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Laboratory Experiment

Byproduct Valorization: From Spent Coffee Grounds to Fatty Acid Ethyl Esters

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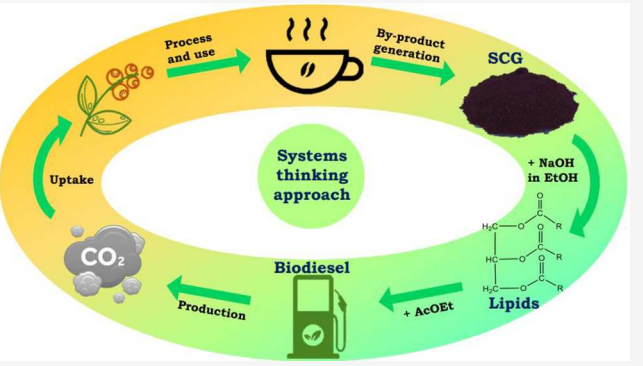
ABSTRACT: A laboratory experiment was designed to provide students with an introduction to byproduct valorization by producing an analogue of biodiesel (fatty acid ethyl esters, FAEE) via lipid extraction and subsequent transesterification from spent coffee grounds (SCG). Valorization is the process of upgrading underutilized or discarded wastes or byproducts into chemicals, materials, and (bio)energy. Upon isolation of the intermediate and FAEE, students analyzed the respective spectroscopic characteristics using infrared and nuclear magnetic resonance spectroscopy as well as evaluated gas chromatography spectra that were provided. Associated green metrics for the reaction were determined to obtain a quantitative measure of the "greenness" of the experiment. In this laboratory experiment, students are introduced to key concepts such as whole systems thinking and the United Nations Sustainable Development Goals where they apply these frameworks to real-world problems such as consumption and waste disposal. In addition to providing a greener alternative to traditional methods for biodiesel analogue production from SCG by solvent alterations, this experiment demonstrates the value of waste that would otherwise be overlooked to generate products that can help reduce the continued use of finite fossil fuels.



KEYWORDS: *Green Chemistry, Second-Year Undergraduate, Analytical Chemistry, Laboratory Instruction, Hands-on Learning/Manipulatives, Fatty Acids, Lipids*

INTRODUCTION

There is a highly significant global issue surrounding landfill sites and waste disposal, with some wastes taking thousands of years to biodegrade and often generating methane and other greenhouse gases or a bad odor. Some may not biodegrade at all; therefore, there is a substantial demand for development of new ways to reuse or recycle waste products to minimize impacts on the environment. The use of waste biomass, such as food and agricultural wastes, offers an alternative to crude oil as a feedstock; this practice also prevents potentially useful products being consigned to waste. This process of converting waste materials into their utilizable constituent parts, which can include chemicals, materials, and fuels, is termed waste valorization[1] and is increasingly being considered as a valuable tool for the next generation to address the growing issue of waste to aid in a transition from a linear economy to a circular economy.[2] This laboratory experiment gives students the opportunity to employ methods and metrics that are used in industrial processes to determine the "greenness" of reactions along with gaining an appreciation that traditional industrial manufacturing processes tend to rely heavily upon crude oil. As a result of this reliance, the impacts on the environment have been greatly accelerated with increasing population and production of goods, causing deforestation, increased landfills, and enhanced global warming; hence, alternatives need to be found.[3] Waste of varying types is generated in vast quantities every day by the growing population with many of these being bioresources that are readily available and have many potential further applications. Examples of transforming waste streams into useful products that are already well documented in the educational literature include bakery waste and meat into poly(3-hydroxybutyrate) (PHB) and biocollagen,[4] sour milk into Bioplastic,[5] corncobs into biofuel and sun cream,[6] lobster shells in Bioplastic and hydrogels,[7,8] extraction of pectin from orange peel,[9] and cooking oils into biofuels.[10]

This laboratory experiment allows students to apply a systems thinking approach and their knowledge to a "closed-loop" valorization system.[11] Systems thinking is an education framework that considers how manufacture, use, reaction

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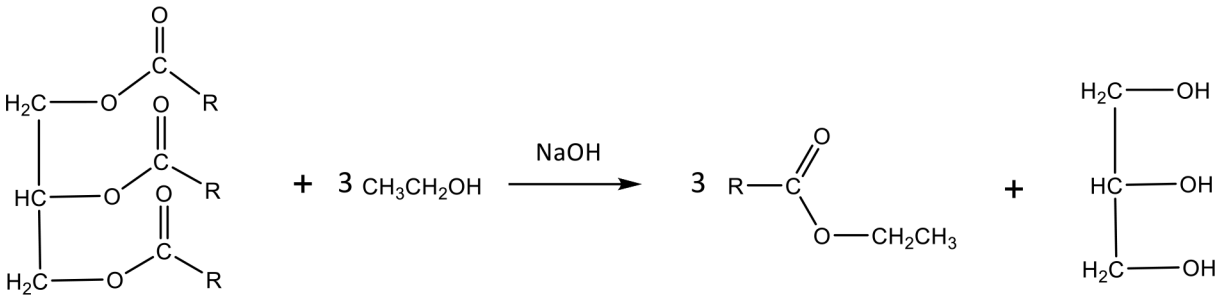

Figure 1. Transesterification of extracted triglycerides to ethyl esters; R groups are long-chain hydrocarbons.

conditions, disposal, and potential impacts upon human health and the environment can interact with another; hence, these components (or subsystems) should be thought of collectively as an entire system.[12] Systems thinking lends itself well to enabling reactions and processes to work toward the application of the United Nations Sustainable Development Goals (UN SDGs) because the goals themselves are connected to one another and often by looking at one problem; this requires analysis of the whole system.[13] These goals encourage prosperity and physical and social well being for all people globally while conserving the long-term stability of our climate and ecosystems.[14] Goal 12 states that responsible consumption and production are important for reducing environmental degradation and allowing for future development.[15] The reuse of existing materials deemed to be waste reduces the reliance upon natural finite resources and increases resource efficiency, leading to a more sustainable future. This experiment shows a real-world approach to the application of the UN SDGs in a way that is accessible to students. In this way, access to quality education (Goal 4) is being provided and will enable students to understand how to enact change to lead to a more sustainable way of developing reactions and processes.[16] This systems thinking approach is also useful for teaching green chemistry principles at a global level;[17,18] there have been numerous educational resources published at the program level[19] as well as the development of games,[20,21] social media interactions,[22] and laboratory experiments.[1,17]

To aid in students adopting a systems thinking approach, a number of the 12 Principles of Green Chemistry can be associated with this experiment; these principles were developed to be applied to the design of new methods which produce molecules, materials, reactions, and processes that have reduced impacts upon the environment and human health.[23] Therefore, with a combination of a systems thinking approach and application of the 12 Principles of Green Chemistry, students can begin to think about laboratory experiments using a holistic real-world approach, considering the associated social and environmental impacts that may result from such experimentation and research. An understanding and practice of the fundamentals of green chemistry using a systems thinking framework can influence the entire life cycle of a chemical from cradle to grave or more beneficially from cradle to cradle, i.e., reusing chemicals and wastes rather than disposing of them, leading to a circular economy.[24]

Spent coffee grounds (SCG), the residue obtained after brewing and filtering, is a good waste stream to demonstrate waste valorization because it is a high-volume, renewable resource. In the 12 months starting August 2020 through July 2021, exports of Arabica beans totalled 4.96 million tonnes compared to 4.73 million tonnes the previous year (4.8% increase).[25] From the initial coffee cherry (fruit), the bean used to make coffee is roughly 50% of the weight with the other 50% comprising of coffee husks, peel, and pulp. Upon using the bean for the purpose of brewing coffee, approximately 45−50% of the weight becomes SCG which are disposed of.[26] In addition, the outside shell of the bean is often disposed of, resulting in nearly 90% of the total weight of the fruit not being used. This waste stream has many sources such as municipal waste, catering companies, and manufacture of freeze-dried coffee. This means that a large quantity of SCG ends up in landfills, which can pose greater issues than simply increasing waste; SCG have the potential to induce mutagenicity which can leach, after disposal, into landfill ground and water supplies.[27] This presents a risk to human and environmental health; hence, the utilization of this waste as a biobased feedstock is beneficial over its disposal. The high nitrogen content also makes SCG problematic for two of the most common alternatives to biomass disposal, incineration for energy and anaerobic digestion. Both of these result in the nitrogen being converted to NO_x and NH_3 respectively, which pose other safety and air quality issues.[28] However, the SCG themselves are a valuable source of a range of compounds such as crude fiber, lipids, nitrogenous compounds, minerals, and bioactive components.[29] As a result, a wide variety of useful products and materials can be made, the most prevalent of which is biodiesel from the lipid content.

The development of the process in this work not only enables the UN SDGs to be a key fundamental for change but also allows students to expand their knowledge of green chemistry using a systems thinking approach. The systems thinking framework for this biorefinery approach to the valorization of SCG allows for emphasis to be applied to the choice of chemicals along with providing students with the tools to consider the whole system and the effects upon the environment and human health. It is important for these principles and frameworks to be used by scientists, engineers, and policy makers to aid in transitioning to a more sustainable future where all interconnected systems are considered when developing new processes and reactions.

In this laboratory experiment, SCG were collected from a local café and dried at 105 °C in an oven. They were then provided to the students (rather than the students producing the grounds themselves, preventing further waste). Students worked individually to extract the lipids from the SCG via reflux in ethyl acetate followed by conducting a base-catalyzed transesterification reaction (Figure 1) with ethanol.

The chemicals for all steps of the reaction were specifically chosen so that they reflect the green nature of the process itself, creating an alternative to crude oil.[30,31] Traditional methods for the production of biodiesel analogues from SCG

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use chemicals, such as heptane, methanol, and potassium hydroxide, that have higher amounts of associated hazards both to human health and to the environment.[32,33] Therefore, to minimize hazards and the variety of chemicals used in this experiment, ethyl acetate was used for the initial lipid extraction and the workup. Sodium hydroxide dissolved in ethanol was used for the transesterification; this differs from traditional methods using potassium hydroxide dissolved in methanol given the reduced hazards.

Associated green metrics can be determined to obtain both quantitative and qualitative measures for the "greenness" of a reaction or process.[34,35] A measure for how effectively a reaction produces the desired product is described by the percentage yield (eq 1).

$$\text{yield} = \frac{\text{actual product amount}}{\text{theoretical product amount}} \times 100 \quad (1)$$

However, percentage yield does not consider the waste, reagent excesses, toxicity, auxiliaries, or energy within the process. The industry standard for efficiency is the process mass intensity (PMI). This metric describes the amount of product formed as a function of the total inputs (eq 2) and so takes into consideration the waste produced throughout the reaction. This improves the measure of greenness; the closer the value is to 1, the less waste is generated and the less impact the process has on the environment because a lower quantity of waste is disposed of. It is a metric often used in pharmaceutical chemistry as it can determine the amount of waste relative to the quantity of product being generated, showing the efficiency of the process.[36,37]

$$\text{PMI} = \frac{\sum \text{input mass(reactant, chemical, catalyst, and solvent)}}{\sum \text{product mass}} \quad (2)$$

Another alternative green metric is the energy consumption of the reaction (eq 3); this can aid in determination of the greenness of a reaction. On the basis of this metric, reactions can be designed with an estimate of the energy consumption, and so strategies can be proposed for improving the energy efficiency to enhance the sustainability of the process.[38]

$$\text{energy consumption} = \frac{\text{power} \times \text{time}}{1000} \quad (3)$$

An introduction and accompanying equations, as seen above in eqs 1−3, are supplied for students and instructors on page 3 of the student laboratory manuscript in the Supporting Information. This laboratory experiment provides students with the opportunity to learn how to extract lipids from SCG, which are used to make biodiesel for use in biorefineries, and upon performing this, students use analytical techniques to determine if the correct product of a multistep reaction is formed. It also allows for the determination of the associated green metrics to ascertain the greenness of the process. Students must demonstrate known practical skills in combination with one another to extract as many of the lipids as possible to obtain the coffee biodiesel analogue in a good yield as well as expert assignment of analytical data to answer the questions posed in the Student Laboratory Manuscript. Hence, this experiment is particularly suited to a second-year undergraduate cohort studying analytical or green chemistry modules.

MATERIALS

SCG (Arabica variety) were obtained from the Park Central coffee shop, University of York, UK, and dried (105 °C) until a constant mass was achieved.

Ethyl acetate (≥99.8%, Analytical Reagent grade), ethanol (absolute, ≥99.8%, Analytical Reagent grade), and NaOH (Analytical Reagent grade) were purchased from Fisher Chemical Ltd.

EXPERIMENTAL METHOD

Lipid Extraction

A mixture of dried SCG (20 g) and ethyl acetate (40 mL), contained in a round bottomed flask (250 mL) equipped with a magnetic stirrer bar, was heated under reflux for 45 min. Thereafter, the mixture was cooled and filtered gravimetrically, and the filtrate was evaporated to dryness in vacuo to afford the desired lipid extract, 1.06 g (5.31%), as a brown oil.

Transesterification

A mixture of sodium hydroxide (210 mg) dissolved in ethanol (100 mL) was added to the oil (15:1 ratio respectively) contained in a round-bottomed flask (100 mL) equipped with a magnetic stirrer bar and heated for 1 h at 60 °C. Following this, the mixture was left to settle and filtered gravimetrically. The filtrate was separated and extracted using ethyl acetate and water before being evaporated to dryness in vacuo to afford the desired FAME, 0.79 g (75.7%), as a light straw-colored oil.

A student laboratory manuscript, instructor guide, and technicians guide are available as part of the Supporting Information. Students were provided with nuclear magnetic (NMR) and IR spectra for the SCG starting material and the NMR of the intermediate along with GC spectra of pure and crude FAEE to allow for full analysis. This experiment can be performed over 2 days by stopping prior to the transesterification process, assuming the intermediate is stored in a fully sealed vial (e.g., with parafilm). The authors have confirmed that the intermediate can be stored up to 1 week ahead of transesterification with no detrimental effects on the outcome of the experiment.

HAZARDS

Ethanol and ethyl acetate are highly flammable liquids and vapors. Furthermore, ethyl acetate and sodium hydroxide pellets cause serious eye irritation, and if chemicals come in contact with the eyes, the eyes should be rinsed cautiously with water for several minutes. Ethyl acetate may cause drowsiness and dizziness and should therefore be used in a well-ventilated area.

ANALYTICAL METHODS

Fourier transform infrared spectroscopy (FTIR) was performed on a PerkinElmer Spectrum 400 IR spectrometer. An initial background scan was run prior to sample analysis with a total of 16 scans performed over the wavelength range of 4000−650 cm^{-1} with a resolution of 4 cm^{-1}. The sample crystal was cleaned with ethanol before acquisition of the background spectrum; the sample scans were then run to the same specification as the background scan.

^{1}H and ^{13}C NMR spectra were acquired by using a JEOL ECS 400 MHz spectrometer. All samples were prepared using $CDCl_3$ as the solvent. For ^{1}H NMR analysis, the samples were

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spun at 300.130 MHz for 8 scans, and for ^{13}C analysis, the samples were spun at 75.468 MHz for 256 scans.

Gas chromatographic measurements were made with an Agilent Technologies HP 6890 gas chromatograph with a flame ionization detector (GC-FID) fitted with a Rxi-5HT capillary column (30 m, 250 mm × 0.25 mm nominal, max temperature 400 °C). Helium was used as the carrier gas at a flow rate of 2 mL/min with a split ratio of 30:1 and a 5 μL injection. The initial oven temperature was 50 °C, increased instantly at a rate of 30 °C/min to 300 °C, and held at this temperature for 5 min with a total run time of 13.3 min. The injection temperature was 250 °C, and the detector temperature was 250 °C.

GC-MS was run the same as described for GC except a 1 μL injection was performed at a flow rate of 10 mL/min and a split ratio of 5:1. For the mass spectrum, measurements were made with a Clarus 560 mass spectrometer with electron ionization initiation. The measurements were taken over 40−500 m/z with a solvent delay of 2 min and a total run time of 13.33 min. MS data were analyzed using NIST library version 2.2.

RESULTS AND DISCUSSION

The laboratory experiment was completed by upper division undergraduate students as part of an open-ended problem-based learning miniproject to assist students in preparing to undertake a substantial independent research project within green and sustainable chemistry. Through this experiment, students embraced a systems thinking-based approach to a waste valorization problem and commented that "The coffee lab was great. Really liked practicing chemistry techniques by making a useful product from waste we were familiar with". This laboratory experiment can be adapted for lower division undergraduate students by ensuring students have expertise in key practical skills such as reflux, liquid−liquid extraction, and spectroscopic analysis as well as an understanding of relevant green chemistry concepts, to include metrics, before undertaking the experiment.

Participating students had undertaken a variety of optional modules in the previous stages of undergraduate study, including (1) green chemistry, (2) materials chemistry, (3) biochemistry, and (4) atmospheric and environmental chemistry, meaning that the background knowledge varied from student to student, demonstrating the utility range of the experiment. Five students performed this reaction individually and completed the experiment within 6 h. This was repeated twice, so a total of 10 full experiments were achieved over two 6 h sessions per student; this was done to demonstrate the reproducibility and repeatability of both the quantity of extracted FAEE and the associated green metrics. Following the completion of the experiment, students presented their work in the form of a written laboratory report, the contents of which included a discussion where the questions posed in the student laboratory manuscript were answered in full. The spectra collected by students (two IR spectra and one NMR spectrum) were also presented and analyzed with a comparison to those given in the supplementary spectra section. The associated green metrics were also calculated, and their suitability to measure the greenness of the reaction was discussed. These reports were then assessed using the instructor manuscript as a guide. Representative data for all aspects of the experiment are presented as follows.

Following the extraction of lipids from the SCG, the intermediate product was characterized via IR spectroscopy (Figure 2). The absorbance band at 1740 cm^{-1} is indicative of

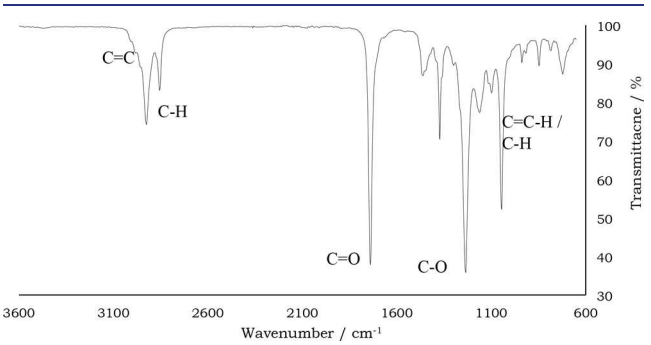

Figure 2. IR spectrum of intermediate lipid extraction.

a C═O stretching frequency of an ester carbonyl; this band is the most intense in the spectrum due to the presence of the lipids. The absorbance bands at 2925 and 2855 cm^{-1} are attributed to C−H asymmetric and symmetric vibrational modes. The strong bands in the fingerprint region between 1200 and 1000 cm^{-1} show the presence of C−O−C stretching frequencies of the alkoxy esters. The presence of the bands discussed demonstrates that the lipids have been extracted from the SCG.

The transesterification reaction was then performed on the extracted lipids from the SCG to produce the desired FAEE. On forming this product, it was characterized by IR spectroscopy (Figure 3) in addition to ^{1}H and ^{13}C NMR

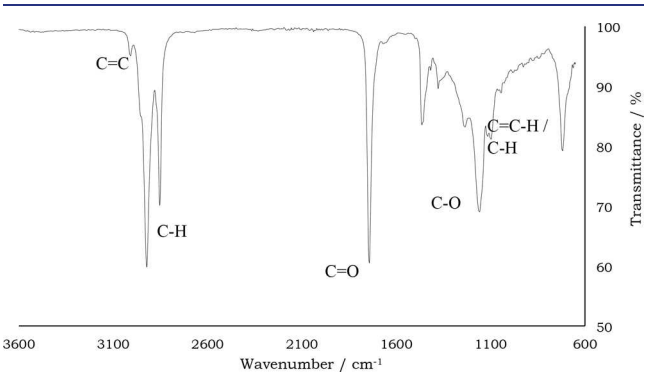

Figure 3. IR spectrum of FAEE produced from SCG.

spectroscopy. Between the triglycerides and the FAEE (Figures 2 and 3), the R groups remain the same and the ester bond being broken is replaced by another ester bond; hence, the peaks above 1600 cm^{-1} remain the same. The two C−H and C═CH absorbance bands located at 2853 and 2922 cm^{-1} and 3009 cm^{-1}, respectively, become more intense as there are more bonds involved relative to bonds present in the triglyceride compared to FAEE.

In addition to Figure 4, Figures 5 and 6 show numerous alkyl peaks between 0.88 and 1.6 ppm and 20.0 and 35.0 ppm for the ^{1}H and ^{13}C NMR results, respectively. These peaks are due to the long-chain carbon R groups of the FAEE, one of which is shown in Figure 4.

The ^{1}H NMR spectrum (Figure 5) contained peaks that are characteristic of FAEE, such as that at 2.1 ppm, which is ascribed to protons alpha to the carbonyl groups (−CH_2−

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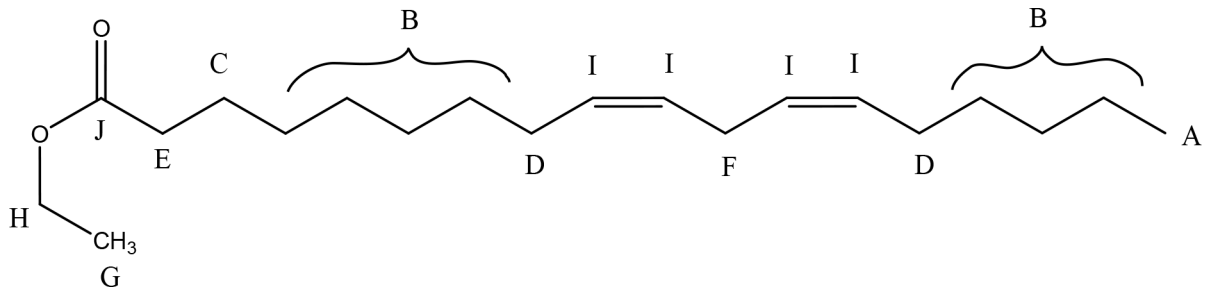

Figure 4. Ethyl ester of linoleic acid with environments labeled A–J.

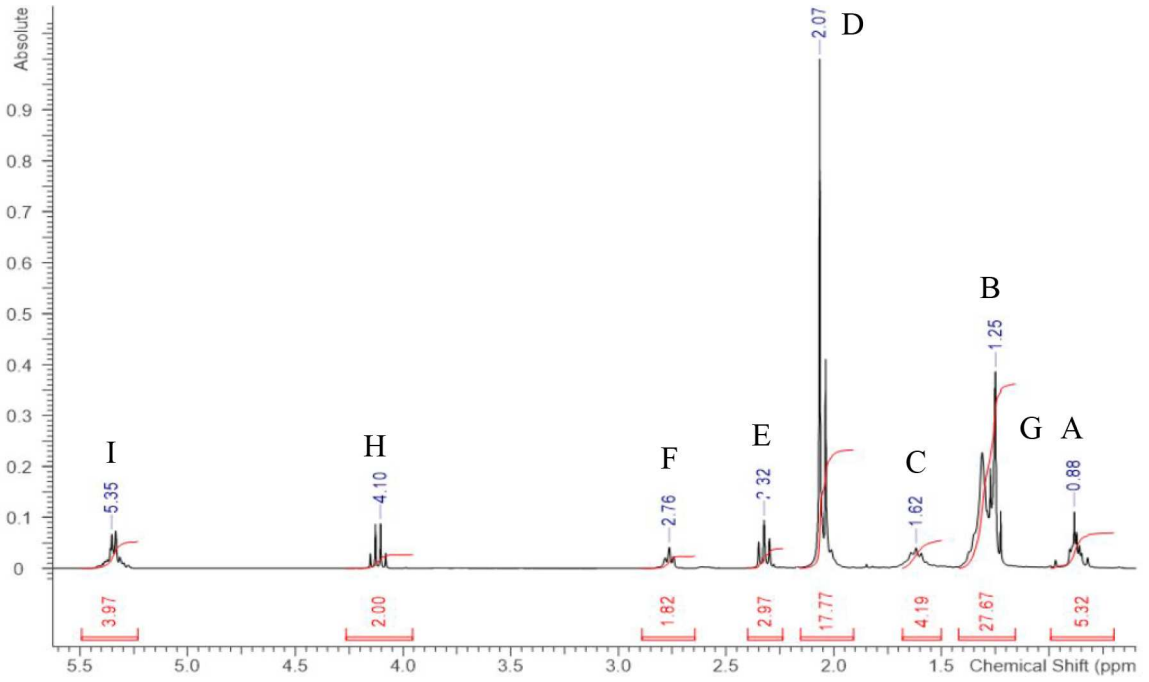

Figure 5. ^{1}H NMR spectrum of FAEE produced from SCG; peak assignments A–I from Figure 4.

C(=O)–), and those at 2.7 ppm responsible for diallylic methylene protons (–C=CH–CH_2–CH=C–), which are present in linoleic acids, as can be seen in Figure 2.[39,40] The quartet at 4.1 ppm is indicative of the CH_2 protons of ethyl esters (CH_3–CH_2–OCOR), while the CH_3 is located in the alkyl region and so not clearly visible.[40,41] The broad signal at 5.4 ppm is due to the alkene protons (–C(H)=C(H)–) present within the R groups.

The ^{13}C NMR results (Figure 6) reveal similar patterns of functional groups present in the spectrum produced. There is the single characteristic carbonyl peak of the ester group present (C=O) at 170.8 ppm, and the four peaks at 129.9, 129.4, 127.7, and 127.5 ppm are all due to ethylenic carbons and are characteristic of the fatty acid ester long chains.[42,43] The peaks at 60.1 and 13.8 ppm are due to the CH_2 and CH_3 of the ethyl ester, respectively, hence proving successful production of the FAEE.[41]

Both the IR and the NMR spectra for the final product showed that the same functional groups are present, including the characteristic ester, alkyl, and alkene groups found in fatty acid esters along with the peaks for the ethyl group, which this biodiesel analogue is comprised of.

As part of the student postlaboratory assessment, students were provided with a gas chromatography (GC) spectrum of both free fatty acid-contaminated product and pure FAEE product. Students were asked to analyze the spectra and determine the separate FAEE produced in this reaction by the retention times and resultant order of elution. This serves as an opportunity to advance the spectroscopic analysis students undertook, adding to their understanding surrounding the reaction and why removal of the free fatty acids is important for obtaining a biodiesel analogue that is aligned with the industry standards. The GC spectrum in Figure 7 indicates that the fatty acid ethyl esters were formed with no presence of free fatty acids and eluted in the order of palmitic acid, linoleic acid, stearic acid, and arachidic acid ethyl esters. This is in agreement with the elution of molecules according to their respective boiling points in the case of these molecules in the order of increasing carbon atoms. Upon comparison to the National Institute of Standards and Technology (NIST) database of chemicals, the resultant mass spectra were all within good agreement with the known spectra of these molecules, as shown in Table 1.[44]

From the metrics provided in eqs 1–3, the greenness of the reaction was determined, and results are shown in Table 2.

The initial lipid extraction reaction produced an average of 1.06 g of intermediate oil, which gave a yield of 5.31%. This low yield is expected due to the low lipid content of 15% per gram of SCG.[45,46] During lipid extraction 2.60 W h of energy was consumed (5.2 W over 30 min), which is a very low value

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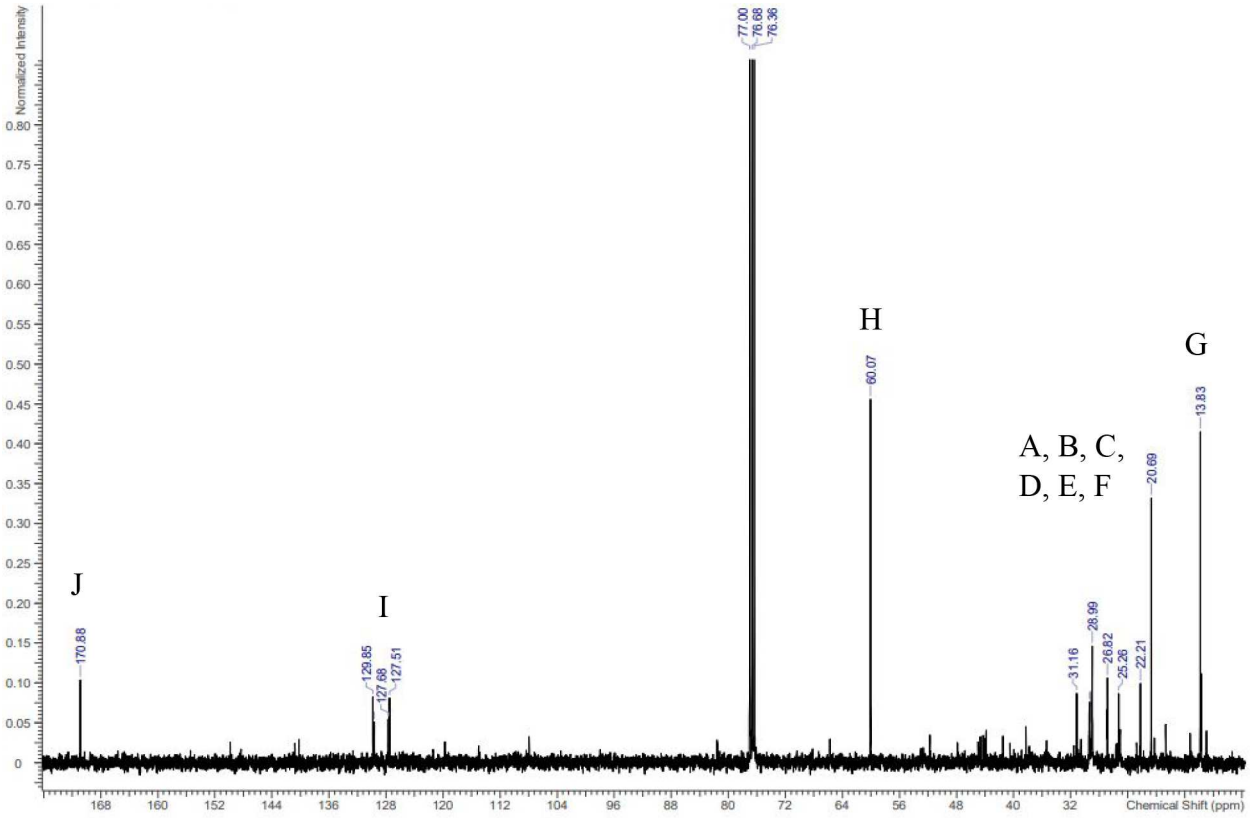

Figure 6. ^{13}C NMR spectrum of FAEE produced from SCG; peak assignments A–J from Figure 4.

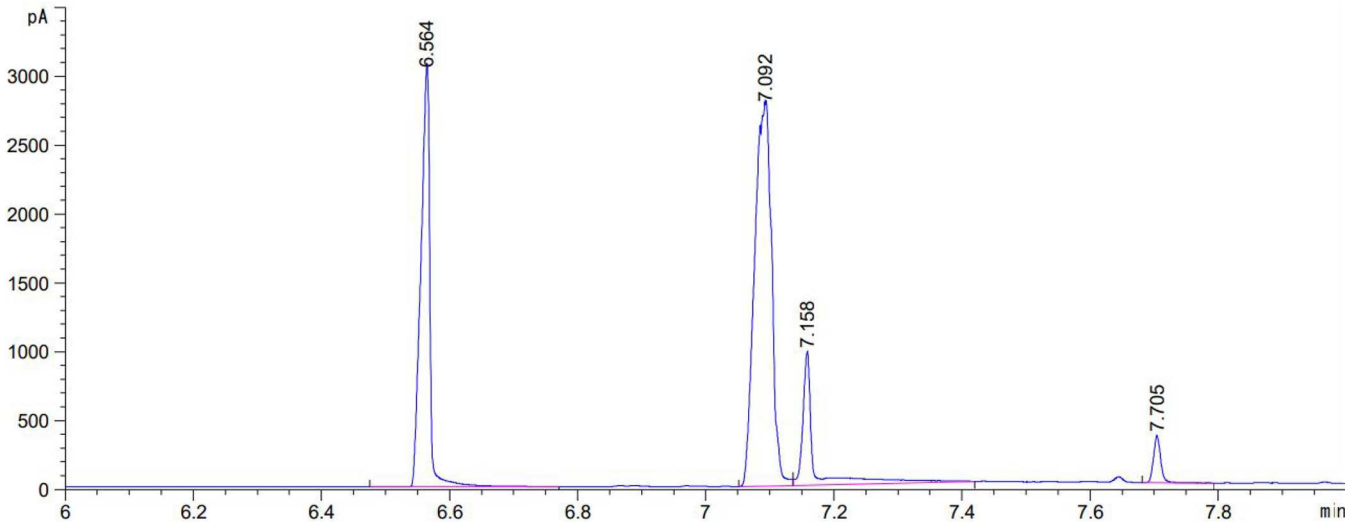

Figure 7. GC spectrum of FAEE from base-catalyzed transesterification (zoomed region).

Table 1. NIST 2.2 Database Percent Probability

chemical	NIST probability (%)
palmitic acid ethyl ester	86.4
linoleic acid ethyl ester	77.6
stearic acid ethyl ester	87.9
arachidic acid ethyl ester	84.7

Table 2. Green Metrics Determined for Each Reaction

	reaction	
metric	lipid extraction	transesterification
yield (%)	5.31	75.70
energy consumption (W h)	2.60	3.38
PMI	54.82	62.56

and so demonstrates that this reaction is sustainable and requires minimal amounts of energy to be produced via fossil fuel combustion. This is beneficial because reduced quantities of greenhouse gases are released as well as reducing consumption of a finite resource. Upon completion of the transesterification reaction, the final mass of FAEE was an average of 0.79 g, giving an improved yield of 75.7%. This reaction had a lower power output (4.5 W) than the lipid

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extraction; however. it ran for a longer time (45 min), so a higher energy consumption of 3.38 W h was obtained. For both reactions combined, the overall energy consumption was 5.98 W h. The final metric assessed was the PMI; the lipid extraction had a value of 54.82 and the transesterification a value of 62.56, giving a value for the total reaction of 144.38. While this value is far from the ideal value of 1, it is similar to that of industrial processes, specifically pharmaceuticals, but much larger than previous literature values for biodiesel production from waste cooking oils in one step.[47,48] However, in comparison to pharmaceutical production and biodiesel from waste cooking oils, the waste associated with this reaction is primarily the extracted SCG, which can be used further in plastic production or as part of fertilizers.[49,50] Furthermore, the solvents that add to the waste content have minimal associated hazards and so have a lower impact upon human health and the environment compared to those used in traditional industrial processes. However, these solvents can be recycled in an industrial setting, which would lead to a lower PMI value.

These green metrics are advantageous to aid in designing and improving reactions or processes. As shown by the metrics used here, this experiment has low levels of associated hazardous waste, meaning that the disposal and resultant impacts on human health and the environment are minimal. Consequently, there are small impacts upon the subsystems related to the experiment, such as the environment on disposal, preparation of chemicals, and energy production, making it a more sustainable overall system. There is the potential for the laboratory experiment to be extended by requiring students to construct and/or analyze systems-oriented concept map extension (SOCME) diagrams related to the valorization of spent coffee grounds.[51]

CONCLUSION

This laboratory experiment enables students to see first hand that many of the substances discarded daily as waste can be used further, minimizing the increase in landfills. In utilizing this waste, students extract lipids to valorize SCG into FAEE. Upon performing this laboratory experiment, students have the opportunity to improve skills using spectroscopic techniques, in conjunction with one another, to determine the intermediate and product of a multistep reaction. Analysis of calculated green metrics allows for students to show the impacts this experiment has on the wider environment with energy consumption and efficiency via PMI. Further to illustrating biodiesel and its analogues as greener alternatives to traditional crude oil-derived fuels, this experiment allows students to begin to think about the consequences of waste not only with respect to the chemicals used but also the entire life cycle of the SCG. In achieving this, students can consider the entire system as a whole and the effects each subsystem has upon one another, hence obtaining a well-rounded understanding of waste valorization and the benefits it can have on the wider environment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.2c00728.

Student lab manuscript (PDF, DOCX)
Instructor manuscript (PDF, DOCX)
Technicians Guide (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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