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Analysis of biodiesel-diesel blends using ultrafast gas chromatography (UFGC) and chemometric methods: Extending ASTM D7798 to biodiesel

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ABSTRACT

Ultrafast gas chromatography (UFGC) along with supervised and unsupervised chemometric methods were utilized for evaluation of biodiesel-diesel blended fuels. A variety of biodiesel feedstocks (soybean, tallow, canola, safflower, sunflower, camelina, flaxseed, etc.) and concentrations (1–20%) were evaluated. The method, which uses a short nonpolar column, falls within ASTM D7798 requirements for diesel and extends the method to include biodiesel-diesel blended fuels. Using Principal Components Analysis (PCA), samples clustered based on concentration and diesel type, and differences in plant and animal feedstocks were apparent. Biodiesel concentration was accurately assessed using Partial Least Squares (PLS) on a training set for B0–B20, while predictions were made with some success on a set of commercial and lab unknowns. k Nearest Neighbors (kNN) was used to describe and predict concentration, plant versus animal feedstock, and to identify biodiesel blends. The combination of chemometric methods alongside UFGC proves an effective and fast technique for the analysis of biodiesel source and composition in biodiesel-diesel blended fuels.

1. Introduction

Biodiesel is most commonly added to diesel fuel to intentionally decrease greenhouse gas emissions. Life cycle analysis reports 74% fewer emissions for 100% biodiesel (B100) compared to petroleum diesel [1]. Even a small addition of biodiesel, say 20% by volume (called B20), can decrease hydrocarbon emissions by about 20% and carbon monoxide emissions by about 13% [1]. The United States government and many U.S. states, along with the majority of countries in the European Union, incentivize adding biodiesel to diesel to decrease greenhouse gases and exhaust pollution [2–4]. Refineries, bulk blending distribution terminals, and even retail outlets must be able to accurately blend biodiesel into the diesel to meet regulatory requirements. The amount of biodiesel that is blended may change throughout the year in order to optimize fuel properties [5–7]. For instance, in the summer, a retail outlet may choose to maximize the amount of biodiesel included in the fuel to maximize profit, while in the winter, they need to decrease the biodiesel content to keep the pour, cloud, and freeze points within specification [7]. In addition, some governments may want to identify feedstock as part of initiatives to utilize feedstocks that have data requirements regarding land use [4]. This places a large demand on the number of fuel samples to be analyzed. Thus, increased speed of analysis and standardization of data interpretation will prove valuable.

On the other hand, fraudulent addition of biodiesel and other materials is on the rise. By adding biodiesel, motor oil, or vegetable oil to diesel, fuel carriers can avoid diesel roadside tax or attempt to increase profit margins [8,9]. This type of fuel adulteration is a problem both for governments who stand to lose important tax dollars and for consumers with possible negative impacts on engine performance [8]. Quick and easy roadside analysis of fuels would be extremely valuable. Thus, having a fast and sensitive method for detection and quick determination of biodiesel concentration is valuable for a variety of fields where biodiesel is blended with traditional diesel.

Diesel, a petroleum distillate, contains saturated hydrocarbons (straight-chain and branched alkanes, naphthenes, etc.), aromatic hydrocarbons (alkylbenzenes, naphthalenes, etc.), and a small number of unsaturated hydrocarbons (alkenes) with molecules ranging from ten to twenty carbon atoms. Traditionally, gas chromatography (GC) has been a preferred method for analysis of diesel [10–14]. A nonpolar column and a fairly straightforward temperature program allow for identification of diesel components and evaluation of the refining process [10]. Conventional GC analysis of diesel, however, can be time intensive, with run times of at least thirty minutes or more [10,15]. Ultrafast GC

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Table 1
Test biodiesel sample composition.

	Label	Diesel Type (Year Acquired)	Biodiesel Feedstock (Producer)	Concen-tration
Lab Created Test Samples	A	Flynns (2013)	Soybean (Western Dubuque)	B3
	B	Phillips 66 (2017)	Soyabean (Bianca Rosa)	B8
	C	Flynns (2013)	Waste Grease (TMT Biofuels)	B12
	D	Phillips 66 (2017)	Tallow (Texas Green)	B15
	E	Phillips 66 (2017)	Unknown (Keystone Biofuels)	B30
	F	Shell (2013)	Soybean (MSP)	B50
True Unknown Commercial Samples	G	Flynns (2015)	Unknown	Unknown
	H	Hess (2013)	Unknown	Unknown
	I	Woosta (2015)	Unknown	Unknown
	J	BP (2013)	Unknown	Unknown
	K	Shell (2015)	Unknown	Unknown
Lab Created Multi-feedstock Blends	L	Flynns (2013)	Canola (ADM): Soybean (MSP) [1:1]	B5
	M	Flynns (2013)	Canola (ADM): Soybean (MSP) [1:1]	B10
	N	Flynns (2013)	Canola (ADM): Soybean (MSP) [1:1]	B20
	O	Flynns (2013)	Tallow (Texas): Soybean (MSP) [3:1]	B20
	P	Flynns (2013)	Tallow (Texas): Soybean (MSP) [1:1]	B20
	Q	Flynns (2013)	Tallow (Texas): Soybean (MSP) [1:3]	B20

(UFGC) methods for diesel utilize the same nonpolar column chemistry but with short (2–10 m), narrow-bore capillaries, allowing for run times of just a few minutes [16–20]. One such UFGC method, which allows for simulated distillation correlation, is ASTM standard method D7798 [17]. D7798 is being used currently by commercial and government labs for fast analysis of diesel for both blending and adulteration purposes.

Biodiesel, a renewable fuel, is produced from vegetable oil or animal tallow via a transesterification reaction with methanol and a base catalyst. The result is a fuel that contains a mixture of fatty acid methyl esters (FAMEs) ranging from C6 to C22, depending on the feedstock used. Analysis of biodiesel is conventionally done using spectroscopy or GC [11,21]. Spectroscopy (IR, Fluorescence, etc.) is used to analyze the bulk material without isolation of the individual components [11,21–24]. GC, however, is used to analyze the individual FAME components in the fuel [25,26]. A long, polar column is best suited for successful separation of individual FAMEs [25]. Both concentration and feedstock type can be determined when GC analysis is combined with chemometric methods [25,27–29]. High speed methods for separation of FAMEs have been reported [30–35]. These fast methods utilize a polar column chemistry and allow adequate resolution of FAME components. However, UFGC methods for biodiesels are not currently well utilized.

Biodiesel-diesel blends have been analyzed using a variety of column chemistries, ranging from nonpolar to polar, depending on the application [25,26]. In this study, we suggest the use of D7798, an ultrafast GC method traditionally used for diesel fuels, to be used for biodiesel-diesel blended fuels. D7798 has until now only been used for diesel fuels. We report that useful information can be obtained from UFGC data by employing chemometric methods, such as Principal Components Analysis (PCA), Partial Least Squares (PLS), and k Nearest Neighbors (kNN). Identification of biodiesel presence, blended concentration, and animal versus plant feedstock can be performed using a method that is already employed in many locations for diesel alone. This method – ultrafast GC in combination with chemometrics – offers users a significantly faster and more sensitive alternative for monitoring fuel blending process performance or for roadside detection of adulterated fuels.

2. Material and methods

2.1. Chemicals

Biodiesel fuel samples were obtained commercially or produced in-house via transesterification. Biodiesels obtained from various manufacturers across the United States include Minnesota Soybean Processors ((MSP) Brewster, MN, soybean), Archer Daniels Midland Company ((ADM) Decatur, IL, canola), TMT Biofuels (Port Leyden, NY, waste grease), Iowa Renewable Energy (Washington, IA, tallow, soybean, canola), Texas Green Manufacturing (Littlefield, TX, beef tallow), Western Dubuque Biodiesel (Farley, IA, soybean), NIST (Gaithersburg, MD, SRM 2772, soybean, and SRM 2773, animal/soybean). Commercial biodiesels were stored in their original containers at 4 °C.

Biodiesels produced in the laboratory originated from the following plant oils: canola, sunflower, safflower, soyabean, flaxseed (Nutrition from the Source), and lena camelina (Lentz Spelt Farms). The transesterification reaction was run adding 100 mL of warmed vegetable oil (40 °C) to 20 mL sodium methoxide solution ((0.35 g finely ground anhydrous NaOH (Fisher Scientific) in 20 mL pure methanol (HPLC grade, Fisher Chemical)) and stirring for 15–30 min. The mixture was then transferred to a separatory funnel where it was left to separate for approximately one hour. The glycerol-containing bottom layer was removed, resulting in the final biodiesel.

Diesel fuel samples were obtained from Phillips 66 (Linden, NJ), Shell (Worcester, MA), Sunoco (Germantown, MD) and Flynn's (Shrewsbury, MA), and transferred to amber bottles stored at 4 °C. Biodiesel-diesel blends (10 mL total volume) were prepared at 1, 2, 5, 10, and 20% biodiesel by volume (B1, B2, B5, B10, B20, respectively).

A set of test samples was used for chemometric evaluation (Table 1). Six laboratory-produced test blends along with five commercial biodiesel-diesel blends were analyzed. In addition, six blends containing two different feedstocks, called multi-feedstock blends, were prepared in three ratios (1:1, 1:3, 3:1). Evaluation of the test blends was conducted in a blind manner. All prepared samples were stored in brown bottles at 4 °C. Samples were brought to room temperature, homogenized via inversion, and an aliquot of each was transferred to an injection vial prior to GC analysis.

2.2. Instrumentation

Separations were performed using a CALIDUS™ Ultrafast Gas Chromatograph (Falcon Analytical, Lewisburg, WV) using the ASTM D7798 Ultrafast GC SimDis Method. The GC was equipped with a nonpolar MXT-1HT column (Restek, 2 m × 320 µm × 0.2 µm). The temperature program began at 40 °C (start hold 10 s) and ramped to 395 °C at 2.0 °C/s (end hold 112.5 s). The end hold was needed to successfully remove high molecular weight components that could be present in biodiesel fuels produced outside a regulated setting or in