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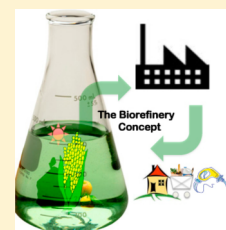
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S Supporting Information

ABSTRACT: Undergraduate curricula have increasingly incorporated sustainable and environmentally friendly approaches in the laboratory. Learning outcomes have emphasized the importance of the principles of green chemistry, but experiments may fail to impress upon the students that large-scale conversions of biomass into a spectrum of value-added products would have a huge impact on a sustainable future. With a lecture and two-session experimental biocatalytic synthesis of functional molecular gelators, students can explore real-world applications of chemistry and become aware of the biorefinery concept.

KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, Laboratory Instruction, Public Understanding/Outreach, Organic Chemistry, Green Chemistry, Materials Science



The prevalence of terms such as green technology, green energy, and the green movement indicates a culture of collective responsibility toward mitigating human impact on the environment. That the green label pervades in the mainstream is a testament to the significance of ensuring an environmentally conscious and sustainable future. Going green is also a crucial motif in research, where chemistry, the central science, is no exception.¹ Chemists have responded to this challenge by adopting a philosophy known as green chemistry with 12 key principles that encourage the minimization of waste (#1), benign synthetic procedures (#3), and the use of renewable resources (#7).² Biorefineries, as industrial manifestations of a sustainable biobased economy, incorporate essential principles of green chemistry and aim to eliminate dependence on petroleum and its derivatives to produce products, fuels, and energy (Figure 1). This article may serve as a suitable review of biorefineries providing sufficient background and information to create a prelaboratory lecture (30–60 min) and laboratory module (two sessions, between 3 and 6 h each) geared toward second-year undergraduates in an introductory organic chemistry or materials science laboratory course.

Green chemistry experiments have been introduced to students to demonstrate various alternatives to conventional chemical reactions; these include the employment of less hazardous solvents and reagents, solvent-free reactions, and enzymatic catalysis.³ However, educators are aware that examples of such green chemical reactions—used for teaching in the laboratory—tend to address only one or two principles of green chemistry and fall short of representing a holistic picture of a biobased economy.³ By employing bioderived products and energy efficient catalytic reactions, the gelator synthesis laboratory can demonstrate the power of coupling the biorefinery method with green chemistry principles. Shedding light on the industrial background and development will help

students grasp a bigger picture and think about the results and consequences of their chemistry.^{1b}

Teaching the biorefinery concept is not difficult in words and pictures; however, the formidable challenge is to convey the significance of an industrial concept in an academic setting accessible to students. Another challenge is to demonstrate in a laboratory experiment the translational aspect of a biorefinery, notably that reactions can directly lead to tangible outcomes (fuel, materials, etc.). By performing a laboratory experiment that takes the students from performing biobased synthesis to witnessing substantial value-added products, students may make a more meaningful connection between the lecture material and their work. Proposed is a set of facile enzyme-catalyzed sugar-based reactions that can be used in an undergraduate organic laboratory to teach important green chemistry concepts and their impact on the environment and economy. The proposed experiment is unique in that it exposes students to the synthesis of soft materials from biobased resources, an experiment that embodies the essential principles of the biorefinery by producing value-added functional products from renewable resources in a simple green chemical methodology.

CLASSROOM DISCUSSION OF THE BIOREFINERY

The prelaboratory discussion is organized into three parts, all of which the instructor may discuss with varying degrees of detail: (1) the biorefinery versus the petrochemical refinery; (2) a historical development of biorefineries and their importance; and (3) the technical development and current status of biorefineries.

Biorefinery versus the Petrochemical Refinery

The instructor may easily start off by presenting the biorefinery in parallel to a petrochemical refinery (Figure 1). A modern

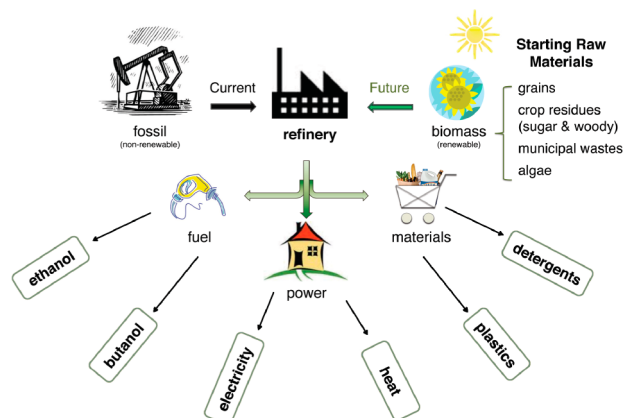


Figure 1. The transition from a petroleum-based economy to biobased economy.

petroleum refinery utilizes fossil fuels to produce a myriad of useful products such as plastics, rubber, solvents, and synthetic fibers. However, the most significant drawback to the traditional refinery is its source materials: fossil fuels, a nonrenewable resource that significantly contributes to environmental pollution resulting from combustion. Nevertheless, the petroleum refinery is a remarkable display of efficiency, utilizing seven primary building blocks: syngas (carbon monoxide/hydrogen gas), ethylene, propylene, butanes, butylene, butadiene, and BTX, (benzene/toluene/xylenes) to produce an array of value-added products.⁴ In an ideal biorefinery, one seeks all of the benefits of a conventional petroleum refinery, namely, its efficiency, versatility, and production scale. The defining feature of a biorefinery is that its starting materials

derive from renewable plant-based matter and wastes, collectively termed “biomass”. For instance, crops such as sugar cane bagasse, wheat straw, rice straw, and corn stover are considered biomass. The American National Renewable Energy Laboratory (NREL) defines a biorefinery as “a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals.”⁵ The key differences between a petroleum refinery and a biorefinery at present include (1) the choice of starting materials, (2) the chemistry of conversion processes, and (3) the diversity of products (the product diversity of biorefineries is limited compared to that of petroleum refinery). An important point the instructor should make is that there is a much higher compositional variety in biomass feedstocks than in fossil-based resources. The composition of fossil-based resources is mostly linear hydrocarbons; distillation can be performed to separate them and yield fuels, while functional groups can be appended to produce chemicals. The chemistry of hydrocarbons is much better understood than that of oxygenated starting materials with widely varying structures that characterize biomass feedstocks. Structural diversity poses a challenge in implementing a facility that needs to process as much local biomass as possible. Therefore, biorefining must include preprocessing, which converts plant raw materials into broadly defined intermediates: carbohydrates, protein, oils, syngas, lignin, and ash.⁶ Such intermediates then undergo the appropriate chemistry to yield further products (fuels, chemicals, polymers, etc.). Some technologies are still in robust development, for instance, the processing technology to efficiently convert lignocellulosic starting material to carbohydrates and other products.

Historical Development and Importance

A presentation of the biorefinery in a classroom is sufficient without discussing its historical development, but giving a backdrop for students may be helpful for both context and content. The idea of extracting and synthesizing chemicals from

The Biorefinery Concept

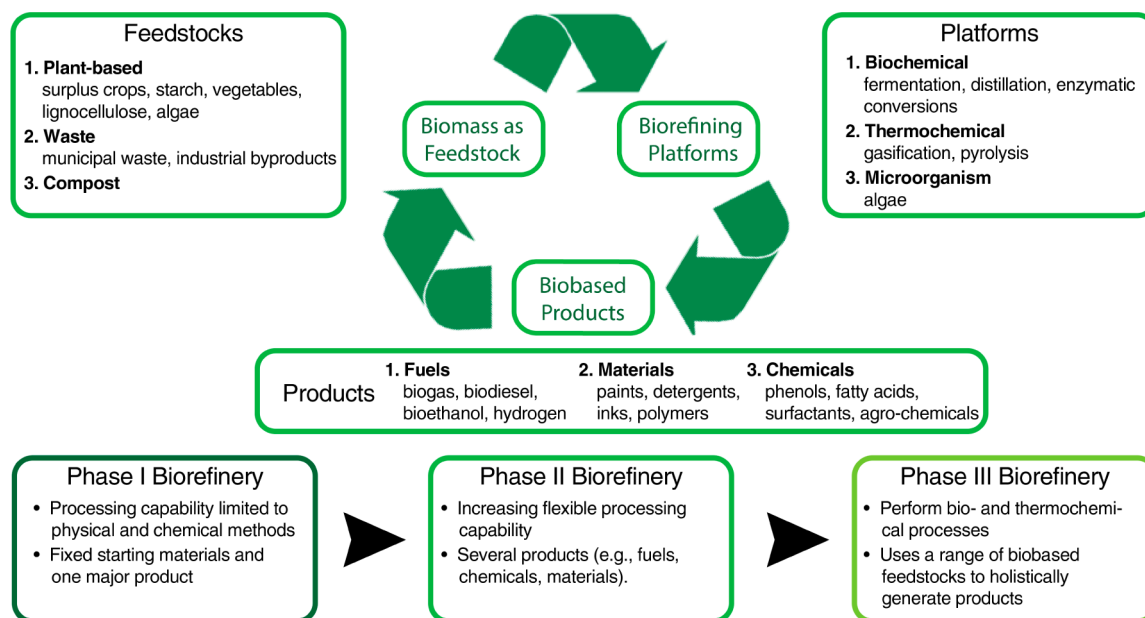


Figure 2. Schematic representation of the biorefinery concept.

biomass is not new. It stems from the age-old ideology that everything we use ought to come from available and renewable resources. For most of the 20th century, however, the biomass industry could not compete against the highly efficient and versatile petroleum-based industries.^{4,6} The wide-ranging composition of biomass limited its integration and processability for the large-scale production of commodities such as feed, chemicals, and fuels. However, with a growing concern for the environment and following the oil crisis of the 1970s, interest in using biomass has grown. Since the late 20th century, scientists and engineers have been working in collaboration to design an integrated system that accommodates different types of biomass to manufacture essential commodities. This concept of integrated biobased production is the "biorefinery concept" (Figure 2). The term "biorefinery" was coined in the 1990s.^{6,7}

Given emergent technologies, the concept that biomass could be used as "an input to produce multiple products with complex processing methods" is new.⁸ Taking a step further, biorefineries are being envisioned to supply fuels and electricity, in addition to chemicals.⁹ Experiments published in this *Journal* have elaborated means of using biomass to generate fuels in an educational laboratory setting.¹⁰ Today, the worldwide production of major crop residues (sugar cane bagasse, wheat straw, rice straw, and corn stover) is over 1000 billion kg per year, while the total U.S. consumption of chemicals is approximately 100 billion kg per year.¹¹ Such disparity, along with current geopolitical situations in areas where oil is most abundant, necessitates the building of efficient biorefineries capable of processing complex mixtures of local biomass, also known as integrated biobased production.

The impact of functional biorefineries as capable as today's petrochemical refineries will be huge. The development of biorefineries would significantly benefit national economies that maintain a heavy dependence on foreign oil.¹¹ Whereas a petroleum-based economy depends on foreign refineries, biorefineries would enable the exportation of more goods produced from domestic resources because biomass is available both locally and domestically. It would give more options to food, fuels, chemicals, and pharmaceutical producers at potentially lower costs, while mitigating their harmful effects on the environment.

The Technical Development and Current Status of Biorefineries

The next appropriate learning point for students focuses on current trends among biorefineries. The biorefinery has begun to evolve over the last century and become increasingly complex and integrated. The evolution of biorefineries can be described in three phases. The phases indicate the extent of versatility and prowess of biorefining operations. The phase I biorefinery, the earliest in development, has fixed processing capabilities. It focuses on utilizing one kind of biomass feedstock to develop one industrially important product. For instance, the Quaker Oats Company, in 1922, developed one of the earliest and most notable examples of an industrial-scale biorefinery.⁶ It involved the production of furfural (IUPAC name: furan-2-carbaldehyde), an industrial organic compound, by treating oat hulls, which are the industrial byproduct of oat dehulling process. As a result, the oats mill produced up to 2.5 tons of furfural per day.⁶

Next is the facility that enables the integration of various processes to produce more than one major product from one

feedstock—the phase II biorefinery. Roquette's site in Lestrem, France, produces proteins, chemicals, sweeteners, and bioethanol all from cereal grains. Roquette is currently using cereal grains from corn, wheat, and peas to manufacture more than 600 different chemicals.¹² In the United States, particularly in the Midwest, there are a number of phase II biorefineries that take local crops for processing, notably in states such as Illinois, Wisconsin, and Michigan.¹³ For example, Mascoma Frontier Biorefinery Project, located in Kinross Charter township, MI, processes pulpwood via enzymatic hydrolysis to sugars, which are simultaneously fermented to ethanol. The list of major biorefinery projects funded by the Department of Energy is available on the Web; readers are encouraged to refer to the provided reference for further reading.¹³

Phase III marks the futuristic vision of the biorefinery, and there still exists a wide gulf between phase II and what researchers envision as phase III biorefineries. Phase III biorefineries will be the powerhouse of a biobased economy. The most advanced and flexible phase III facilities include an integrated system that could produce fuels, power, and materials from a variety of natural resources. Feedstocks are significantly more diverse than for phase II and may include agricultural residues and energy crops (corn stover, switch grass, rice hulls, sorghums), algae, municipal solid waste, and forest material (woody waste, bagasse, mill residues). The phase III biorefinery is an engineering challenge, for it has to process wide-ranging biomass feedstocks with appropriate technologies. Additionally, the facility must reflect what resources are most available in the vicinity. Hence, it must use processing technologies that suit the raw materials. Technologies include the already developed biochemical processes (bacterial conversion and enzymatic conversion routes) and thermochemical processes (gasification and pyrolysis). The more exciting aspect is the emergence of hybrid technologies, well-exemplified in the production of cellulosic ethanol and other intermediate chemicals by ZeaChem, Inc.¹³ ZeaChem uses chemical fractionation to separate sugar and lignin from cellulose; sugar is converted to acetic acid by bacterial conversion and then to cellulosic ethanol. Such is the need for product versatility and process/feedstock flexibility that will make the biorefinery economically competent to the petroleum refinery. At present, no phase III biorefinery exists in the commercial realm. However, due to extensive ongoing research, it is predicted that by the second decade of this century they will be established and commissioned for operation.¹¹ A key message for students here is that biorefining operations are transitioning from phase II into phase III.

Currently, NREL defines three platforms or methods to refine biomass.¹⁴ The three platforms are biochemical, thermochemical, and microorganism (Figure 2). The biochemical platform encompasses processes such as fermentation and distillation, and is the most widely used platform today. Ethanol production is achieved by the fermentation of sugars extracted from plant-based sources and subsequent distillation. The thermochemical platform uses gasification and pyrolysis of biomass feedstocks. One example is the production of charcoal by gasifying wood. Lastly, the microorganism platform involves production of biofuels from algae, and other whole cells.

■ EXPERIMENTAL APPROACH TO THE BIOREFINERY

Amphiphiles and Molecular Gels from Biobased Resources

The practice of chemistry that embodies the ideals of biorefinery can extend to academic research and science education alike. In laboratories across the world, efforts are underway to figure out how to best harness biomass, and it will be the next generation of scientists and engineers who will develop the future of the biorefinery.

As a hands-on exercise for the students, the synthesis of amphiphiles from sugar alcohols, a readily available and inexpensive starting material can be performed. Amphiphiles, molecules with both a hydrophilic head and a hydrophobic tail, have been an integral component of chemical technology including agrochemicals, consumer products, and industrial processes. They also serve as an interesting case study as the saponification of triglycerides from natural oils is an early example of the chemistry of biomass. Amphiphiles may serve as building blocks for a number of functional materials (e.g., fibers, liquid crystals, and gels as shown in Figure 3). The scale of their

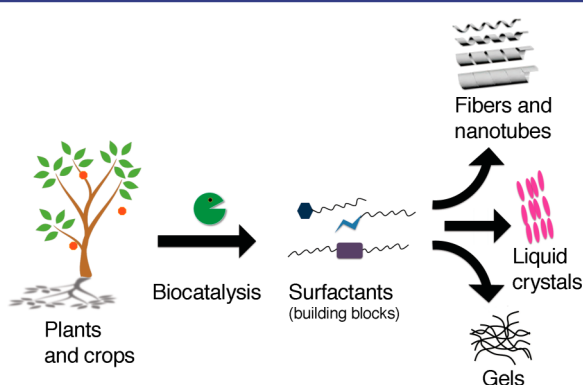


Figure 3. Biorefinery concept shown through the synthesis of surfactants, generally classified as amphiphiles. When placed in a liquid medium, surfactants aggregate in a manner dependent on their chemical structure and liquid medium, giving rise to the products shown on right.

production is highly significant, with the world market of surfactants, a type of amphiphile, having reached over U.S. \$24 billion in 2009.¹⁵ However, petroleum-based resources have historically been the primary starting material. Switching to biobased reagents has been preliminarily proven to reduce the overall environmental impact without affecting the manufacturing economy and the surfactant performance efficiency. Thus, the adoption of biorefinery concept will have a significant impact on the qualitative evolution of the surfactant market.

Many other laboratory experiments involving biomass conversion have been detailed in chemical education literature to date. Examples range from synthesis of important industrial intermediates from biobased sources to developing biofuels via distillation.^{10,16} The proposed experiment is unique in that the product of reaction serves as a building block for a tangible gel material, the final outcome of the experiment.

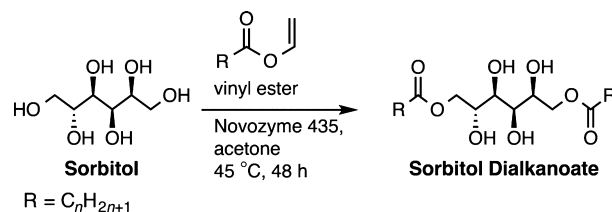
A Pedagogical Tool for Undergraduate Organic Laboratories

In the laboratory, a green method in which biobased reagents are the starting material for amphiphiles was developed (Figure 3). The proposed set of reactions can easily serve as a pedagogical tool for undergraduates to demonstrate the biorefinery concept in a small-scale laboratory setting. The

overall focus here is (1) a starting material derived from natural resources is used; (2) green methods and pathways to synthesize amphiphile molecules are used; and (3) the synthesized amphiphiles are used to create a functional material (in this case, a gel, through self-assembly). In particular, one important facet of the biorefinery concept—that biobased feedstocks can directly afford value-added materials—is stressed (Figure 1). Conveying such ideas requires the use of a suitable reaction that demonstrates green principles and easily translates organic chemistry to material synthesis.

In an industrial setting, the sugar-based crops are preprocessed to yield chemical intermediates (e.g., glucose, sucrose, sugar alcohols) that could be further modified. Chosen reactants include the open-chain sugar alcohols, sorbitol ((2S,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol) and its isomer, mannitol ((2R,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol). Due to its remarkable availability as an intermediate, sorbitol is identified as one of the 12 identified building blocks that “could serve as an economic driver to the integrated biorefinery”.⁷ Moreover, sugars serve as versatile starting materials, as one or more of their hydroxyl groups could easily be modified. In the following reaction, sorbitol or mannitol is reacted with long-chain vinyl ester, derived from fatty acids, to create two-tailed diester gemini amphiphiles (Scheme 1). The sugar-fatty acid

Scheme 1. General Reaction of Sorbitol-Based Amphiphiles from Sorbitol and Vinyl Ester



conjugates serve as molecular gelators, which are able to congeal a liquid via self-assembly. This lab is also well suited as a gateway to introduce students to self-assembled soft nanomaterials (for further information review the Supporting Information).

The diester product is a two-tailed amphiphile because with both hydrophilic and hydrophobic components on the same molecule—two hydrophobic chains on its extremities and a polar region at its center. Lipase (Novozyme 435; *Candida antarctica* Lipase B immobilized on acrylic resin), one of nature’s many biocatalytic proteins, is used for a regioselective transesterification at the primary hydroxyl groups of the sorbitol. Though catalysis is a foundational pillar of green chemistry, using enzymes instead of a chemical catalyst stems from the principles of the biorefinery. Both of these methodologies allow for catalyst recycling in comparison to a consumed stoichiometric chemical reagent. Furthermore, using a heterogeneous solid-phase catalyst allows for incorporation into an introductory organic chemistry lab as simple gravity or vacuum filtration may be used to recover the catalyst. Care must be taken as to prevent water from entering the reaction matrix, as water could drive the reaction backward by breaking the ester bonds and promoting fatty acid formation, which reacts much less efficiently than the vinyl ester derivative.

Materials and Methods

Mannitol, sorbitol, and caprylic acid vinyl ester were purchased from TCI America and used as received. Novozyme 435, a

commercially available immobilized lipase, was obtained from Novozymes, and acetone was purchased from ThermoFisher and used after drying over activated molecular sieves (size 4A). Mannitol or sorbitol (0.4 g, 2.2 mmol) and 0.85 mL of caprylic acid vinyl ester (vinyl *n*-octanoate, 4.4 mmol) were reacted with 0.300 g of Novozyme 435 in 50 mL of acetone. The reaction mixture was incubated at 250 rpm in an orbital shaker at 45 °C for 48 h. The simple work-up procedure, precluding column chromatography, was performed on the white and cloudy resultant reaction mixture; vacuum filtration was first performed to recover the solid lipase, which was subsequently washed thrice with acetone and left to dry while the mixture was washed thrice with hexane (25 mL) and filtered again to isolate the white powder product with an approximately 75% yield. Should time and resources allow, ¹H NMR spectroscopy may be used to identify and confirm the diester product and may be compared to the spectra included in the Supporting Information available online.

The synthesized amphiphiles were used as precursors to a material, a self-assembled organic solvent or oil gel. With the use of a conventional heating–cooling gelation method, amphiphiles formed gels with various organic solvents and oils. A small glass vial with 15 mg of amphiphile in 300 μL of liquid was heated to disperse the amphiphile in the liquid, and then the solution was allowed to cool to room temperature to determine the gelation capability of a 5 wt %/v solution. To heat the mixture, a heat gun was used under the fume hood or a hot water bath for most low boiling organic solvents (bp <100 °C) or an oil bath set to 125 °C for oil gels. Gel formation afforded a versatile soft material from a sugar-based amphiphile. After it was cooled, the glass vial was inverted to check whether the content flowed against gravity, following the inverted vial method (Figure 4).¹⁷ If it did not flow, the gelation of a liquid is

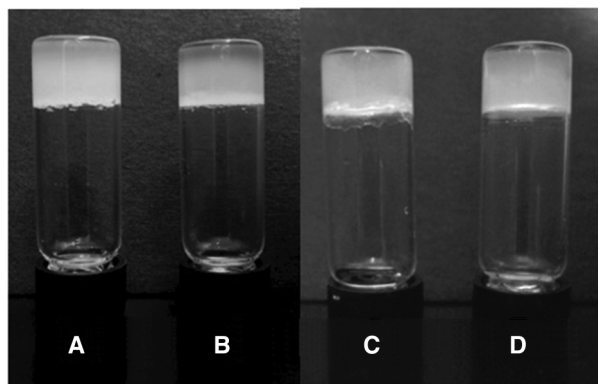


Figure 4. Photographs of 5 wt %/v organogels made using (A) mannitol dioctanoate and toluene; (B) mannitol dioctanoate and 1,8-dibromooctane; (C) sorbitol dioctanoate and toluene; and (D) sorbitol dioctanoate and 1,8-dibromooctane.

explained by molecular self-assembly; upon cooling, amphiphile molecules, which were forced to dissolve, aggregated and formed fibrous structures in the liquid, creating a three-dimensional network that trapped liquid molecules in its interstices. Students may create a table such as Table 1 to record gelation properties of amphiphiles by testing their gelation capability in different solvents. The amphiphiles are not observed to form gels in water; thus it has been proposed that the amphiphiles could potentially be used to clean up oil spills as they selectively gel oil in oil/water mixtures.¹⁷ The

Table 1. Gelation Data for Mannitol and Sorbitol Amphiphiles

| Solvents or Oils | Mannitol dioctanoate (R = C ₇ H ₁₅) | Sorbitol dioctanoate (R = C ₇ H ₁₅) |
|----------------------------------|---|---|
| Benzene | G ^a | G |
| Toluene | G | G |
| Cyclohexane | G | G |
| Dodecane | G | G |
| Heptane | P ^b | P |
| Mineral Oil | G | G |
| Canola Oil | G | G |
| Pump Oil | G | G |
| Silicone Oil | PG ^c | PG |
| Hydrocarbon Mixture ^d | G | G |

^aG = gel at 5 wt %/v. ^bP = precipitate. ^cPG = partial gel at 5 wt %/v.

^dMixture of hydrocarbons refers to aliphatic (pentane, hexane, octane) and aromatic (benzene, toluene, xylene) solvents in 1:1 volume ratio.

sorbitol/mannitol amphiphile belongs to a class of molecules known as phase-selective gelators. The premise is that gelled oil could be removed, and then recovered, from oil/water mixture.

HAZARDS

Fatty acid vinyl esters and the acetone solvent are volatile organic liquids that should be handled with gloves and proper eye protection. All reagents should be kept within a fume hood during handling, synthesis, and work-up. When using a heat gun to dissolve the product in a liquid, caution is advised. It should be done in a fume hood and laboratory tongs should be used to tightly hold the glass vial during heating. The vial must remain undisturbed when cooling back to room temperature.

IMPLEMENTATION AND ASSESMENT

The lecture information and laboratory experiment are well suited for incorporation into a modular organic chemistry lab, which has been successfully demonstrated by numerous undergraduates in our research lab, and easily assessed via journal-style laboratory report. Due to the breadth of information in the lecture portion, this may be an ideal exercise in which instructors incorporate the introduction section of the laboratory report by allowing the students to further research green chemistry and biorefineries.¹⁸ Additionally, because students are invited to collect gelation data in a variety of solvents, it represents an opportunity to build their results section, practice formatting and incorporating tables, charts, and images into their report, an obvious but sometimes overlooked aspect of report writing. Lastly, though gelation is briefly introduced, it serves as a starting point for the discussion section and may allow students to develop a complete story, often seen as one goal of the journal-style laboratory report.¹⁹ Should a full report not be ideal, sample questions based off of pertinent topics are included in the Supporting Information.

CONCLUSION

The proposed discussion and experiment will give an opportunity for students to relate to an industrial concept in the teaching laboratory. Students gain a heightened sense of the current and future impact of biorefineries by practicing a small-scale biobased organic synthesis, where the translational aspects from organic synthesis to material synthesis are clear. This laboratory experiment may benefit a wide range of students, because of its interdisciplinary nature incorporating catalysis,

soft materials, and renewable resources that connect students to a range of relevant scientific issues.

■ ASSOCIATED CONTENT

● Supporting Information

Provided are ^1H NMR spectra for both mannitol and sorbitol dicaprylate which instructors and advanced students may use to compare to their products. Additional information on important discussion topics and questions to be used in lab, or as a template for developing assessment materials is provided. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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