Journal of Chromatography A 1667 (2022) 462903

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Analysis of biodiesel-diesel blends: Does ultrafast gas chromatography provide for similar separation in a fraction of the time?☆

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ARTICLE INFO

Article history:
Received 19 January 2022
Revised 9 February 2022
Accepted 12 February 2022
Available online 13 February 2022

Keywords:
Biodiesel
Diesel
Ultrafast gas chromatography
UFGC
Gas chromatography
GC
PCA

ABSTRACT

Ultrafast gas chromatography (UFGC) using a moderately polar column was compared to traditional gas chromatography (GC) for evaluation of biodiesel-diesel blended fuels. Several biodiesel feedstocks (soybean, tallow, canola, palm, camelina) and concentrations (1–20%) were evaluated, with specific attention to the separation of fatty acid methyl esters (FAMEs) from the biodiesel component. UFGC is compared to traditional GC using a similar column chemistry. Principal component analysis (PCA) is performed to identify clustering based on feedstock and concentration. UFGC proves an effective and fast technique, comparable to traditional GC, for the analysis of biodiesel-diesel blended fuels.

1. Introduction

Gas chromatography (GC) with a nonpolar column has long been the preferred method for analysis of diesel, a petroleum distillate containing various hydrocarbons [1–5]. Conventional GC analysis of diesel can be time intensive, with run times of at least thirty minutes or more [1,6]. Ultrafast GC (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 [7–11]. Biodiesel is commonly added to diesel fuel in response to the need for greener fuels and lower emissions [12]. Biodiesel is produced from vegetable oil or animal tallow via transesterification and yields fatty acid methyl esters (FAMEs). GC paired with a long, polar column is best suited for successful separation of individual FAME isomers in the biodiesel-diesel blends [13]. High speed methods for separation of biodiesel blends have been reported [14–15]. These fast methods utilize a polar column chemistry and allow adequate resolution of FAME components. However, ultrafast methods for analysis of biodiesel-blends are not well utilized and the literature regarding use of UFGC for FAME analysis is limited. The work of Bergamaschi Tercini et al. is one of the only studies that evaluates biodiesel-diesel blends using UFGC; they employed a very polar column for the analysis of total FAMEs [16]. UFGC relies on quick temperature ramps and high final temperatures, which in combination with a very polar column, can yield column degradation in a short number of cycles. Previous research in our lab evaluated a nonpolar column for the analysis of diesel fuels mixed with various concentrations of biodiesel [17]. Resolution of the FAMEs was poor on a nonpolar column. An alternative approach may be to utilize a moderate polarity column, where increased polarity may improve FAME separation along with increased maximum temperatures may prolong column lifetime. In fact, use of a moderate polarity GC column for the separation of FAMEs has been reported in this journal [18]. A moderate polarity column has also been utilized for analysis of diesel fuels, when additional information regarding the chemical composition is desired [19]. In this research, we employ UFGC with a moderately polar column to investigate the separation of biodiesel-diesel blended samples. A comparison to the separation of the same samples using a traditional length GC column with similar column chemistry is performed.

2. Material and methods

2.1. Chemicals

Biodiesel fuel samples included in this study were obtained from Iowa Renewable Energy (Washington, IA, tallow, soybean, canola) and NIST (Gaithersburg, MD, SRM 2773, tallow/soybean).

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https://doi.org/10.1016/j.chroma.2022.462903
0021-9673/

Two biodiesels were produced in house from the original plant oil (palm (Bianca Rosa) 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 was obtained from Phillips 66 (Linden, NJ). Samples were stored in their original containers at 4 °C. A series of biodiesel-diesel blends (10 mL total volume) were prepared for each biodiesel type by mixing with the Phillips 66 diesel in blend ratios of 1, 2, 5, 10, and 20% biodiesel by volume (B1, B2, B5, B10, B20, respectively). Samples were brought to room temperature, homogenized via inversion, and an aliquot of each was transferred to an injection vial prior to GC analysis. Each sample was injected and analyzed in triplicate.

2.2. Instrumentation

2.2.1. UFGC

Separations were performed using a CALIDUS™ Ultrafast Gas Chromatograph (Falcon Analytical, Lewisburg, WV). The GC was equipped with a moderately polar MXT-50 column (50% phenyl polydimethylsiloxane, Restek, 4 m x 180 μm x 0.2 μm). The temperature program began at 40 °C (start hold 10 s) and ramped to 275 °C at 2.0 °C/s, followed by a second ramp to 345 °C at 1.0 °C/s (end hold 27.5 s), yielding a total run time of 3.75 min. Ultra high purity hydrogen was used as a carrier gas under constant pressure mode (15.0 psi). The flame ionization detector (FID) was operated using ultra zero grade high purity air (17.6 psi) and ultra-high purity hydrogen (22.0 psi) at 350 °C. Each sample was analyzed at room temperature. Injections (70 nL, splitless) occurred via a PALARUS™ GC autosampler (Falcon Analytical) at 350 °C. Chromperfect™ (v6.0.14, Chromperfect, Denville, NJ) was used to control all instrument parameters.

2.2.1. Traditional GC

Separations were performed using an Agilent 6890 gas chromatograph coupled with an Agilent 5973 mass spectrometer (Agilent Technologies, Santa Clara, TX) and have been described previously [27]. The GC was equipped with a moderately polar RTX-50 column (crossbond 50% phenyl polydimethylsiloxane, Restek, 30 m x 0.25 mm x 0.25 µm). The oven temperature was optimized for separation of FAME components in the biodiesel as follows: 80 °C (hold 1 min) to 180 °C at 30 °C/min to 290 °C at 5 °C/min, yielding a total rum time of 26.5 min. High purity helium was used as a carrier gas at a flow rate of 1.5 mL/min. Each sample was manually injected in triplicate (1µL from 10 µL syringe, Hamilton Company) with a split ratio of 50:1. The inlet and transfer line temperatures were held at 250 °C and 280 °C, respectively. An electron-impact ionization source was utilized with a quadrupole mass analyzer operated in full-scan mode (m/z 20 – 600) with a sampling rate of 4.94 scans/s. The mass spectrometer source and quadrupole were held at 230 °C and 150 °C, respectively.

2.3. Data analysis

Peak identification was performed by comparing to the NIST 2773 soybean/tallow biodiesel standard and using a NIST database. All chromatograms were aligned using Lineup™ (Infometrix, Bothell, WA) to a representative diesel chromatogram with warp of 2 and segment size of 100 for the UFGC data and warp of 4 and segment size of 15 for the GC data. Aligned files were imported into Pirouette® (v4.5, Infometrix). Mean centering and vector length normalization were applied prior to chemometric analysis using Principal Component Analysis (PCA). The data are plotted in principal component space using Microsoft Excel.

3. Results and discussion

3.1. Separation of biodiesel-diesel blends by UFGC

Representative chromatograms showing the separation of biodiesel blends using the moderately polar MXT-50 column in UFGC are presented in Fig. 1. Fig. 1A displays various feedstocks at B20 concentration, and Fig. 1B displays the tallow/soybean feedstock at different concentrations.

FAMEs from the biodiesels elute between 1.2 and 2.2 min. The C12:0, C14:0, C16:0, C20:1, and C22:1 FAMEs are resolved from other FAMEs and diesel peaks. The C18:0 and C18:1 FAMEs are unresolved from one another. In some feedstocks, the C18:2 is a shoulder peak overlapping with the C18:0 and C18:1, while in other feedstocks, like the camelina, the C18:2 is a more distinct peak yet still not baseline resolved. For most feedstocks, the C18:3 FAME is not baseline resolved from the C18:0/C18:1 peak. Interestingly, the C18:3 FAME is baseline resolved for the camelina feedstock. Elution order here is characteristically based on both boiling point and polarity [18].

Peak heights for FAMEs increase with concentration. For the most abundant FAMEs in a given feedstock, peaks are typically noticeable at low concentrations of biodiesel (B1 and B2). For example, C16:0 and C18:0/C18:1 peaks are present in the B1 tallow chromatogram. At the low concentrations, it can be more challenging, however, to identify FAMEs that are present in smaller concentrations (e.g. C20:1 in camelina) or those that overlap with diesel peaks (C12:0 in palm).

In comparison to UFGC with a nonpolar column, the separation of FAMEs is not greatly improved [17]. The main difference is the ability to perhaps identify the presence of C18:3 FAME, but otherwise the separation is similar. Thus, if detailed information concerning FAME composition is needed, UFGC with a moderately polar column would not necessarily be a better choice than a nonpolar column, and use of a polar column chemistry would be warranted [16]. However, if detailed FAME identification is not needed, perhaps for determination of an adulterated fuel or calibration of a biodiesel concentration, this UFGC method could be appropriate.

3.2. Separation of biodiesel-diesel blends by conventional GC

For comparison, representative chromatograms showing the separation of biodiesel blends using the moderately polar RTX-50 column in conventional GC are presented in Fig. 2. Fig. 2A displays various feedstocks at B20 concentration, and Fig. 2B displays the tallow/soybean feedstock at different concentrations.

FAMEs from the biodiesels elute between 5.6 and 17.5 min. The C12:0, C14:0, C16:0, C20:1, and C22:1 FAMEs are resolved from other FAMEs and diesel peaks. The C18:0 and C18:1 FAMEs are unresolved from one another, as was the case with the UFGC method. A large difference here is that the C18:2 and C18:3 FAMEs are baseline resolved from the C18:0/C18:1 peak and from one another, a major improvement in the separation. In fact, a much clearer description of the FAME composition for each biodiesel and the differences across the set can be identified. Elution order is again characteristically based on both boiling point and polarity [18]. These results are somewhat consistent with Yamomoto et al., who were able to achieve some resolution between saturated and monounsaturated FAMEs but did not achieve baseline separation using a 50% phenyl column [18].

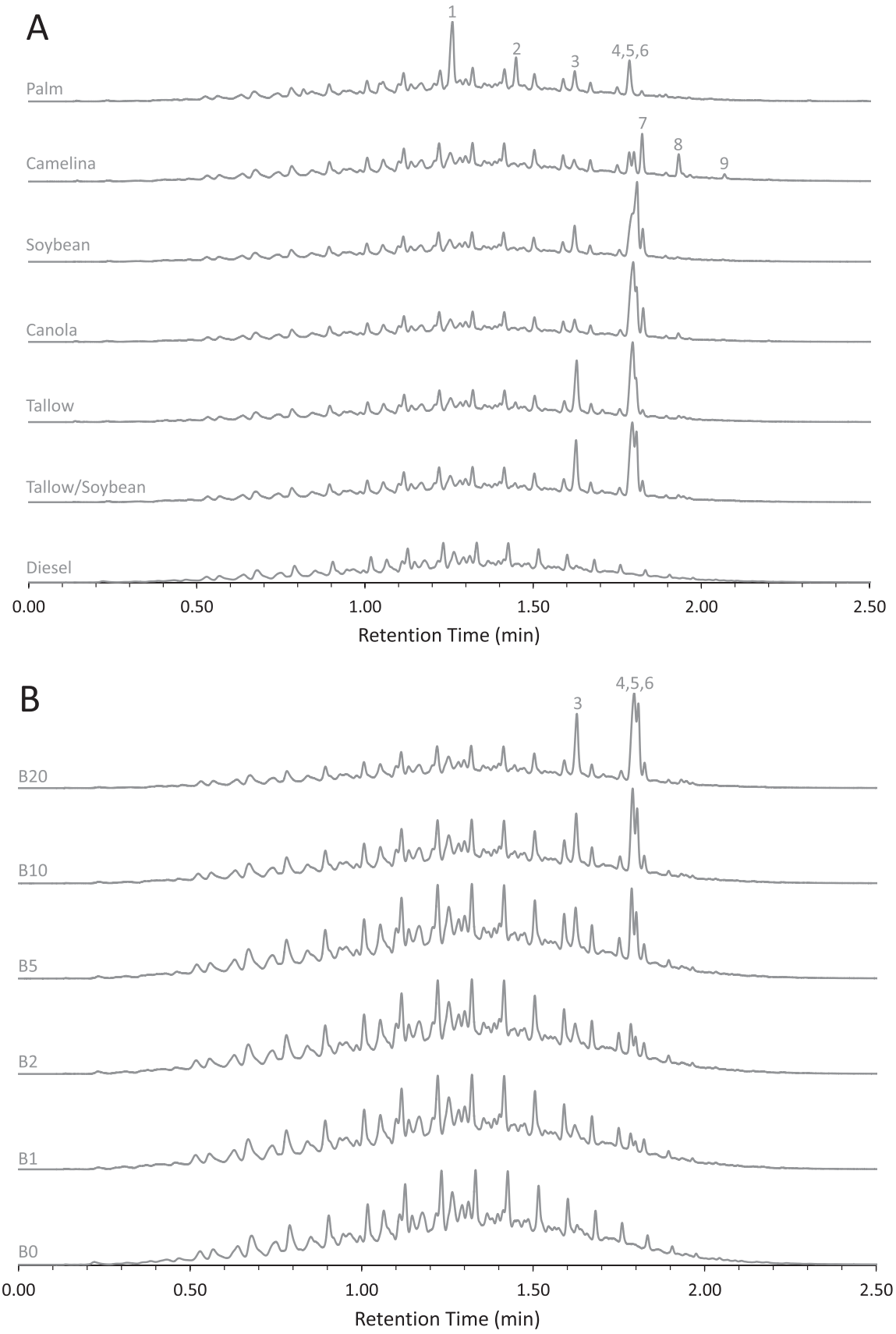

Fig. 1. UFGC chromatograms displaying (A) various feedstocks at the B20 blend ratio and (B) various blend ratios of the tallow/soybean biodiesel. FAME peaks are labeled: 1- C12:0, 2- C14:0, 3- C16:0, 4- C18:0, 5- C18:1, 6- C18:2, 7-C18:3, 8- C20:1, 9-C22:1.

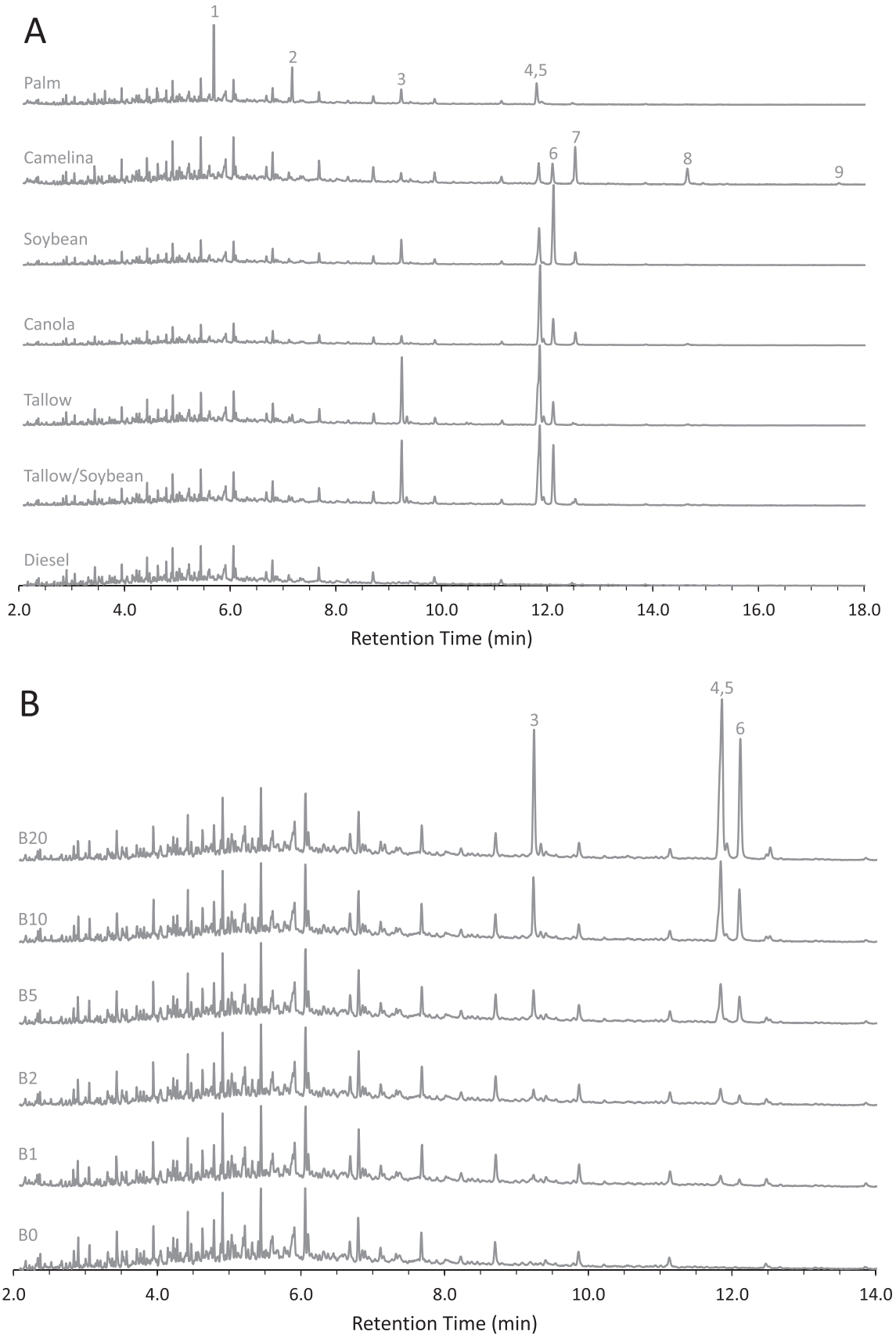

Fig. 2. Conventional GC chromatograms displaying (A) various feedstocks at the B20 blend ratio (B) various blend ratios of the tallow/soybean biodiesel. FAME peaks are labeled: 1- C12:0, 2- C14:0, 3- C16:0, 4- C18:0, 5- C18:1, 6- C18:2, 7-C18:3, 8- C20:1, 9-C22:1.

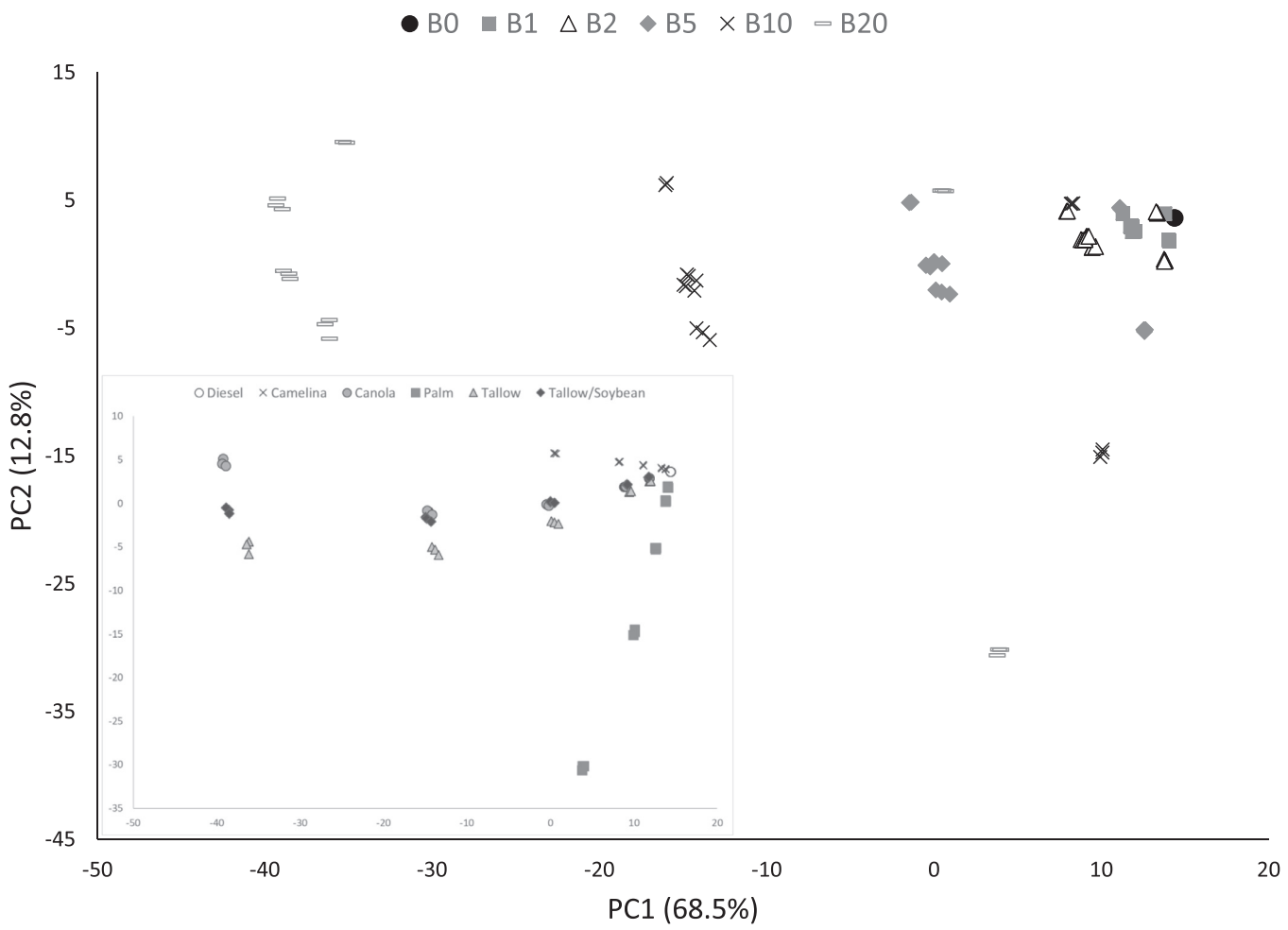

Fig. 3. PCA of UFGC dataset showing clustering based on concentration. The inset figure displays feedstock type.

Peak heights for FAMEs increase with concentration, with similar trends compared to UFGC. For the most abundant FAMEs in a given feedstock, peaks are typically noticeable at low concentrations of biodiesel (B1 and B2). For example, C16:0 and C18:0/C18:1 peaks are present in the B1 tallow chromatogram. Again, at the low concentrations, it can be more challenging, however, to identify FAMEs that are present in smaller concentrations (e.g. C20:1 in camelina) or those that overlap with diesel peaks (C12:0 in palm).

3.3. Principal component analysis of UFGC data

PCA is a multivariate technique that is useful in determining trends in large data sets. In this research, PCA was used to investigate if concentration and feedstock type could be grouped together using the data obtained from a moderately polar column where the resolution between FAMEs is not complete. PCA was performed on the UFGC data set; the first two principal components are plotted in Fig. 3. Biodiesel-diesel blends are clustered based on concentration across PC1. Diesel (B0) samples are clustered in the upper right with B1 and B2 samples clustering nearby. The overlapping B0, B1, and B2 groups are likely based on very small differences in concentration of the FAMEs present in the B1 and B2 samples. B5, B10, and B20 samples are clustered more distinctly from one another and spread from right to left across the first principal component axis. The differences in B5, B10, and B20 FAME concentration are more pronounced than in the smaller concentrations. The loadings for PC1 indicate C12:0, C16:0, and C18:0/C18:1 FAME peaks are responsible for the concentration clusters observed. The only exception to these concentration clusters comes from the camelina feedstock (far upper right in Fig. 3). The camelina samples are still clustered distinctly based on concentration, but are not as spread out across PC1 as the other samples.

Biodiesel-diesel blends are clustered based on feedstock type across PC2, almost as spokes from a central origin, as shown in the inset of Fig. 3. On PC2, from most positive to least positive, the feedstocks are identified as camelina, soybean, canola, tallow, tallow, palm. The soybean, canola, and tallow samples all contain similar FAMEs: C16:0, C18:0, C18:1, C18:2, and C18:3, albeit in different concentration ratios [13]. The camelina biodiesel has a large concentration of C18:3 FAME and is the only feedstock in this data set that contains the longer C20:1 and C22:0 FAMEs. The palm biodiesel has a large concentration of C12:0 and C14:0, making it the only biodiesel in this set with these FAMEs. The loadings on PC2 indicate C12:0, C18:0/C18:1 and C18:2/C18:3 contribute the most, with C14:0, C16:0, and C20:1 contributing to a smaller extent. The differences in these FAME concentrations are important for differentiating the biodiesel-diesel feedstock type, thus it is an important that these FAMEs are separated on this column chemistry. Similar groupings based on concentration and feedstock type were obtained for the conventional GC with a moderately polar column (not shown).

4. Conclusions

The use of UFGC with a moderate polarity column was successful for the analysis of biodiesel-diesel blends when considering both concentration and feedstock. Bulk determination of identity of a blend (concentration and feedstock) can be performed using UFGC, with some analysis of FAME composition, in a very short period of time. The UFGC method, while comparable to conventional chromatography, was limited in its ability to resolve C18:0, C18:1, C18:2, and in many cases C18:3. The use of conventional GC with a moderate polarity column was also successful for the analysis of biodiesel-diesel blends. While bulk determination of the identity of a blend can be performed, additional resolution of the C18:2 and C18:3 FAMEs provided for a more comprehensive analysis. Both methods are somewhat limited if detailed analysis of FAME composition (positional isomers and/or saturated and monounsaturated FAMEs) in the biodiesel-diesel blends is desired. However, the use of PCA allows for differentiation of both concentration and feedstock type, despite the limited resolution of some FAME peaks in both UFGC and conventional GC modes using a moderately polar column. While PCA itself cannot provide classification or quantitative assessment of biodiesel blending ratio, additional multivariate regression techniques, such as PCR or PLS, could potentially be used in combination with either UFGC or conventional GC to predict blend ratio. Combined with a difference in run time of nearly 23 min for each injection, a difference of 42 h of total run time for the samples included in this study, UFGC provides a faster analysis of biodiesel-diesel blends. Overall, this study shows that a moderate polarity column paired with UFGC may be beneficial for quick determination of biodiesel feedstock and concentration.

Declaration of Competing Interest

None.

Acknowledgments

The authors are appreciative of the generous loan of the UFGC system and MXT-50 column by Falcon Analytical. The Weiss Summer Research Program (donors for this project included Dr. Timothy Babineau, Mr. Wendell P. Weeks, and Mrs. Kim Weeks) supported three summer undergraduate students. The College of the Holy Cross provided additional funding. We also thank Phillips 66, Iowa Renewable Energy, and the National Institute of Standards and Technology for providing samples of commercial diesel or biodiesel.

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