



Forensic analysis of biodiesel



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ABSTRACT

The analysis of four different biodiesel blends, as well as homemade biodiesel prepared from vegetable oil, has been performed using gas chromatography-mass spectrometry. The identification of methyl esters within the biodiesel along with any background components is made possible by recognizing their mass spectral fragmentation patterns. These fuels were subjected to typical fire scene environments, specifically weathering and microbial degradation, to investigate how these environments affect the analysis. A matrix study was also performed on wood, carpet, and clothing in order to identify any interferences from these substrates. The data obtained herein will provide the forensic science community with the data needed to help recognize these increasingly common ignitable liquids.

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1. Introduction

The use of alternative fuels has increased dramatically over the last several years, as more people look for ways to save money, reduce environmentally harmful emissions, and decrease their dependence on fossil fuels. Specifically, biodiesel made from either waste vegetable oil (WVO) or straight vegetable oil (SVO) has become popular since it is inexpensive, readily available, and renewable. In 2014, the United States biodiesel industry produced over 1.27 billion gallons of biodiesel [1]; in Europe over 7 billion gallons were produced [2]. Most of this biodiesel is produced from some kind of vegetable oil (soybean and canola oils are the most commonly used feedstocks). There are currently 120 plants in the United States that are members of the National Biodiesel Board [3], and over 50 members of the European Biodiesel Board [2]. In addition, more people are making biodiesel in their homes, using inexpensive WVO or SVO and other household materials. Typically these materials include methanol and a strong base such as sodium hydroxide or potassium hydroxide, all of which are easy to obtain in large quantities. The reaction is a straightforward transesterification of triacylglycerides (fats) to fatty acid methyl esters (FAMES, Fig. 1), but involves the use of corrosive and flammable materials.

Because of the increasing use and manufacture of biodiesel, both commercially and in people's homes, it is expected that these fuels will be present in increasing numbers of submissions to fire

debris analysts. Many people who make biodiesel at home are working with several gallons of fuel at a time. Many recipes for making biodiesel at home can be found very easily on the Internet; an online search for "make biodiesel at home" returned over one million results [4]. Consequently, many people who are relatively inexperienced at working with corrosive and flammable materials in large quantities are doing just that, and the potential for fires and explosions is high. There are already several reports of fires starting at homes and at biodiesel processing plants, where large amounts of methanol, oils, and strong bases are stored and heated [5]. These fires have led to hundreds of thousands of dollars in damage. Because of this, fire investigators and fire debris analysts will be encountering biodiesel in more routine casework.

While analysts are comprehensively trained in identifying a wide variety of petroleum-based products, it is relatively rare to see non-petroleum based samples (e.g., oxygenated products and terpenes). Currently, there is little training or experience with biofuels. This point was made in 2007 by Stauffer and Byron in their excellent introduction to biodiesel for fire debris analysts [6]. These authors addressed the basic analytical profiles of biodiesel and noted several considerations that are unique to biodiesel and vegetable oil, such as aging effects and decreased volatility. Since this introduction, there has not been a thorough study of the analysis of biodiesel. The effects of weathering, degradation, and substrate involvement have been systematically studied for petroleum products [7,8], but these and other effects have not been examined with respect to the analysis of biofuels.

Herein we report what is to the best of our knowledge the most complete forensic analysis of biodiesel to date. Following

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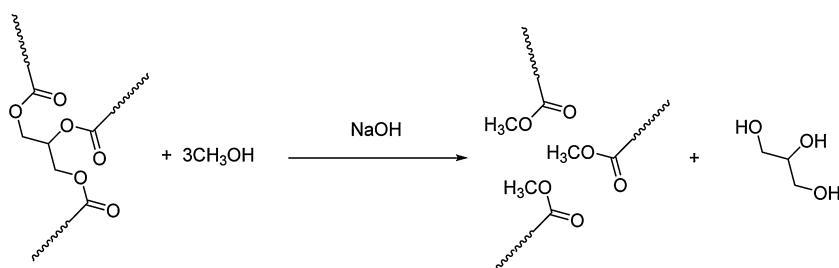


Fig. 1. General reaction scheme of the production of FAMEs that make up biodiesel from a triacylglycerol. Glycerol is the other product formed in the reaction.

modifications of the procedures set by ASTM international [9] which are commonly used in routine fire debris analysis, we set out to understand the forensic aspects of biodiesel at the same level as our current understanding of petroleum products. Specifically, we have studied: (i) neat liquid samples of homemade biodiesel along with commercial samples of B5, B20, B50, and B99 blends, as compared to regular diesel fuel; (ii) heated-headspace extraction samples of each type of biodiesel, at two different temperatures; (iii) the effects of microbial degradation on analysis; (iv) the effects of evaporation on analysis; and (v) the potential for matrix effects to interfere with the identification of biodiesel. We also examined the differences encountered when biodiesel is made using different types of oils. It is our goal to provide the forensic science community with as complete a profile as possible of a wide range of biodiesel products. We predict that the increasing use of biofuels and subsequent increase in their appearance in fire debris will eventually warrant the formation of a new class of ignitable liquids [10], or at least a sub-classification within oxygenated products.

We have chosen to focus on the analysis of the B20 biodiesel blend herein for two reasons. First, this blend is the most commonly used, at least in the United States [11]. Second, chromatographically it is the most interesting blend because it contains significant amounts of both diesel and FAMEs. This makes B20 ideal for studying the differences of the behavior of biodiesel compared to well-known petroleum-based (especially diesel) samples.

2. Materials and methods

2.1. Materials

Carbon disulfide (ACS grade) and 1-chlorohexadecane (99%) were purchased from Aldrich and used as received. A stock solution containing 0.1% 1-chlorohexadecane in CS_2 was prepared and used to elute the charcoal strips when comparisons to an internal standard were desired. Methanol (ACS grade), dichloromethane (99%), and sodium hydroxide were purchased from Fisher Scientific. Unlined metal paint cans were purchased from House of Cans (www.houseofcans.com). Activated charcoal strips ($8 \times 20 \times 1$ mm) were purchased from Albrayco Technologies. Heet[®] (a methanol-based fuel additive), Drano[®] (an NaOH-based drain cleaner), and Miracle-Gro[®] potting soil were purchased at local hardware stores and used as-is.

Homemade biodiesel was prepared from commercial vegetable oil using a common, publicly available procedure [12]. Briefly, 3.52 g of Drano[®] professional strength crystals was added to 210 mL of Heet[®]. This mixture was shaken to dissolve the crystals, and the metal shavings from the Drano[®] were filtered. This solution was slowly added to 1 L of new vegetable oil and the solution was heated to 55 °C with stirring. After stirring for 20 min, the mixture was left overnight to allow two layers to separate. The

top biodiesel layer was removed in 300 mL portions and each portion was washed three times with 100 mL of deionized water. The biodiesel layers were combined and heated to 100 °C to remove any remaining water, and the final product was characterized by infrared spectroscopy and nuclear magnetic spectroscopy. Spectral data of the final product are available in the Supplementary Information.

Biodiesel was also prepared from coconut, safflower, peanut, and cottonseed oils on a smaller scale using methanol and sodium hydroxide instead of Heet[®] and Drano[®]; the experimental procedure was the same as that described above.

Commercial biodiesel samples (B5, B20, B50, and B99) were obtained from various fueling stations in the Seattle, WA area.

2.2. Instrumentation

GC–MS data were collected using a Hewlett-Packard 6890 gas chromatograph with a 5973 mass selective detector (MSD). The MSD was operated in electron ionization mode with an ionization potential of 70 eV and a scan range of 50–550 amu. The ion source temperature was maintained at 230 °C.

Chromatographic separation was carried out using a capillary column Restek Rxi-35Sil ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). The GC was operated at a 50:1 split ratio (1 μL injection volume) with a constant helium flow of 1.0 mL/min. The GC injector temperature and transfer line were both maintained at 280 °C. The oven temperature was programmed as follows: initial temperature, 60 °C, held for 2 min; ramp rate, 10 °C/min to 200 °C, 5 °C/min to 240 °C, held for 6 min; total run time 30 min.

2.3. Methods

2.3.1. Analysis of neat samples

Neat samples were analyzed by placing 10 μL of biodiesel fuel in a 1.5 mL gas chromatography vial. Carbon disulfide (1.5 mL) was added to the vial and the sample was analyzed by GC–MS.

2.3.2. Heated headspace analysis: General procedure

The material to be analyzed was placed in an unlined metal can. An activated charcoal strip was suspended in the can's headspace using an alligator clip inside the can lid held in place with a magnet on the outside of the lid. The can was sealed and placed in an oven set at either 75 °C or 100 °C for 6 h. The can was allowed to cool to room temperature and the charcoal strip was removed. The strip was placed in a GC vial and eluted with 1.5 mL of CS_2 . This sample was analyzed by GC–MS.

2.3.3. Preparation of samples for microbial degradation

For each sample, approximately 50 g of potting soil was added to a can. Approximately 1 mL of the biodiesel sample was added to the soil and the can was sealed for 2, 7, 14, 30, or 60 days at room temperature. After that time, the can with the sample inside was

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