Estimating Biodiesel/Diesel Blend Percent Composition Using Gas Chromatography - Mass Spectrometry and MATLAB

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ABSTRACT

The goal of this project was to emulate the educational article “An Advanced Analytical Chemistry Experiment Using Gas Chromatography−Mass Spectrometry, MATLAB, and Chemometrics To Predict Biodiesel Blend Percent Composition” by Pierce, Karisa M., et al. Our goals were to obtain both biodiesel and petrol diesel, run a comprehensive GC/MS analysis, and use chemometric techniques to estimate concentrations of known biodiesel/diesel blends. Firstly, both petrol diesel and biodiesel were synthesized/obtained. Secondly, both the petrol diesel and biodiesel were characterized via GC/MS. Finally, biodiesel/diesel blend concentration was to be estimated using chemometric techniques and MATLAB software.

INTRODUCTION

As environmental concerns increase, so does the demand for alternative, non-petroleum based fuels. Because of these increasing concerns, biodiesel -- defined by chemical engineer Donk-Shik Kim as “vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl esters,” is surging in popularity. The process for synthesizing biodiesel falls under the category of transesterification, where fatty acids are transformed into fatty ester molecules. Biodiesel synthesis was first completed in 1853 by Patrick Duffy, many years prior to the first diesel engine. In comparison to petroleum diesel, biodiesel is composed of much fewer components and sports an ester functional group on the end of its long hydrocarbon chains. Diesel, on the contrary, has no functional groups and is composed of thousands of chains varying in length and configuration.

The goal of the project was to predict biodiesel blend composition using GC/MS and MATLAB. To accomplish this goal, every scrap of data needed to be extracted from the GC/MS chromatogram. However, each one of those chromatograms contains millions of data points. To harvest them effectively, chemometric techniques such as PLS and PCA were employed. Principal Component Analysis (PCA) identifies significant data. Partial Least Squares (PLS) is essentially multivariate line of best fit. PLS regresses the data, making it uniform and easy to interpret. Together, PLS and PCA are able to create effective models for just about anything. For example, the store TARGET famously identified a woman as pregnant before her own father even knew. This was no shot in the dark on TARGET’s part, it was their sales models that tracked her purchases, recognized a correlation, and ordered her maternity promotions. In the case of biodiesel/diesel blends, these chemometric techniques can function as quality control for booming biodiesel industries that produce premade blends such as B20 and B10. Therefore, these PCA PLS are the future of many fields of work; biodiesel blends and retail being only a filament of what they can ultimately accomplish.

EXPERIMENTAL

Section I: Synthesis of biodiesel

Canola oil based biodiesel was synthesized via base-catalyzed transesterification over a period of three days. Firstly, the canola oil was titrated with NaOH to ensure a basic reaction medium. According to Utah Biodiesel Supply, pH 8 was the optimal condition for base catalyzed transesterification. Separately, NaOH and MeOH were mixed to ensure a basic reaction medium in the canola oil. For this specific synthesis, 1L of canola oil was mixed with 0.22L of MeOH NaOH solution. The reaction was then aggressively mixed and left for a period of three days with daily mixings. After the three day period, the biodiesel had separated glycerol and biodiesel. The biodiesel was separated from the glycerol. The biodiesel was then heat dried, transforming from a translucent yellow color to a transparent amber color.

Section II: GC/MS of biodiesel and diesel

A tetradecane sample (10ul tetradecane in 1ml hexane) was used as a GC/MS standard (Fig. S). The GC/MS sample was created with 10ul of biodiesel in analytical grade hexane. Total sample volume was 1ml. Quadrupole GC/MS was then conducted with the biodiesel sample. Initially, a GC column temperature ramp rate of 10°C/min was used.

To optimize separation, a different GC column temperature ramp was used.

	Rate (°C/min)	Final Temp(°C)	Hold time (min)
0	-	40.0°C	1.00
1	10.00	230.0°C	1.57
2	0.50	233.0°C	1.00
3	5.00	300.0°C	5.00

Biodiesel GC/MS column temperature ramp method:

A petroleum diesel (cetane rating=40) sample was created using 55ml of diesel in analytical grade hexane. Total sample volume was 1ml. To distinguish the individual parts of diesel, increased sample concentration was used. The petroleum diesel GC/MS column temperature ramp was set to a constant rate of 10°C/min.

Section III: Exportation into ASCII and MATLAB

The software, Shimadzu GCMSsolution v4.41, was unable to export 3 dimensional mass chromatograms. To circumvent this problem, individual MS were selected by peak height using the "MC Fragment Table." Additionally, individual MS were also selected in increments of 1 min. The gathered MS were then manually entered into a spreadsheet.

RESULTS

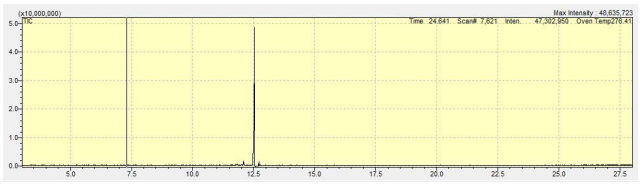

Fig. S: Tetradecane Standard GC/MS

Section I: Biodiesel GC/MS chromatograms

Fig. A: Initial GC column temperature method

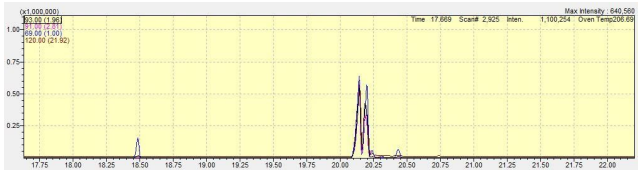

Fig. B: Optimized GC column temperature method

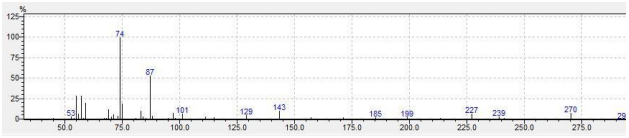

Fig. B-1: RT 18.51min MS

Section II: Diesel GC/MS chromatograms

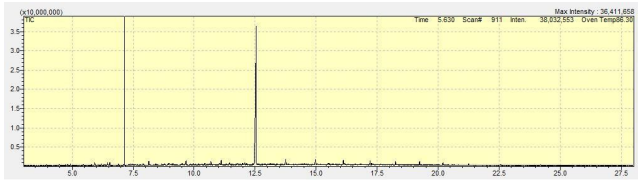

Fig. C: 10ul/ml concentration diesel sample

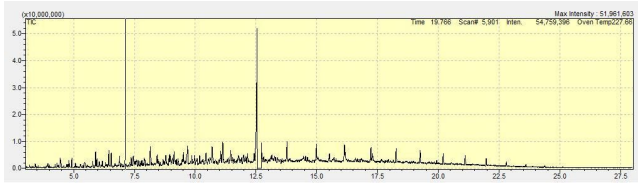

Fig. D: 55ul/ml concentration diesel sample

DISCUSSION

Post synthesis, the canola based biodiesel was characterized using GC/MS. The primary component

of biodiesel are long hydrocarbons terminated with ester functional groups. In this case, using methanol, methyl ester production was expected. According to lipid chemist Dr. William Walker Christie in his article "Mass Spectrometry of Methyl Esters," the fragment 74m/z is key to identifying methyl esters (Fig. E). The MS of the canola based biodiesel (Fig. B-1) showed a major fragment at 74 m/z. Additionally, a contemporary project showed that algal based biodiesel had the same fragmentation patterns at the same retention time (Hogan). Furthermore, a flame test was conducted using a primitive atomizer and bunsen burner. Thankfully, the canola based biodiesel was able to combust similarly to petrol diesel.

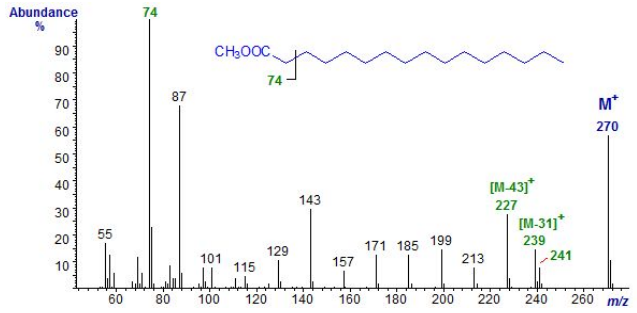

Fig. E: Fragmentations pattern of methyl ester "Christie, Mass Spectrometry of Methyl Esters"

GC/MS of the diesel showed a very different chromatogram than biodiesel. Since biodiesel is derived from fatty acids, the long alkyl chain portion of the biodiesel remained relatively uniform in length and structure. The uniform alkyl chain length explains the concentrated distribution of fragments on the GC/MS chromatogram (Figs. A &B). On the other hand, diesel is a mixture of thousands of different alkyl chains differing in both length and structure. This mixture of thousands of alkyl chains explains why there is such a wide distribution of ions throughout the chromatogram. This distribution of ions throughout the chromatogram also explains why the diesel concentration in the sample had to be inflated for observable results.

With both biodiesel and diesel characterized via. GC/MS, the goal of the project shifted from synthesis and characterization to exportation and MATLAB work. To begin, a 3-D GC/MS chromatogram had to be exported in an ASCII readable format (example Fig. F) . Unfortunately, the Shimadzu GCMSsolution software was not capable of exporting a 3-D GC/MS chromatogram. The software was able to export individual chromatograms. Therefore manual selection of MS, both by increments of time and TIC peak height, was required to create a 3-D chromatogram in an ASCII format. The manual entry came with its caveats; for instance, the goal of PCA and PLS regression models is to use all of the data in order to establish correlations between variables. With the manual entry solution, much of the data was lost in translation.

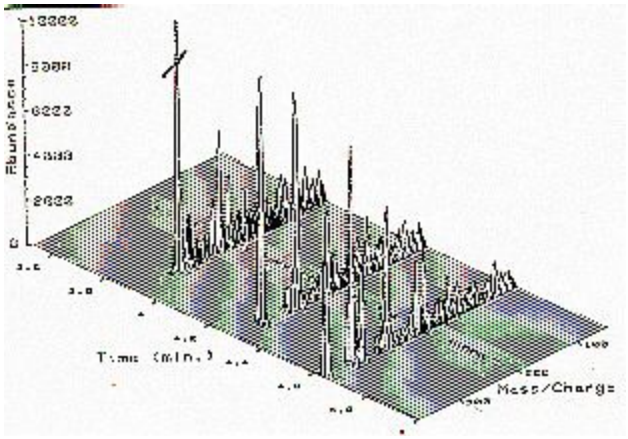

Fig. F: Example of GC/MS output "SRIF GM University"

MATLAB was able to read the file correctly. However, the file was unable to be located by the python script used to run PCA and PLA by Pierce, Karisa M., et al. This was not a problem with the python script, nor was is a problem with MATLAB. It was a formatting problem with the manually entered 3-D GC/MS chromatogram. The solution to these formatting issues is to obtain the same software used by Pierce, Karisa M., et al during their research.

CONCLUSION

The goal of the project was to emulate the educational article "An Advanced Analytical Chemistry Experiment Using Gas Chromatography−Mass Spectrometry, MATLAB, and Chemometrics To Predict Biodiesel Blend Percent Composition" by Pierce, Karisa M., et al. By extension, our goals were to obtain both biodiesel and petrol diesel, run a comprehensive GC/MS analysis, and use chemometric techniques to estimate concentrations of known biodiesel/diesel

blends. Unfortunately, the goal was not met. However, a solution was devised. To properly emulate Pierce, Karisa M., et al., it is imperative that an identical software is used.

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