiesel.<sup>9,10</sup> The use of waste cooking oil in biodiesel production on a large scale would partially decrease the dependency on petroleum-based fuel and ease the

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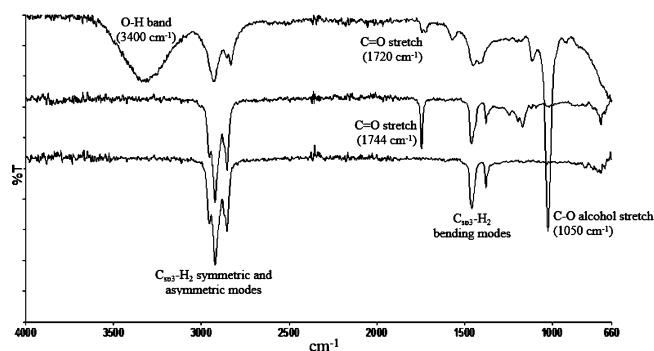
challenge of waste oil disposal and possible contamination of land and water resources, providing a more carbon neutral approach to combustion-based energy sources.<sup>3,7</sup> Differences in the production processes have been reported including varied molar ratios of alcohols to fatty acids, enzymatic and chemical catalysis, or noncatalytic transesterification, whereas a catalyst, homogeneous or heterogeneous, is commonly employed in the biodiesel production.<sup>11–13</sup>

As the use of biodiesel increases, it is important to meet the standards for biodiesel as a fuel. Therefore, the nature of the feedstock in the production of biodiesel needs to be clearly identified, and the complete characterization of the produced biodiesel has been an important aspect of biodiesel research.<sup>14–17</sup> The performance of the biodiesels from different sources and their exhaust gas emissions have been studied as well.<sup>18–20</sup> Different characterization methods have been employed to determine various chemical and physical properties of the generated biodiesel.<sup>2,21–24</sup> The characterization methods include monitoring of the transesterification process [Fourier transform infrared (FT-IR)], fatty acid methyl esters (FAMES)' composition analysis [gas chromatography–mass spectrometry (GC–MS)], liquid chromatography–mass spectrometry (LC–MS), and nuclear magnetic resonance (NMR)], trace metal analysis [inductively coupled plasma–mass spectrometry (ICP–MS)], kinematic viscosity, and heat of combustion (calorimeter).

The objectives of this study were to conduct extensive experiments on the biodiesel production from waste cooking oil and grease and to characterize the properties of the synthesized biodiesel and its blends with commercial diesel, along with the generator combustion exhaust gas characterization. This research utilized the vehicle of undergraduate researchers under the supervision of faculty in the campus environmental research cluster.<sup>25</sup> Although other studies have investigated the production, composition, and characteristics of biodiesel from waste cooking oil and grease, this work is the first report, to the authors' knowledge, of such extensive and integrated research activities led by undergraduate student researchers, investigating locally sourced and sustainable alternative fuels including synthesis, blending, combustion, exhaust capture, and detailed characterization at each stage of the project. The synthesized biodiesel was characterized for its physical and chemical properties by measuring kinematic viscosity and heat of combustion and utilizing instrumental analysis including GC–MS, ICP–MS, FT-IR, and NMR. The characteristics of the produced biodiesel, commercial diesel, and their blends with the detailed comparison are provided herein.

## RESULTS AND DISCUSSION

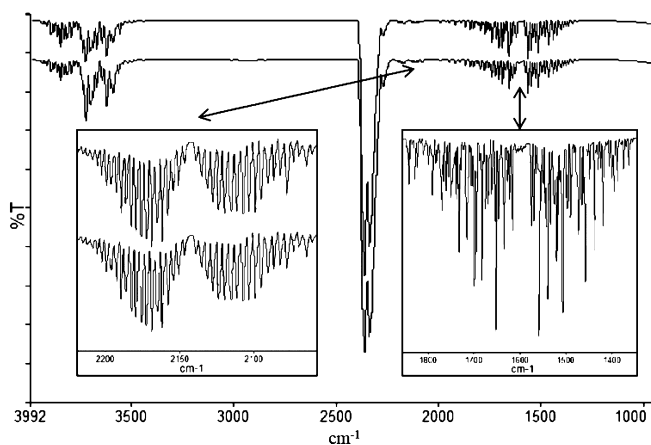
**FT-IR Analysis.** FT-IR spectra of the glycerol layer after biodiesel synthesis (top), synthesized biodiesel product after washing (middle), and commercial ultralow sulfur diesel (ULSD) fuel (bottom) are shown in Figure 1 with detailed vibrational mode assignments summarized in Table S1 in the Supporting Information. Mode assignments for the three layers were made using standard techniques and previous FT-IR studies of biodiesel.<sup>26–31</sup> Noteworthy in the glycerol layer, are the broad O–H alcohol/water band at  $3400\text{ cm}^{-1}$ ,  $C_{sp^3}-H_2$  asymmetric ( $2900\text{ cm}^{-1}$ ) and symmetric ( $2800\text{ cm}^{-1}$ ) stretching modes,  $C_{sp^3}-H_2$  ( $1450\text{ cm}^{-1}$ ) bending mode, C–O alcohol ( $1050\text{ cm}^{-1}$ ) stretch, and  $C_{sp^3}-H_2$  ( $725\text{ cm}^{-1}$ ) rocking modes. The glycerol layer also contains a low-intensity



**Figure 1.** FT-IR spectra of glycerol layer after synthesis (top), synthesized biodiesel product after extraction and washing (middle), and commercial ULSD fuel (bottom).

C=O ( $1720\text{ cm}^{-1}$ ) stretch from the ester, indicating that a small quantity of the synthesized biodiesel is solvated in the glycerol layer. The biodiesel layer indicates no O–H alcohol/water ( $3400\text{ cm}^{-1}$ ) stretching band, indicating that the extraction and washing steps of the synthesis effectively removed glycerol and water from the synthesized biodiesel. The biodiesel exhibits the  $C_{sp^2}-H$  ( $3050\text{ cm}^{-1}$ ) of the vinyl hydrogens,  $C_{sp^3}-H_2$  asymmetric ( $2924\text{ cm}^{-1}$ ) and symmetric ( $2854\text{ cm}^{-1}$ ) stretching modes, high-intensity C=O ( $1744\text{ cm}^{-1}$ ) stretch of the ester, low-intensity C=C ( $1651\text{ cm}^{-1}$ ) alkene,  $C_{sp^3}-H_2$  ( $1440\text{ cm}^{-1}$ ) bending mode,  $C_{sp^3}-H_3$  ( $1375\text{ cm}^{-1}$ ) bending mode, C–O ester ( $1200\text{ cm}^{-1}$ ) stretch,  $C_{sp^3}-H_2$  ( $725\text{ cm}^{-1}$ ) rocking, and the low-intensity C=C cis ( $680\text{ cm}^{-1}$ ) bending of the alkene. The ULSD layer shares features similar to the biodiesel layer but is missing the C=O ( $1744\text{ cm}^{-1}$ ) and the C–O ( $1200\text{ cm}^{-1}$ ) stretches of the ester functional group, indicating that ULSD is a typical diesel hydrocarbon mixture containing no ester moiety.

The FT-IR spectra of the diesel generator gaseous combustion exhaust running on 100% commercial ULSD fuel (top) and B30 blend (bottom) are shown in Figure 2. The blend with mixture of 90% ULSD and 10% biodiesel (vol %) is referred as B10, mixture of 80% ULSD and 20% biodiesel as B20, and mixture of 70% ULSD and 30% biodiesel as B30. The left inset in the figure is an expansion of the weak CO rotation–vibration band, and the right inset is an expansion of



**Figure 2.** FT-IR of the gaseous diesel generator combustion exhaust running on commercial ULSD fuel (top) and B30 blend (bottom). The left inset is the CO rotation–vibration band, and the right inset is the  $H_2O$  rotation–vibration band.

the medium intensity H<sub>2</sub>O rotation–vibration band. The spectra of gaseous H<sub>2</sub>O and CO<sub>2</sub> have been extensively characterized,<sup>32–38</sup> and our experimental exhaust gas spectral features<sup>39</sup> for both ULSD and the B30 blend are summarized in Table S2. Note that the spectra of the ULSD and the B30 blend are virtually identical and that there are no C–H mode features (2750–3150 cm<sup>-1</sup>), indicating complete fuel combustion to H<sub>2</sub>O and CO<sub>2</sub> and a small quantity of CO. The intense CO<sub>2</sub> asymmetric stretching mode (2349 cm<sup>-1</sup>) dominates the spectrum, with the corresponding asymmetric stretching mode (2283 cm<sup>-1</sup>) for the isotopic <sup>13</sup>CO<sub>2</sub> as a low-intensity shoulder of the 2349 cm<sup>-1</sup> feature. The major H<sub>2</sub>O features are a combination band (3852 cm<sup>-1</sup>), the asymmetric stretch (3756 cm<sup>-1</sup>), symmetric stretch (3657 cm<sup>-1</sup>), and the bending rotation–vibration band (centered at 1595 cm<sup>-1</sup>). The CO spectrum displays the rotation–vibration band<sup>40,41</sup> of diatomic molecules and enables construction of the CO rotation–vibration P-branch/R-branch energy diagram as shown in Table S3 and Figure S1.

**GC–MS Analysis.** The FAME profile of the biodiesel generated from waste cooking oil and grease was determined by the GC–MS analysis method described in the experimental section. The retention times of individual peaks of the gas chromatogram were verified against a FAME standard mixture, and individual FAMEs were identified using the MS database (NIST library data). The waste cooking oil and grease obtained from the campus dining facility contained a mixture of canola and peanut oil. C18 fatty acids are the major fatty acid constituents of the synthesized biodiesel, and the identified FAMEs in the biodiesel were methyl oleate, methyl linoleate, methyl palmitate, methyl linolenate, and methyl stearate. The FAME composition is shown in Table 1, and the

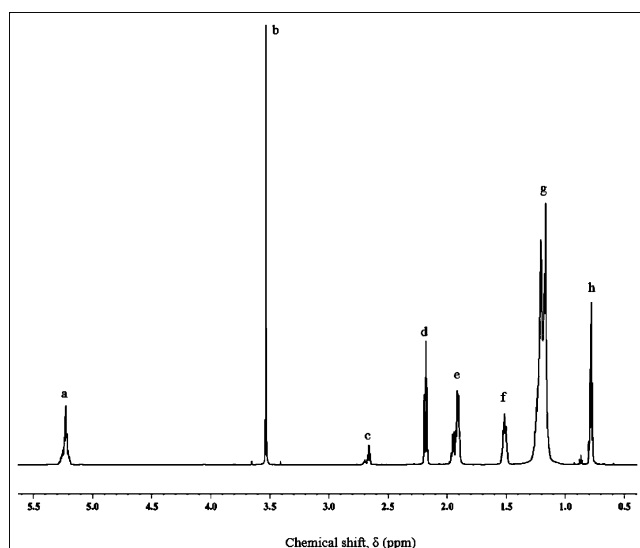
**Table 1. FAME Composition of Biodiesel Synthesized from Waste Cooking Oil and Grease**

retention time (min)	FAMEs	structure	molecular weight	weight (%)
6.7	methyl palmitate	C16:0	270	10.0
7.9	methyl stearate	C18:0	298	1.5
8.9	methyl oleate	C18:1 ( <i>cis</i> -9)	296	64.9
10.5	methyl linoleate	C18:2 (9 <i>Z</i> , 12 <i>Z</i> )	294	20.1
12.3	methyl linolenate	C18:3 (9 <i>Z</i> , 12 <i>Z</i> , 15 <i>Z</i> )	292	1.9
9.0	others <sup>a</sup>	C18:1	296	1.7

<sup>a</sup>Indicates small amount of additional fatty acid species.

GC chromatogram is shown in Figure S2. The FAME composition values are in good agreement with previous studies.<sup>42,43</sup> The FAME composition analysis was confirmed by <sup>1</sup>H NMR results which will be explained in the next section.

**NMR Analysis.** The <sup>1</sup>H NMR spectrum of the biodiesel synthesized from waste cooking oil and grease is shown in Figure 3, and the <sup>13</sup>C NMR spectrum is in Figure S3. The NMR results are referenced to the GC–MS results, which indicate that the biodiesel is a mixture of five FAMEs: 64.9% methyl oleate, 20.1% methyl linoleate, 10.0% methyl palmitate, 1.9% methyl linolenate, and 1.5% methyl stearate. Initial proton and carbon assignments for both spectra were made using standard techniques<sup>44–47</sup> and specific NMR studies of



**Figure 3.** <sup>1</sup>H NMR of a biodiesel mixture of five FAMEs. Detailed proton assignments are presented in Figure 4.

methyl oleate,<sup>48–50</sup> methyl linoleate,<sup>51,52</sup> methyl palmitate,<sup>53,54</sup> methyl linolenate,<sup>55–57</sup> and methyl stearate.<sup>58,59</sup>

To elucidate <sup>1</sup>H spectral features of the FAME mixture, the singlet at 3.52 ppm with an integrated area of 9.00 corresponding to the three methyl hydrogens of the methyl esters (labeled “b” in Figure 4) was used as a reference from

FAME	GC-MS wt %	Structure and Proton Assignments
methyl oleate	64.9 %	
methyl linoleate	20.1 %	
methyl palmitate	10.0 %	
methyl linolenate	1.9 %	
methyl stearate	1.5 %	

**Figure 4.** Biodiesel mixture, FAME structure, and <sup>1</sup>H NMR assignments.

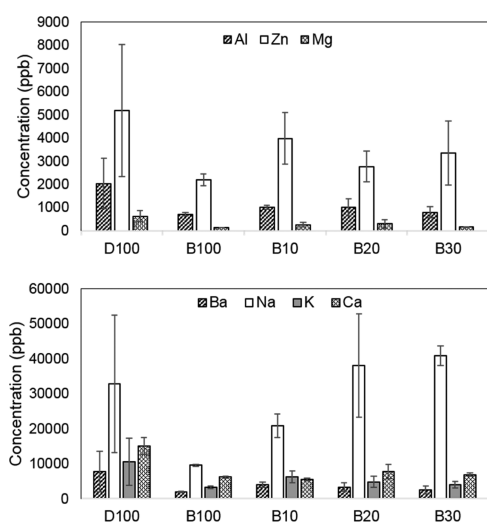
which other peaks were compared. Using the GC–MS mixture percentages of the five FAMEs, the corresponding hydrogens in the structures as shown in Figure 4, and normalizing predicted integrated peak areas, we determined the GC–MS-Predicted Integrated Peak Ratio (x/b) for each type of hydrogen (x) in the mixture relative to the methyl hydrogens of the methyl esters (b) shown in Table 2. On the basis of the experimental <sup>1</sup>H NMR spectrum integrated peak areas, we determined the NMR peak area ratio (x/b). Using the GC–MS-Predicted Ratio as the “theoretical” and the NMR peak area ratio as the “experimental,” we calculated % error NMR versus GC–MS, as shown in Table 2. On the basis of the low % errors, the <sup>1</sup>H NMR spectrum strongly supports the GC–MS results for the percentage of each FAME in the biodiesel

Table 2.  $^1\text{H}$  NMR Proton Areas vs GC–MS Predicted Areas

H	$\delta$ (ppm)	peak shape	peak area	NMR peak area ratio x/b	GC–MS predicted ratio x/b	% error NMR vs GC–MS
a	5.22	singlet	6.69	0.743:1.00	0.750:1.00	0.9
b	3.52	singlet	9.00	1.00:1.00	1.00:1.00	0.0
c	2.66	triplet	1.50	0.167:1.00	0.159:1.00	4.9
d	2.18	triplet	6.29	0.698:1.00	0.667:1.00	4.6
e	1.93	quartet	10.59	1.18:1.00	1.18:1.00	0.0
f	1.52	pentet	6.38	0.709:1.00	0.667:1.00	6.2
g	1.21	multiplet	60.01	6.67:1.00	6.36:1.00	4.8
h	0.78	triplet	9.12	1.05:1.00	1.00:1.00	5.0

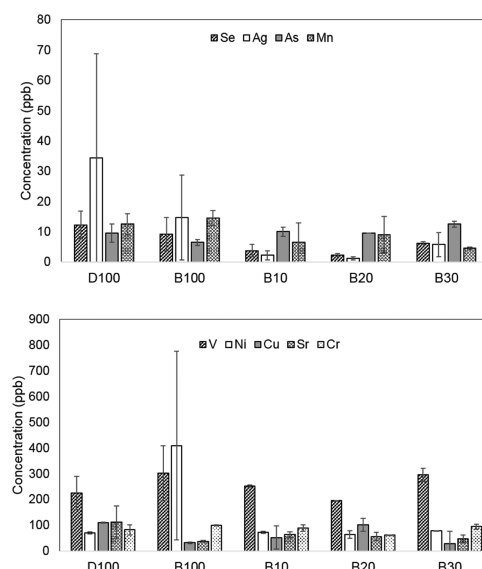
mixture, as does the  $^{13}\text{C}$  NMR spectra and analysis in the [Supporting Information](#).

**ICP–MS Analysis.** Measured concentrations for each element were corrected for the average acid blank digest concentrations ( $n = 4$ ) and dilutions of samples. Analyzed elements were categorized in three groups, low concentration, mid concentration, and high concentration. Low-concentration elements ranged from 1.25 ppb (Ag) to 409 ppb (Ni), mid-concentration elements ranged from 139 ppb (Mg) to 5.18 ppm (Zn), and high-concentration elements ranged from 4.84 ppm (Ba) to 32.86 ppm (Na). [Figures 5](#) and [6](#) show the concentrations for primary elements found in each category.



**Figure 5.** Distribution of mid-concentration elements (top) and high-concentration elements (bottom) found in commercial diesel, synthesized biodiesel, and corresponding blends analyzed using ICP–MS. Error bars represent the full range of measured values for replicates ( $n = 2$ ).

For the low-concentration elements, V and Ni were measured in greater concentrations in the synthesized biodiesel than those in the commercial diesel. These two metals are the only instance in this study of metal concentrations found higher in the synthesized biodiesel than those in the commercial diesel. This is in contrast to Ag, Sr, and Cu, which were present in lower concentrations in the synthesized biodiesel than those in the commercial diesel. Mid-concentration elements included Al, Zn, and Mg, all of which were measured in higher concentrations in the commercial diesel samples than those in the biodiesel. High-concentration elements included Ba, Na, K, and Ca. All of these measured elements were found in higher concentrations in the commercial diesel samples than those in the biodiesel.



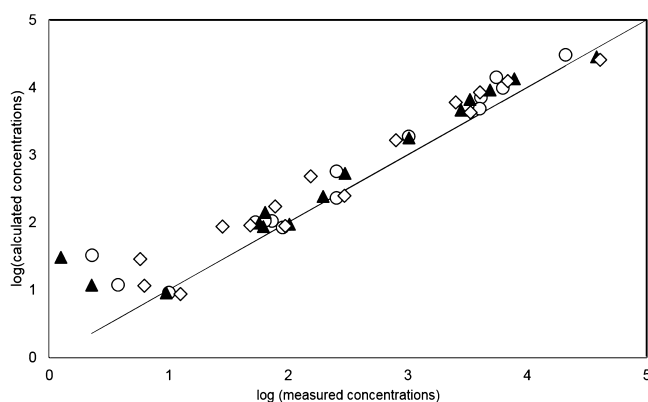
**Figure 6.** Distribution of low-concentration elements found in commercial diesel, synthesized biodiesel, and corresponding blends analyzed using ICP–MS. Error bars represent the full range of measured values for replicates ( $n = 2$ ).

Na was consistently measured as the highest concentration element found in the synthesized biodiesel.

On the basis of the v/v percentages for the commercial diesel and synthesized biodiesel fuels used to create the B10, B20, and B30 blended samples, estimated concentrations for the blends were calculated using a linear combination of the measured data for the original commercial diesel and synthesized biodiesel samples. These calculated (estimated) concentrations of blends for each element are shown in [Figure 7](#) in comparison of measurement data acquired using ICP–MS for each blend. Calculated concentrations were consistently higher than measured concentrations, suggesting a possible matrix effect (a change in the analytical signal which is not attributed to changes in analyte concentrations, possibly due to isobaric interferences) during the measurement of blended samples that dampened the measurement of elemental concentrations. This is also supported by the percent recovery experiments conducted and described in the [Supporting Information](#) section.

Trace elements and minerals found in commercial diesel and biodiesel can originate from sources such as petroleum additives or contamination during the refining process.<sup>60</sup> They can also be present, naturally, as a result of the source, location, and type of the feedstock used in the creation of the biodiesel.<sup>61–65</sup> Regardless of the source, the presence of trace elements and minerals in biodiesel can form soaps and insoluble deposits on vehicle filters, cause issues with corrosion





**Figure 7.** Comparison of measured concentrations vs calculated concentrations (calculated using linear combinations of percentages). The solid line represents a 1:1 ratio. ○ represents B10, ▲ represents B20, and ◇ represents B30.

within the engine, or increase the rate of oxidation within the biodiesel fuel.<sup>15,60,62,66–69</sup> Certain metals, which could be emitted via engine exhaust, also need to be monitored from the environmental and human health perspective.<sup>70,71</sup> Although several studies have focused on elemental determination in biodiesel and their associated feedstocks,<sup>15,60,62,66,67,72–74</sup> this is one of the few studies to measure the elemental composition of biodiesel created from waste cooking oil and grease. Table 3 shows the concentrations determined for the locally synthesized biodiesel (feedstock of waste cooking oil and grease) compared to literature values of previous studies.<sup>15,62,66,75</sup> As shown in Table 3, the elemental composition of biodiesels can vary drastically based on sources, preparation method, and feedstock. For example, the high concentration of Na in the locally synthesized biodiesel can be attributed to the NaOH catalyzed reaction used during synthesis. General guidelines and standards for elemental composition of biodiesel fuels are based on the major minerals (Na, K, Ca, and Mg). ASTM 6751 and EN 12412 standards of biodiesel limit the concentration of Na and K to 5.0 mg/kg.<sup>73</sup> The locally synthesized biodiesel has a higher concentration for Na than recommended by the ASTM 6751. However, the K

concentrations fall below the limits set by this standard. The monitoring of Ca, K, Mg, and Na amount is necessary because of their ability to form undesirable compounds in engines and because of the use of KOH and NaOH catalysts during biodiesel synthesis.<sup>73</sup> Other measured trace elemental and mineral concentrations fall within the wide ranges of values previously reported for biodiesel. Percent recovery experiments were conducted using an organometallic standard in soybean oil. The results of these replicate experiments are listed in Table S4 and explained in detail in the Supporting Information.

**Viscosity and Combustion Analysis.** Kinematic viscosity and heat of combustion are the important fuel properties that affect the engine performance.<sup>76,77</sup> Mixing the biodiesel with diesel and pre-heating the biodiesel can improve the viscosity of the biodiesel.<sup>76</sup> Moreover, both density and viscosity are highly dependent on changes in temperature.<sup>78</sup> Viscosity analysis was conducted to investigate the effect of temperature on kinematic viscosity of biodiesel, diesel, and their blends over the temperature range of 30–100 °C. The analyzed fuels were commercial ULSD, the synthesized biodiesel (100%), and its blends of B10, B20, and B30. The biodiesel (100%) is referred to as B100 and ULSD (100%) as D100.

The kinematic viscosity of biodiesel was 4.86 cSt at 40 °C, meeting the viscosity range from international standards of biodiesel (ASTM D6751) which was 1.9–6 cSt.<sup>79</sup> The ULSD exhibited a kinematic viscosity of 2.59 cSt at 40 °C which lies in the range of (ASTM D 975) standard which is 1.9–4.1 cSt.<sup>79</sup> The viscosity of biodiesel is about 1.8 times higher than that of the diesel. Table 4 lists the kinematic viscosity of test

**Table 4.** Kinematic Viscosity of Biodiesel, Commercial Diesel, and Their Blends

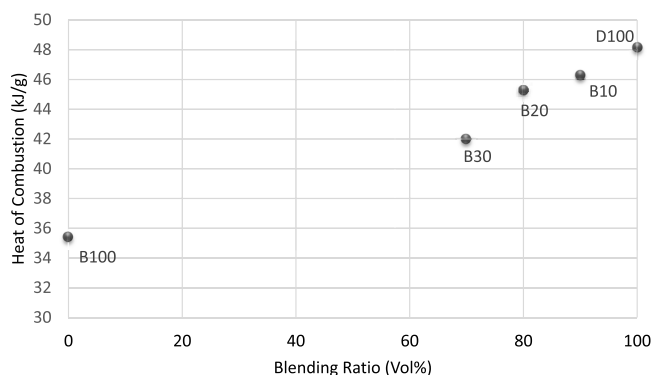
temp (°C)	kinematic viscosity (cSt)				
	B100	B30	B20	B10	D100
30	6.13	3.83	3.58	3.38	3.14
40	4.86	3.1	2.91	2.76	2.59
60	3.28	2.15	2.06	1.95	1.82
80	2.37	1.64	1.54	1.46	1.38
100	1.83	1.3	1.22	1.15	1.07

**Table 3.** Concentrations of Trace and Mineral Elements in Previous Studies and in This Study

element	literature concentrations (ppb)				GGC mean biodiesel concentration (ppb)
	75	15	66	62	
ref	75	15	66	62	
Na	1180–1510	$1.2 \times 10^5$ to $1 \times 10^6$	127–1430	900 to $2.9 \times 10^4$	9542
K	130–2300	15.4–50.6			3335
Ca	100–5340	3–50	20.8–131	400–800	6247
Mg	64–520	$1.2 \times 10^4$ to $2 \times 10^5$	6.16–12.1	160–330	139
Mn		$1.1 \times 10^4$ to $8 \times 10^4$	0.114–0.450	4.9–76	15
Ba		$1.1 \times 10^4$ to $1 \times 10^6$	4.64–55.8		1988
Cu		$1.2 \times 10^4$ to $1.1 \times 10^5$	0.752–11.5	13.8–142	33
Sr		$5 \times 10^0$ to $4.0 \times 10^4$	0.339–4.59		37
Cr		$3 \times 10^4$ to $7 \times 10^4$	0.376–1.09		99
V		5000 to $9 \times 10^4$	0.186–1.36		302
Ni		$2 \times 10^4$ to $5 \times 10^4$	0.397–3.64	6.5–14.1	409
Al		$5 \times 10^0$ to $2 \times 10^6$			713
Zn		$5 \times 10^5$ to $3 \times 10^6$	2.80–27.4	2700	2194
Ag		2–1200	0.257–3.15		15
As		3–2000	1.02–1.29		6
Se		$\sim 1 \times 10^5$			9

fuels and their blends with temperature. The viscosity of biodiesel, each blend, and diesel decreases as the temperature increases. Also, at a fixed temperature, the viscosity decreases as the diesel volume percent in the fuel blend increases.

Because energy released during combustion determines how far a vehicle containing a fixed amount of fuel travels, the higher heat of combustion is an important property of fuel.<sup>80,81</sup> The heat of combustion of B100 synthesized from waste cooking oil and grease was 35.411 kJ/g, roughly 40% less than that of D100 which was 48.083 kJ/g. Heat of combustion increased with the increase of the ULSD fuel in the blends. Figure 8 shows the plot between blending ratio (vol %) and



**Figure 8.** Heat of combustion vs blending ratio between the synthesized biodiesel and ULSD. The *x*-axis (vol %) denotes the volume percent of ULSD.

heat of combustion. The heat of combustion increases linearly with the increase of diesel (vol %). The B30 blend exhibits deviance from the linear trendline, roughly 2 kJ/g lower than that expected. Deviance could be due to interactions on a molecular level when mixing biodiesel to diesel in larger volume ratio.

**Economic and Sustainability Analysis.** Although several studies show analysis of economic feasibility of biodiesel production from waste cooking oil and grease at an industrial level,<sup>82,83</sup> our discussion rather focuses on the economic feasibility of small scale, continuous biodiesel production for on-campus diesel fleet operation. Scale-up biodiesel production from the current bench scale requires installation of the pretreatment system (filtration of waste oil feedstock and neutralization of free fatty acids), 60-gallon biodiesel processor with heating element, wash tank, drain system, and control panel. Operating cost includes methanol and other chemicals, human operator labor, electricity, and other utility fees. The relatively low cost of initial equipment installation for small-scale production, free waste oil and grease feedstock from on-campus dining operations, cost savings from eliminating the current waste oil and grease disposal contract, low labor costs with volunteers and paid student workers, and the operation supervision by environmental cluster faculty enable us to estimate our local biodiesel production costs at less than \$2.00 per gallon. A biodiesel production rate of 30 gallons per week would provide enough biodiesel for B20 fuel to power the on-campus diesel vehicles used by the maintenance and security personnel. This scale-up biodiesel production may be a meaningful action plan for moving toward carbon neutrality on campus as it increases the use of alternate, locally sourced, and sustainable energy resources. Incorporating the biodiesel scale-up operation into a sustainability course in the

curriculum may provide a relevant and exciting sustainability initiative on campus that students across science, business, economic, and political science majors may pursue.

## CONCLUSIONS

Much work in the production and characterization of biofuels begins with using “pure” feedstocks, such as rapeseed oil, from which the biofuel is synthesized. In this study, we attempted to maximize the principles of local sustainability by synthesizing biofuel from waste cooking oil and grease from our on-campus dining facility. This local sustainability approach is especially meaningful for students at our Primarily Undergraduate Institution as they are universally interested in sustainability, especially the idea of locally sourced resources, in their application of science to positively impact their lives. As such, we successfully synthesized useful biodiesel as a mixture of FAMEs using waste cooking oil and grease generated from the cooking process, eliminating the campus expense of shipping and processing the waste cooking oil and grease off campus. The FT-IR, GC-MS, and NMR (<sup>1</sup>H and <sup>13</sup>C) analyses establish the biodiesel as a mixture of five FAMEs, and ICP-MS investigation indicates that heavy metal contamination as a result of the cooking process, and its potential for release into the atmosphere during combustion, is not a concern as the level of contaminants is far below that of the environmental concern. Thermodynamic and viscosity studies of the biodiesel attest to its suitability as a fuel, and upon combustion in our diesel generator, exhaust gas analysis indicates virtually complete combustion to CO<sub>2</sub> and H<sub>2</sub>O with no hydrocarbons remaining. The results of our study open additional avenues of investigation into scale-up of production and characterization so that the biodiesel from local campus waste cooking oil and grease might be used to more economically power diesel vehicles currently operated on campus by operations, maintenance, and security personnel and their potential cost savings to the college.

## EXPERIMENTAL SECTION

**Materials.** Waste cooking oil and grease, composed of a mixture of peanut and canola oil, was obtained from the on-campus dining facility. Methanol (certified ACS, Fisher Chemical), sodium hydroxide (certified ACS, Fisher Chemical), standard mixture of 37 FAMEs (Restek Corporation), dichloromethane (HPLC grade, Acros), and nitric acid (69%, Veritas, redistilled) were purchased from Fisher Scientific (Somerville, NJ). The ULSD fuel was obtained from a commercially available petrol station.

**Biodiesel Synthesis.** The waste cooking oil and grease were filtered under vacuum (Fisherbrand filter paper, P4 grade) prior to use. The biodiesel was synthesized from waste cooking oil and grease via transesterification reaction with methanol. Sodium hydroxide was used as a catalyst, and the reaction proceeded at 65 °C for 2.5 h under reflux. After separation of glycerol and biodiesel, an additional heated reaction of the isolated biodiesel was carried out for 45 min at 65 °C, followed by extraction, washing, and drying.

**FT-IR Spectroscopy.** The FT-IR spectra of the glycerol synthesis by-product, the synthesized biodiesel, and commercial ULSD were taken on a PerkinElmer Spectrum One spectrometer using attenuated total reflection and signal averaging eight scans over the range 4000–660 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution and background subtraction. ULSD and B30

blended fuel were used to power a Generac 5 kW diesel generator, and the combustion exhaust gas was captured for analysis. The FT-IR spectra of the gaseous combustion exhaust from the diesel generator were taken on a PerkinElmer Spectrum Two spectrometer with transmission through a 10 cm gas cell with CaF<sub>2</sub> windows at 1.0 atm pressure, 298 K, signal averaging 64 scans over the range of 4000–1000 cm<sup>-1</sup> with a 0.5 cm<sup>-1</sup> resolution and background subtraction.

**Gas Chromatography–Mass Spectrometry.** The biodiesel samples were analyzed using a Shimadzu QP2010S Gas Chromatography–Mass Spectrometer with a HP 88 column (60 m, 0.25 mm, i.d., 0.20 μm film thickness) in the scan mode to determine FAME composition. The carrier gas was helium with a constant flow rate of 2.0 mL/min. The sample of 2.0 μL in methylene chloride was injected using the split mode with a split ratio 1:50 at the injection temperature of 250 °C. The GC oven temperatures were held at 175 °C for 10 min, ramped at 3 °C/min to 220 °C with a final hold for 5 min. The GC–MS interface was maintained at 250 °C, and the MS ion source temperature was 230 °C.

**NMR Spectroscopy.** <sup>1</sup>H NMR spectra of the biodiesel mixture were taken with a Bruker spectrometer in the CDCl<sub>3</sub> solvent operating with 600 MHz at 300.0 K with 2.7 s acquisition time, 16 scans, 65 536 data points, 12 019.230 Hz spectral width, 10.30 μs pulse length, and 0.183399 Hz FID (free induction decay) resolution. <sup>13</sup>C NMR spectra of the biodiesel mixture were taken with a Bruker spectrometer in the CDCl<sub>3</sub> solvent operating with 125 MHz at 301.2 K with 1.1 s acquisition time, 48 scans, 65 536 data points, 30 030.029 Hz spectral width, 11.50 μs pulse length, and 0.458222 Hz FID resolution.

**Inductively Coupled Plasma–Mass Spectrometry.** Samples of ULSD, synthesized biodiesel, and corresponding blends were digested using concentrated HNO<sub>3</sub> (69%, Veritas, redistilled) in a 1/9 volume ratio (0.5 mL of sample to 4.5 mL of HNO<sub>3</sub>) using PTFE beakers (Sallvex). These mixtures were heated under gentle reflux at 110 °C for ~120 h. Digests were then filtered (Whatman GD/X nylon syringe filters, 0.45 μm) and diluted to 50 mL using MilliQ water (resistivity = 18.2 MΩ cm). Replicate digests (*n* = 2) were created for each sample. Acid blanks (*n* = 4) were created using the same procedure using 0.5 mL of concentrated HNO<sub>3</sub> in place of the biodiesel sample. Replicate aliquots of 0.5 mL (*d* = 1.25 g/mL) of a metallo-organic standard in soybean oil (High Purity Standards, Charleston SC, CRM-TMSO) were digested using the same method to investigate percent recovery of metals from an organic matrix using this digestion method. Replicate digests and acid blanks were analyzed using a PerkinElmer Elan DRC II ICP–MS (PerkinElmer, USA). Details of instrument parameters and quality control can be found in Tables S5 and S6 in the [Supporting Information](#).

**Kinematic Viscosity Measurement.** Kinematic viscosity was measured using the Cannon-Ubbelohde viscometer and a PolyScience viscosity bath (Figure S4). The viscometer and bath were operated at temperatures of 30, 40, 60, 80, and 100 °C, with 20 min provided for each temperature equilibration. Efflux time (for biodiesel to flow a specified distance in the viscometer under gravity) was then recorded as it flowed from mark E through F in Figure S4a. The kinematic viscosity was calculated by multiplying the efflux time with a viscometer constant.

**Calorimetry.** A Parr System 6725 semimicro calorimeter with a 6772 calorimetric thermometer and a 1109(A)

semimicro oxygen combustion vessel (bomb) with a 45C10 fuse wire of nickel alloy (heat of combustion of 9.6 J/cm) was used to measure the heat of combustion of the biodiesel, ULSD, and B10, B20, and B30 blends. Benzoic acid pellets were used as a standard to determine the calorimeter heat capacity, and the heat of combustion was determined by combusting samples ranging between 0.100 and 0.200 g.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsomega.9b00268](https://doi.org/10.1021/acsomega.9b00268).

IR assignments (cm<sup>-1</sup>) of glycerol layer, synthesized biodiesel product after washing, and commercial ultra-low sulfur diesel fuel; IR assignments of diesel engine combustion exhaust gases; analysis of CO rotation–vibration band; schematic rotation–vibration energy diagram for the CO based on the FTIR exhaust gas spectrum and experimental data summarized in Table S3; GC chromatogram of FAMES of biodiesel synthesized from waste cooking oil and grease; <sup>13</sup>C NMR of biodiesel mixture of 5 FAMES; percent recovery values for method validation for ICP–MS; quality control information for elements measured using ICP–MS in biodiesel and blended samples; ICP–MS instrument parameters; and viscometer pictures (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ ACRONYMS

B10 blend	90% ULSD and 10% biodiesel (vol %)
B20 blend	80% ULSD and 20% biodiesel (vol %)
B30 blend	70% ULSD and 30% biodiesel (vol %)
B100	100% biodiesel
D100	100% ULSD
GGC	Georgia Gwinnett College
ULSD	ultralow sulfur diesel



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