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Biodiesel Synthesis from Vegetable Oils Using a Recyclable Heterogeneous Catalyst: Employing Active Learning to Implement Education for Sustainable Development

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Abstract We report here on a project regarding the synthesis and properties of biodiesel (BD) from two Brazilian vegetable oils, babassu- (BO), cottonseed oil (CSO), and bioethanol (EtOH). The project was given to our chemistry major students as an introduction to Education for Sustainable Development (ESD). It took seven weeks, 4-hour/week, including the final presentation by the students. In order to introduce the subject, we used active learning, by giving two questionnaires, and by encouraging the students to decide on: the vegetable oils, the heterogeneous catalyst, a simple and fast technique (viscosity) to determine the transesterification reaction yield. An important feature of this project is the use of design of experiment (DOE) to calculate the dependence of BD yield on two experimental variables, namely, reaction time and the molar ratio EtOH/vegetable oil. The outcome of this project is that important knowledge related to ESD is gained from a simple experiment. It is recommended, in its present or modified form, for science students.

Keywords Biodiesel, Synthesis of, Babassu oil, Cottonseed oil, Transesterification, Heterogeneous catalysis, Design of experiment

1. Introduction

The introduction of electric-powered vehicles raises questions about the future of their diesel-powered counterparts. However, a combination of enhanced performance, flexibility, higher power-density, and longer operational range means that diesel engines will still be in use for some time [1,2], especially in large countries like Australia, USA and Brazil, where most cargo (> 70%) is moved by trucks [3,4,5]. Another important factor is that the use of (petroleum-based) diesel-biodiesel mixtures lower the emission of greenhouse gases. Depending on the source of biodiesel (BD), its greenhouse gas emissions are 40 to 86% less than those generated by burning diesel oil [6]. In addition to be essentially sulfur-, and nitrogen-free fuel, and has a higher cetane number range than diesel oil [7], use of BD dramatically reduces emission of carbonaceous particulates and formaldehyde as compared with diesel oil [8]. These characteristics have a considerable impact on air quality, as Brazil consumed 63.23 billion liters of diesel fuel, containing 6.62 billion liters of BD in 2022 [9].

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In summary, the subject of BD is relevant to an everyday situation, less air pollution and better fuel performance in cargo transport, hence it is important for the undergraduate curriculum.

We report here on a project regarding the synthesis and properties of BD from vegetable oils using a recyclable heterogeneous catalyst. It was implemented within an advanced experimental course given to our chemistry major students (Chem 1405). We used active learning to implement Education for Sustainable Development (ESD) as indicated by the United Nations Educational, Scientific and Cultural Organization (UNESCO), and further advanced by the Global Action Program on ESD. Among other goals, these programs give "learners of all ages the knowledge, skills, values and agency to address interconnected global challenges including climate change, loss of biodiversity, unsustainable use of resources, and inequality" [10,11,12].

We used active learning to implement ESD by outlining our goals, and helping the students during their discussion/ decision on: the vegetable oils to be employed; the heterogeneous catalyst, and the experimental technique to calculate BD yield. The students chose to use babassu oil (BO) from the Amazon region and cottonseed oil (CSO), see **Figure 1**. Bioethanol, hereafter referred to as EtOH, was chosen as the alcohol, while a macroporous strongly basic ion exchange resin (Ambersep-900, OH^- form) was

used as the catalyst. Viscosity was employed to determine BD yield. The student´s evaluation was rewarding because of the active learning approach, introduction of new material, especially DOE, and because the project is directly related to an environmentally important issue, namely, greenhouse gas emissions.

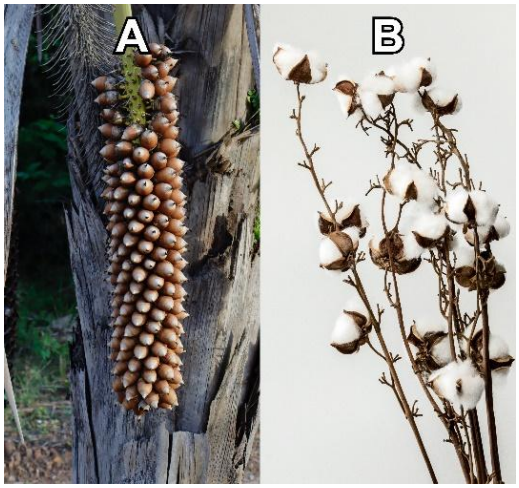


Figure 1. Illustration of Babassu (Attalea speciosa) nut (Part A) and cotton plant (Part B). The oils derived from these plants, namely babassu oil and cottonseed oil, are obtained through hydraulic pressing of babassu nut kernels, and cottonseeds, respectively

The main activities and targeted learning objectives are shown in **Table 1**.

Table 1. Activities and Targeted Learning Outcomes of the Project on the Synthesis and Properties of Biodiesel

Activity	Targeted Learning Outcomes
Questionnaires	Assessment of student´s previous knowledge of green chemistry, with emphasis on renewable materials, catalysis, and DOE.
Assignments	Review/analysis of relevant literature; decision making on the experimental part (reaction variables, techniques, and catalyst).
Group seminars	Improving skills in information organization and presentation; work collaboratively with others in a group.
Chemistry laboratory	Applying good laboratory practices; conducting experiments; organization and analyses of experimental data.
Computer room	Development of experimental protocols; data analysis and interpretation.

2. Experimental

2.1. Starting Materials

Refined BO (CAS 91078-92-1) and CSO (CAS 8001-29-4) were from Cooperativa Central Do Cerrado Maranhão, Brazil, and Cargil Agricola SA, respectively. The average molecular weights employed were 654.4 and 860.6 $g.mol^{-1}$, for BO and CSO, respectively [13,14]. Absolute ethanol (CAS 64-17-5), n-hexane (CAS 110-54-3) and standardized analytical solutions (HCl, CAS 7647-01-0; KOH, CAS 1310-58-3; $Na_2S_2O_3$, CAS 7772-98-7) were from Synth Chemical, São Paulo. Ambersep-900, macroporous anion exchange resin (CAS 9017-79-2; Res-OH form) was from Aldrich. Its capacity (0.8 meq/mL resin) was determined using potentiometric titration [15]. Anhydrous $MgSO_4$ (CAS 7487-88-9) was from Merck. The internal standards for GC analysis, namely, ethyl undecanoate and ethyl tridecanoate were available from a previous study [16].

2.2. Equipment

Potentiometric titration was carried out using Metrohm 827 pH meter. Gas chromatographic analysis was carried out at the Analytical Center of this Institute, using Shimadzu model CG-MS QP2010 gas chromatograph, equipped with BPX5 (5% phenyl methylpolysiloxane) 30m capillary column. Viscosity was determined at 25°C using a Brookfield model R/S-CPS cone-plate rheometer; the density was determined at 25°C using Anton Paar DMA 4500 M digital density meter. A Rudolph Research J357 digital refractometer (operating at 488 nm) was employed to measure the refractive indices at 25°C.

2.3. Ion-exchange Resin Activation and Recycling

Before use, the (new) resin was washed (in a column) with two volumes of ethanolic KOH solution (ca. 1 mol/L), then with water, and dried at ≤ 40°C, under reduced pressure, over P_4O_{10} until constant weight. The dried resin absorbs air humidity only slowly; it can be weighted in stoppered bottles and transferred easily to the reaction flask.

The catalyst employed in the synthesis of BD was regenerated and activated using a modification of the published procedure, as follows [17]: After the experiment, the ion-exchange beads were left to dry, then washed twice with n-hexane at 40-45°C, air dried, and then washed once with alcoholic KOH, ca. 1 mol/L KOH at room temperature (Erlenmeyer flask; base volume = thrice the resin volume; magnetic stirring). The wet resin was transferred to a glass column washed with water until free from the retained KOH, and then dried under reduced pressure, as given before.

2.4. Synthesis of Authentic Biodiesel Samples

We employed a published procedure to synthesize BD samples from BO and CSO [18]. Based on the analysis of CG data, these BD samples were ≥ 99.5% pure.

2.5. Work Carried out by the Students

The students were divided into 8 groups, G1-G4 and G5-G8 worked on BO and CSO, respectively. In parallel with BD synthesis under different experimental conditions (2.5.1), the students determined the properties of the starting oils and BD by titration, calculated the cetane number of BD (2.5.2), and determined the densities and viscosities of the staring vegetable oils and of the mixtures (starting oil + corresponding biodiesel; 2.5.3).

2.5.1. Synthesis of Biodiesel

Briefly, the students used the densities of BO, CSO and EtOH to calculate the required vegetable oil and alcohol volumes; pipetted these into a 125 mL round-bottom flask, provided with a magnetic bar, introduced the flask into a diethylene glycol bath, and heated the latter to 85 ± 5°C. When the bath temperature was reached, the solid, dry catalyst was introduced, the mixture was refluxed for the required time, cooled, washed extensively with water, and the oil phase was separated and (partially) dried with anhydrous $MgSO_4$. The products (mixtures of vegetable oil + BD) were given to the instructor for further drying, vide infra section 3.4.

2.5.2. Determination of Acid-, Saponification-, Iodine Number of the Starting Oils, and Calculation of the Cetane Number of Biodiesel

Acid and saponification numbers were determined by acid-base titration, as indicated elsewhere [15,19]. Iodine number was determined using aqueous ethanol solvent instead of CCl_4, as reported elsewhere [20].

Values of the acid number (AN) and saponification number (SN) were calculated from:

$$\frac{56{,}1\ (V_a - V_b)C}{m} \quad (1)$$

where: Va is the standardized KOH solution volume used in sample titration; Vb is the corresponding volume used in blank titration; C is molar concentration of the standardized KOH solution; m is the mass of oil used, in g.

$$\mathrm{SN} = \frac{56.1(Vb - Va)\mathrm{C}}{\mathrm{m}} \quad (2)$$

where: Vb is the standardized KOH solution volume required to titrate the blank sample, in mL; Va is the corresponding volume required to titrate the ethanolic oil solution, in mL; C is the concentration of HCl, in $mol.L^{-1}$; m is the mass of oil used, in g. Value of the iodine number (IN) was calculated from:

$$\mathrm{IN} = \frac{(Vb - Va)\mathrm{C}\ 12.69}{\mathrm{m}} \quad (3)$$

where: Vb is the standardized $Na_2S_2O_3$ solution volume required to titrate the blank sample, in mL; Va is the corresponding volume required to titrate the oil and biodiesel samples, in mL; C is molar concentration of the standardized $Na_2S_2O_3$ solution; m is the mass of the vegetable oil and BD employed, in g.

Using the values of (IN) and (SN) of BD, the students calculated the cetane number (CN) of the biofuel.

$$\mathrm{CN} = \frac{58.48 + (46.3 - 0.225.\mathrm{IN})\mathrm{SN}}{\mathrm{SN}} \quad (4)$$

2.6. Statistical Design of Experiment: Dependence of Biodiesel Yield on the Experimental Variables

The students used the Statistica software (version 13.0, Dell, Austin, USA) to generate a table of randomized-order for experiment execution. Because there are two variables, e.g., the molar ratio of EtOH/vegetable oil ($\chi_{EtOH/oil}$) and time, each one has three values (or levels), e.g., 60, 90 and 120 minutes, the minimum number of experiments is 9 (= 3^2), increasing to twelve because the center point ($\chi_{EtOH/oil}$ = 9; 90 minutes) was repeated three more times to obtain robust experimental data.

2.7. Hazards

Ethanol poses hazards of flammability and toxicity. The vegetable oils and the corresponding biodiesels are combustible. There are no significant hazards in this project that require precautions other than wearing personal protective equipment. All liquid wastes were discarded by the safety division of this Institute.

3. Results and Discussion

3.1. The Questionaries

Scheme 1 shows the activities of this project. Questionaries **Q1** and **Q2** and their results are given in the Supplementary Information (SI) section. The answers to **Q1** showed little knowledge, (for Brazilian students!) of oils and fats from the Amazon region. **Q1** also shows little contact with catalysis of the transesterification reaction, and of chemometrics. Therefore, the present project was a "hands-on" opportunity to remedy this lack of knowledge of important subjects.

Regarding **Q2**, gas chromatography (alone or coupled with a mass detector) is probably the most employed technique for quantitative and structural analysis of BD [21]. In view of the limited laboratory time, and the availability of one GC equipment in the undergraduate laboratory, use of this technique was considered unfeasible. Taking account of the large difference between the viscosities of the starting vegetable oils and their corresponding BD samples, the simplicity and fast determination of the viscosity (ca. 5 minutes/analysis), the students opted to use viscosity for the determination of BD yield. We explained that use of viscosity is based on the assumption that the students´ samples contain only unreacted vegetable oil, and the corresponding BD. That is, the concentrations of mono- and diglycerides formed (by partial transesterification) are negligible. This assumption is acceptable in view of the large excess of EtOH employed, and the fact that the transesterification rate constants follow the order: monoglycerides > diglycerides > triglycerides. That is, the intermediate products of transesterification react with EtOH react faster than the original oil to produce BD, probably because of the associated decreased in steric hindrance [22,23].

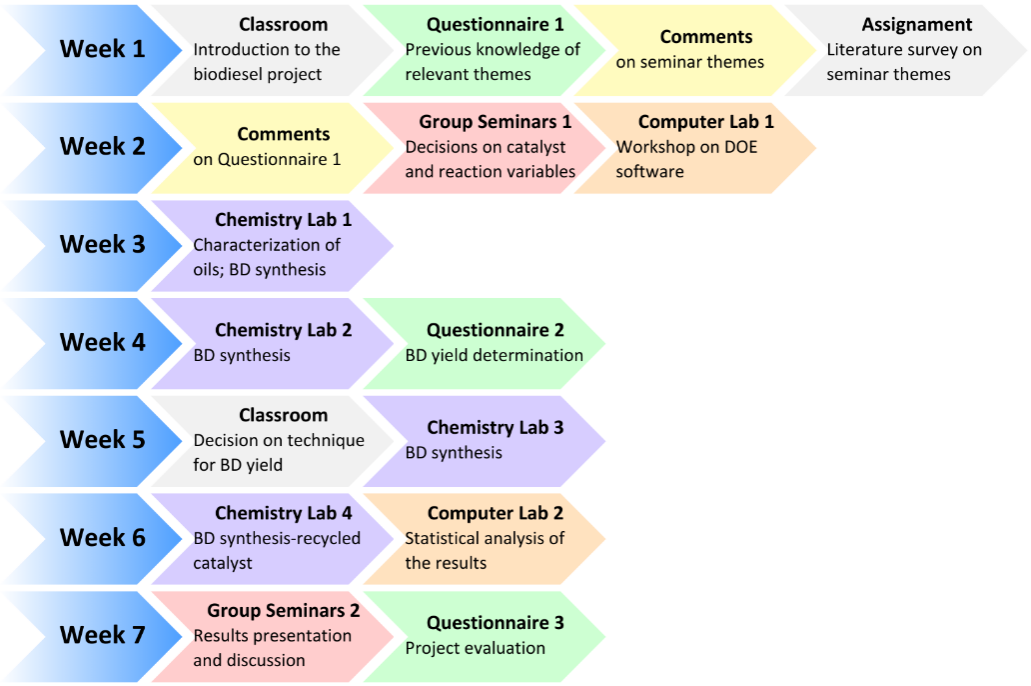
3.2. Group Seminars

As shown in SI-3, the titles of the seminars served to cover important aspects of the theme BD, including: fuels for diesel engine, renewable material in BD production;

mechanistic aspects of the transesterification reaction, analysis of BD and its performance as a diesel-engine fuel.

3.3. Choice and Properties of the Vegetable Oils

The babassu (Attalea speciosa) fruits have an ellipsoidal form (see **Figure 1**), weighing 90-280 g each. These are roasted and crushed in order to separate the inner white kernels; BO is extracted by hydraulic pressing of the kernels; the oil yield is ca. 7% of the fruits´ weight [24]. Cotton (gossypium Hirsutum) bolls weighing 3-6 g (see **Figure 1);** the seed accounts for about 60% of this weight, out of which 15-20% is oil. After removal of the lint, the cottonseed is crushed; crude cottonseed oil is extracted by pressing, or by solvent extraction, followed by bleaching and deodorization [14]. BO is a highly saturated (ca. 89%) oil [13], whereas CSO is highly unsaturated one (ca. 77%) [25]. Consequently, the former is typically used in cosmetic products, and for soap making [26], whereas the latter is used for salad, food frying, etc [27]. This composition difference has consequence on fuel performance; the corresponding CNs are ca. 63, and ca. 56, for BD from BO, and CSO, respectively [28]. The values calculated by our students were 65.8 ± 1 and 53.4 ± 1, for BD based on BO, and CSO, respectively. These CN values are superior to those (47 to 52) determined for Brazilian diesel oil [29].



Scheme 1. Flowchart of the Activities Carried out during the Course

Table 2. Conditions and biodiesel yield for student groups

Experiment number[a]	Reaction time (min)	Ethanol/oil molar ratio ($\chi_{EtOH/oil}$)	Yield for babassu oil (m%)[b]	Yield for cottonseed oil (m%)[b]
1	60	6	15.42	30.60
2	60	9	15.36	36.10
3	60	12	15.80	38.29
4	90	6	32.65	45.83
5	90	9	34.45	48.09
6	90	9	41.29	49.63
7	90	9	43.35	49.57
8	90	9	42.72	50.85
9	90	12	48.32	52.25
10	120	6	36.21	54.32
11	120	9	52.78	55.60
12	120	12	65.21	62.53

[a]The order of experiments were randomized, as generated by the Statistica software. For convenience, we grouped the experiments for each reaction time, using variable $\chi_{EtOH/oil}$.
[b]BD yield was calculated by viscosity measurements.

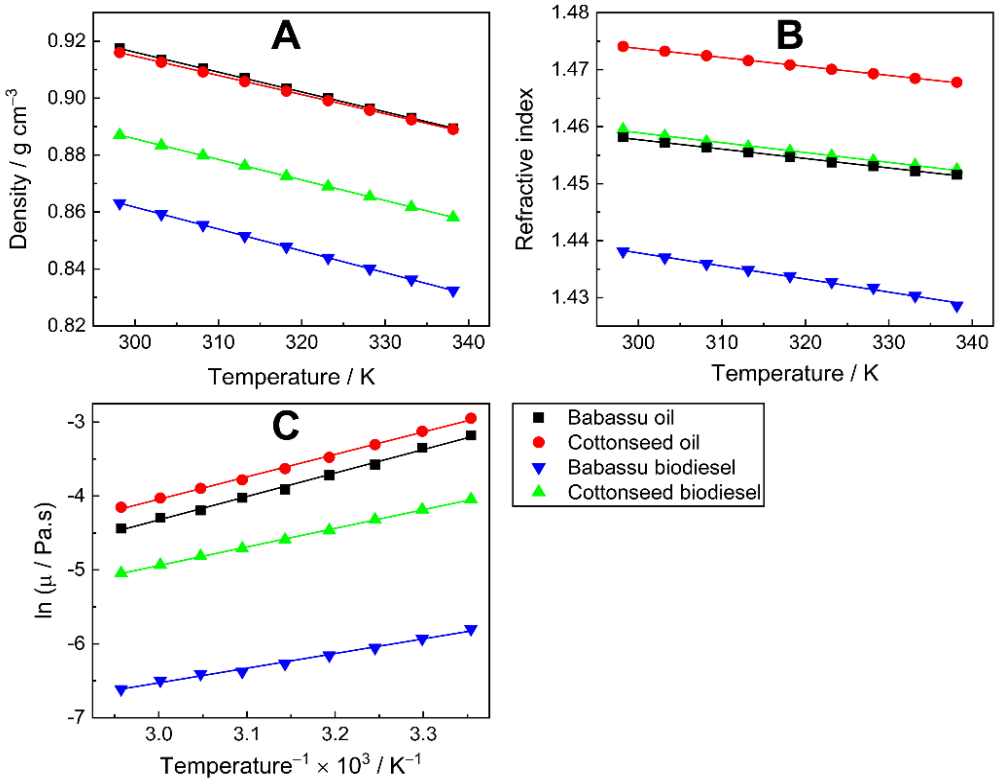
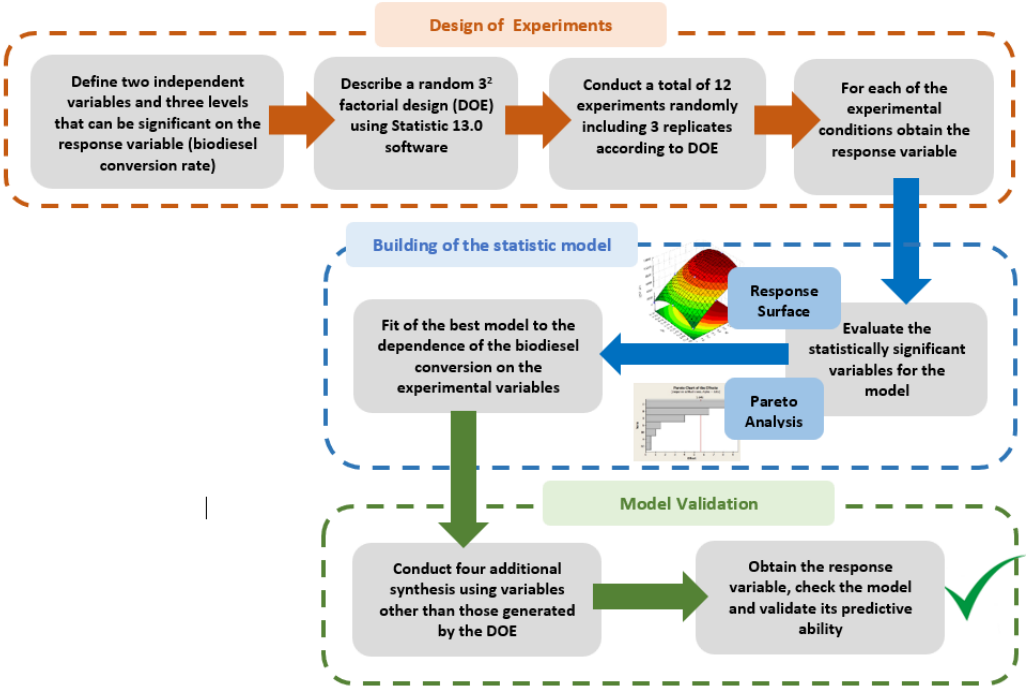


Figure 2. Dependence of the density (A), refractive index (B) and Arrhenius-type plot of viscosity (C) of the studied oils and biodiesels on the temperature



Scheme 2. Simplified scheme with the steps for the design of experiments analysis with Statistica 13.0

Vegetable oils and the corresponding BDs are typically characterized by their properties, such as density, refractive index, viscosity, and IN. The differences in these properties are related to the contents of saturated/unsaturated fatty acids [30,31,32]. The properties of both oils and the corresponding BDs at different temperatures (25-65℃) are listed in **Table SI-2**, and plotted in **Figure 2**. Due to time constraints, these experiments were conducted by the instructor, and the results were sent to the students. At 25℃, the refractive index and viscosity of CSO are larger than those of BO due, as discussed above, to the higher content of unsaturated fatty acids in CSO [33,34]. The effect of temperature on the viscosity can be described by an Arrhenius-type equation whose slope (Ea) is the energy of viscous-flow, whose values

are 16.5 and 20.9 kJ/mol for the biodiesel of BO and CSO, respectively. This result agrees with the reported dependence (an increase) of (Ea) on oil unsaturation [33].

3.4. The Biodiesel Synthesis Experiment

Table 2 shows the (randomized) experiments carried out by the students on BO, as generated by the Statistica software, along with the corresponding BD yields. The latter were calculated from the plots shown in **Figure 3**. These plots generated **Eq. 5** and **Eq. 6** that were employed for calculating the BD yields.

One practical aspect of this BD project is the relatively long time required for phase separation under gravity, although centrifugation and membrane filtration were employed to accelerate phase separation [35,36,37]. Due to this problem, some BD is lost during separation, and the product (vegetable oil + BD) still contains some water at the end of the laboratory period. Consequently, the instructors removed all volatiles after the laboratory class; the BD yield was calculated from viscosity measurements, i.e., not gravimetrically.

The ESD aspect is central to this experiment. In this regard, the students should appreciate the relative importance of experimental variables to the BD yield obtained. This appreciation was achieved from information generated by design of experiment (DOE), including the Pareto plot, and the response surface. The variables defined by G1-G8 groups for the factorial design for biodiesel synthesis are described in **Table SI-3**, and the steps for the DOE analysis are shown in **Scheme 2**.

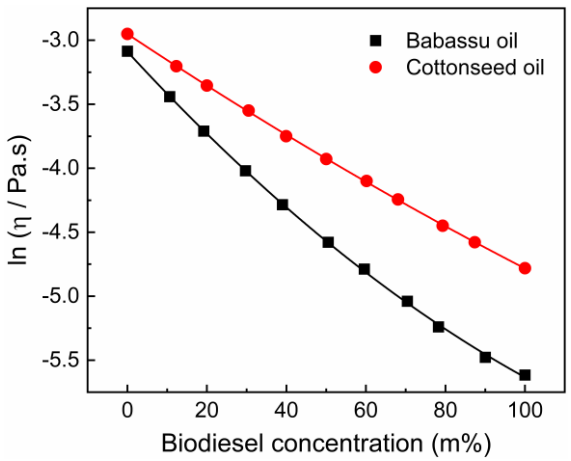


Figure 3. Calibration curve showing the dependence of viscosity on the concentration in m% of authentic mixtures of babassu oil and cottonseed oil with the corresponding biodiesel

$$\ln(\eta / \text{Pa.s}) = -3.089 - 0.0338\ \text{babassu BD (m\%)} + 8.3 \times 10^{-5}\ \text{babassu BD (m\%)}^2 \quad (5)$$

$$\ln(\eta / \text{Pa.s}) = -2.951 - 0.0206\ \text{cottonseed BD (m\%)} + 2.3 \times 10^{-5}\ \text{cottonseed BD (m\%)}^2 \quad (6)$$

The Pareto principle (Vilfredo Pareto) is also known as the 80/20 rule, i.e., 80% of effects arise from 20% of the causes [38]. As the number of variables was limited to two, the Pareto chart shows the relative importance to BD yield of reaction time (t) and reaction mixture composition. As **Figure 4** shows, (t) affects the reaction much more than $\chi_{EtOH/oil}$. perhaps because the minimum value for the latter variable was 6, i.e., was already high. Note that the quadratic term in (t) was calculated by the software merely to produce a better statistical fit.

An efficient approach to quantify the dependence BD yield on the two reaction variables tested is the color-coded, 3D response surface shown in **Figure 5**. This analysis produced Eq. 7 and Eq. 8 for this dependence. Note that the latter equations were generated using reduced values for both variables, due to the very different scales of each, namely, 6 to 12 for $\chi_{EtOH/oil}$ and 60 to 120 minutes for reaction time. Again, the quadratic term in (t) was included by the software merely to upgrade quality of the fit. These results are qualitatively similar to those of **Figure 4**, i.e., reaction time is more important that reaction composition, within the ranges studied.

Additional experiments were carried out by the students, including yield prediction and catalyst recycling. In principle, Eq. 7 and Eq. 8 permit calculation of reaction yield under conditions different from those employed by the students, but still within the ranges given in **Table 2**. This was carried out for BO, using reaction time = 75 minutes and $\chi_{EtOH/oil}$ = 7.5. The expected BD yield and that calculated from Eq. 7 differed by 5%. Additionally, repeating experiment 9 of **Table 2** using recycled catalyst gave 46.43% yield, showing 96% catalytic efficiency. This high efficiency is due, in part, to the macroporous nature of the resin employed, as the gel-type resins are not efficient for BD synthesis. [39]

In the presentation of their final results, the students showed some relevant and interesting data. For example, they stressed that repeated washing of the BD sample with water is crucial in order to remove the produced glycerol, whose viscosity at 25℃ is 308 times that of BO! They showed that a sample of CSO used for frying (collected from a street market) contains 6 times more free acid than a fresh oil sample. They also discussed the power of CG/MS for structural determination of BD components, especially when authentic carboxylic esters with odd carbon numbers are used as "markers", see **Figure SI-1**. ^{1}H and ^{13}C NMR spectra offer not only additional information about the structure of the oil/BD [40], but is a reliable tool to detect adulteration of oils, especially olive oil with soybean oil [41].

$$\text{Biodiesel yield (m\%)} = 15.2 + 54.4\ (t) + 28.6\ (t)\cdot \chi_{EtOH/BO} - 32.8\ (t)^2 \quad (\text{G1-G4};\ R^2 = 0.996;\ \textstyle\sum Q^2 = 1.12) \quad (7)$$

$$\text{Biodiesel yield (m\%)} = 31.3 + 36.0\ (t) + 7.44\ \chi_{EtOH/CSO} - 13.5\ (t)^2 \quad (\text{G5-G8};\ R^2 = 0.986;\ \textstyle\sum Q^2 = 1.28) \quad (8)$$

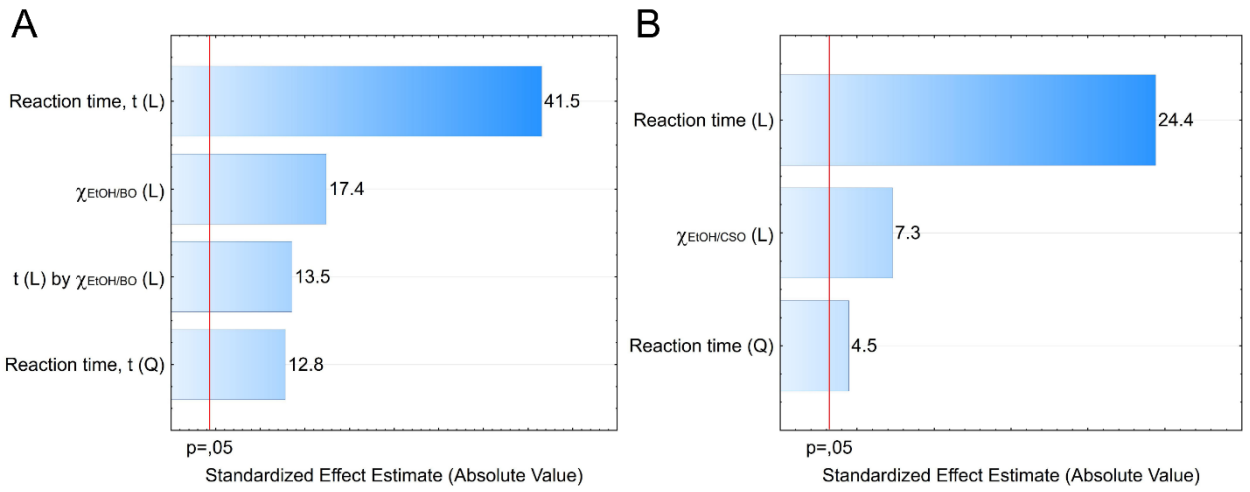


Figure 4. Pareto plot showing the effect of reaction composition, given by ethanol/oil molar ratio, and reaction time on biodiesel yield. Babassu oil results are shown in Part A, while cottonseed oil results are shown in Part B. Only variables that significantly affect biodiesel production (above the red vertical line) are shown. The terms are labeled with (L) for linear and (Q) for quadratic

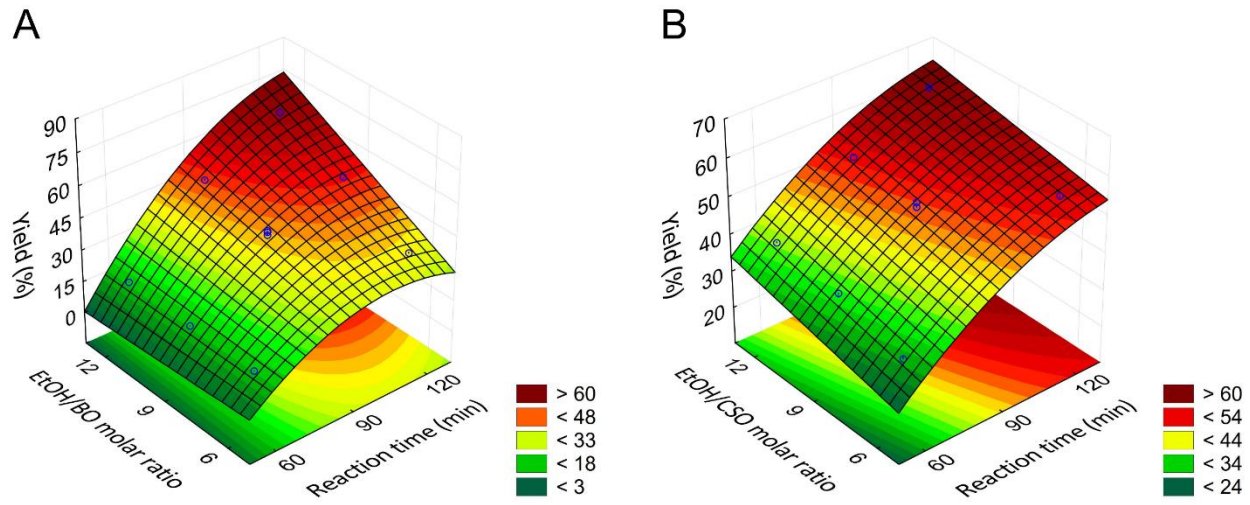


Figure 5. Response surface plots of the data showing the dependence of biodiesel yield on ethanol/oil molar ratio and reaction time at a fixed catalyst concentration. Part A illustrates the results of babassu oil, and Part B shows the results of cottonseed oil

4. Conclusions

The project reported served for discussing several important aspects of biofuels. We used active leaning to introduce BD production/properties, within the scope of ESD. BO is an Amazon region oil that is not used in foods, EtOH is produced by sugar molasse fermentation [42] and the catalyst is easily recyclable. The project requires simple infrastructure, thanks to the use of viscosity to determine BD yield. The biofuels produced perform better than petroleum-based diesel oil due to their higher CN (between 56 and 63 for BDs, compared to 47 to 52 for diesel oil [29], and are essentially sulfur and nitrogen free. During the project, the students learned new information from the quizzes and gained "hands-on" experience in the use of statistics to enhance a reaction yield. In their final evaluation, 90% classified the project as interesting, motivating and innovative. Because of its versatility and green chemistry features, this project is suitable for any science students (biology, chemistry, engineering and pharmacy), and can be modified according to the objective, time available and conditions of the laboratory.

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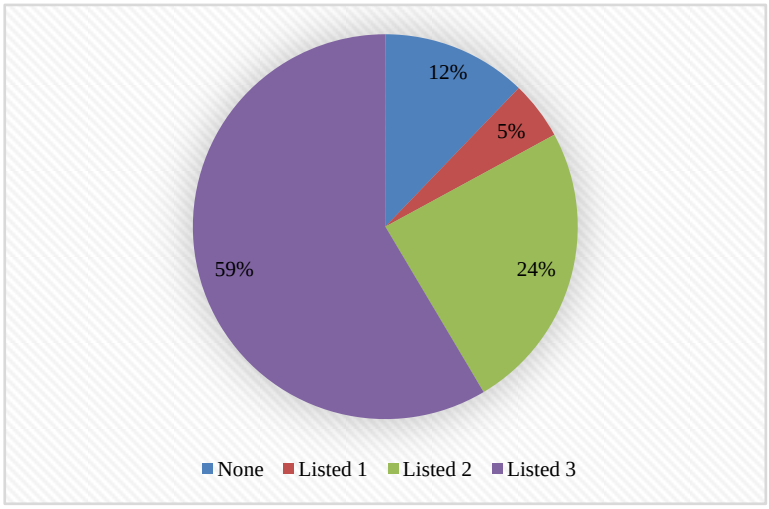
Supplemental Information-SI

SI-1-Questionnaire 1

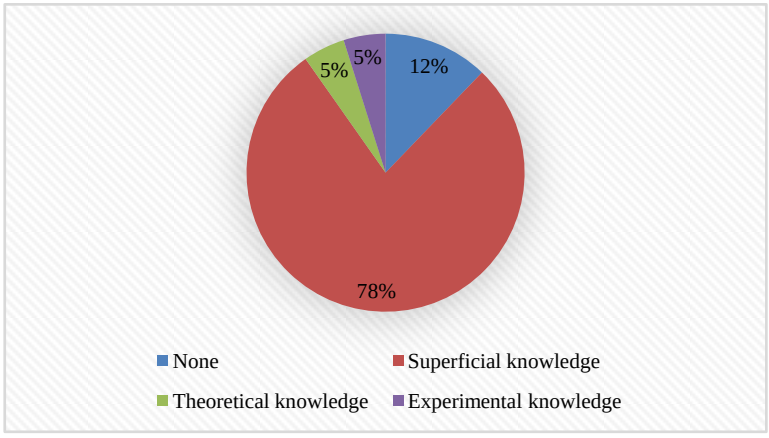
Questionnaire 1: Previous Contact with Topics Relevant to Biodiesel Project

1. Name three sources of Brazilian oils or fats other than soybean, canola, corn, sunflower and palm.



Oils listed by students: Avocado, cotton, almond, peanut, rice, babassu, buriti, cocoa, canola, chestnut, Brazil nut, coconut, copaiba, cupuaçu, shea, flaxseed, castor, melon, murumuru, olive, palm, peroba, primrose, and castor oil.

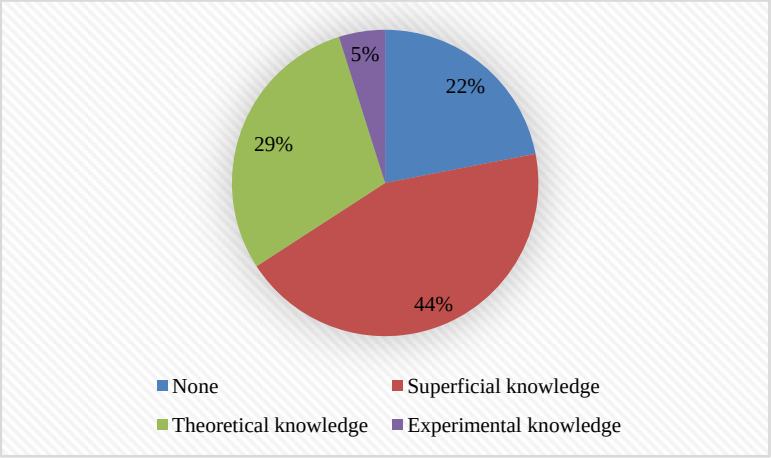
2. What is your previous contact with biodiesel?



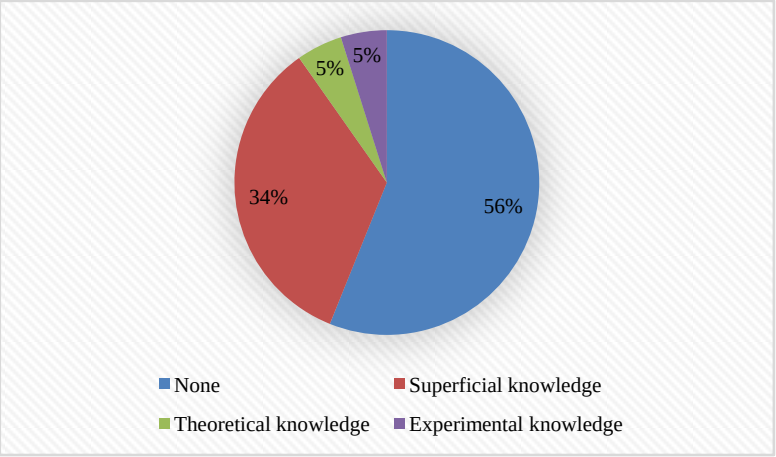
3. Name two instrumental techniques, either single or tandem, that can be used in the analysis of biodiesel.

Techniques listed by students: Gas Chromatography (GC), High-Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance (NMR), UV-Visible Spectroscopy (UV-Vis), Rheometry, Infrared Spectroscopy, Gravimetry, Gas Chromatography-Mass Spectrometry (GC-MS), High-Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS).

4. What is your previous contact with catalysis of transesterification reactions?



5. What is your previous contact with chemometrics?



SI-2-Questionnaire 2

Questionnaire 2: Decision on Alternative Techniques for Biodiesel Yield Determination

At the end of the transesterification reaction of a vegetable oil, the reaction mixture was repeatedly washed with water to remove excess ethanol, catalyst, and the glycerol produced. This leaves product containing unreacted vegetable oil and the corresponding biodiesel. The next step is to determine the composition of this product to determine the yield of biodiesel.

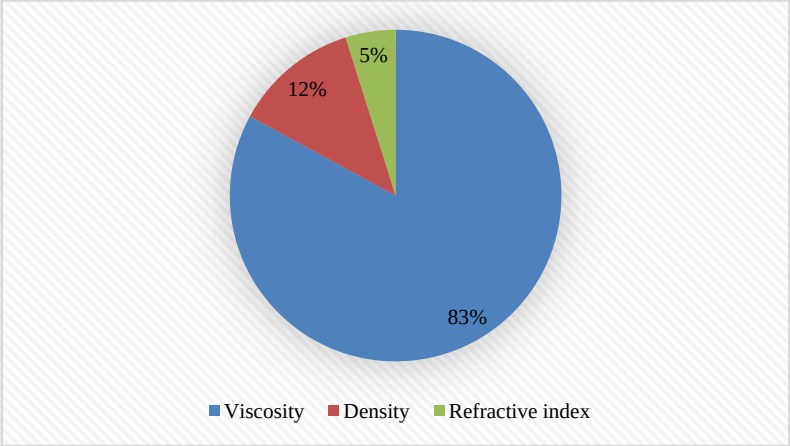
Several techniques can be used, e.g. gas chromatography alone or coupled with a mass detector are robust techniques to determine the biodiesel yield. However, our interest is to use another,simple instrument.

So far, you have determined the density (ρ), refractive index (n), and dynamic viscosity (η) of babassu and cottonseed oil. The following Table shows the values of these properties for babassu oil, cottonseed oil, and the corresponding (authentic) biodiesels.

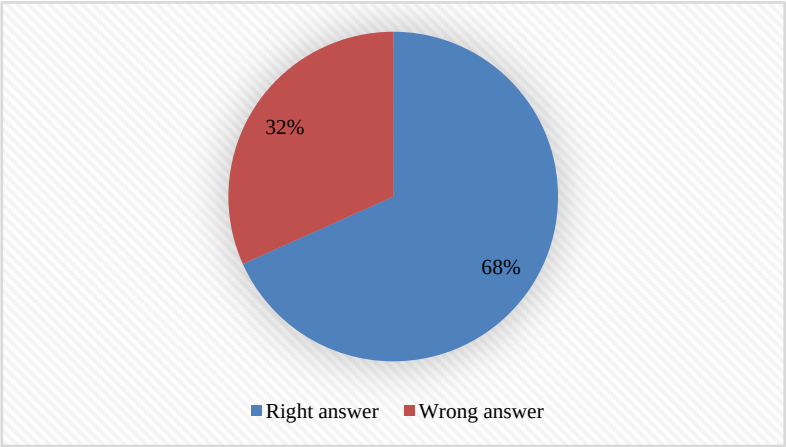
Table SI-1. Physicochemical properties of vegetable oils and the corresponding biodiesels at 25℃

Property	Starting Babassu oil	Babassu oil-based biodiesel	Starting Cottonseed oil	Cottonseed oil-based biodiesel
Density, ρ (g cm^{-3})	0.91758	0.86311	0.91600	0.88704
Refractive index, n	1.45817	1.43814	1.47408	1.45952
Dynamic viscosity, η (mPa s)	41.67	3.03	52.49	17.52

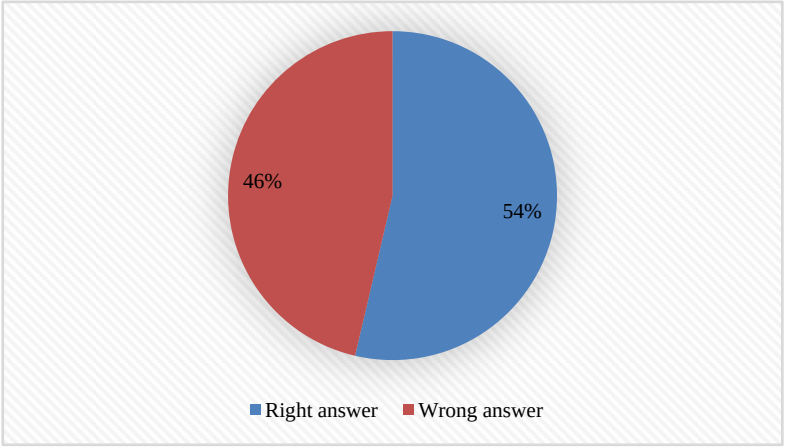
Q-2.1 - Choose one of the techniques listed in the Table SI-1 above to determine the yield of the biodiesel. Justify your choice.



Q-2.2 - Explain how you would carry out the experiment to determine the yield of biodiesel. Break your answer intosteps: 1, 2, 3, etc.



Q-2.3 - Given your choice of technique, briefly discuss an advantage and a potential practical limitation of using it to determine the yield of biodiesel.



SI-3-Themes of Students' Seminars

List of seminar themes assigned to student groups, G1 to G8. Some references were offered on these themes; the students did more literature search.

Introduction to diesel engine fuels:

Group 1- How does the diesel engine work? What is biodiesel (BD)? Discuss economic aspects (Brazilian and global) and environmental impact of the use of diesel (petroleum) and BD as fuels.

Use of renewable material in the production of BD:

Group 2- Discuss the most important properties of starting materials, and the relationship between chemical structures of BD and its performance as a fuel (discuss cetane number).

Group 3- Choose two Brazilian oils that will be used to obtain BD, and an alcohol (methanol, or ethanol) and justify your choices.

Note: as candidates, exclude the following oils: soybean, canola, corn, sunflower and palm oil.

Mechanistic aspects of the BD production reaction:

Group 4- Show the mechanisms of BD production reactions under *homogeneous* conditions, using Brønsted-Lowry and Lewis acid catalysts.

Group 5- Show the mechanisms of BD production reactions under *homogeneous* conditions, using basic Brønsted-Lowry and Lewis type catalysts.

Group 6- Show the mechanisms of BD production using *heterogeneous* acid- and base catalysts.

BD Analytics and Performance:

Group 7- Discuss the use of chromatographic methods (gas chromatography, HPLC) in the determination of the structure/yield of the BD.

Group 8- Shows the use of non-chromatographic methods of determining the BD yield. Discuss instrumental methods for determining the quality/performance of BD, compared to diesel oil.

SI-4-Tables and Figures

Table SI-2. Physicochemical properties (density, refractive index, and dynamic viscosity) of vegetable oils and the corresponding biodiesels at different temperatures (25-65 °C, ΔT = 5°C)

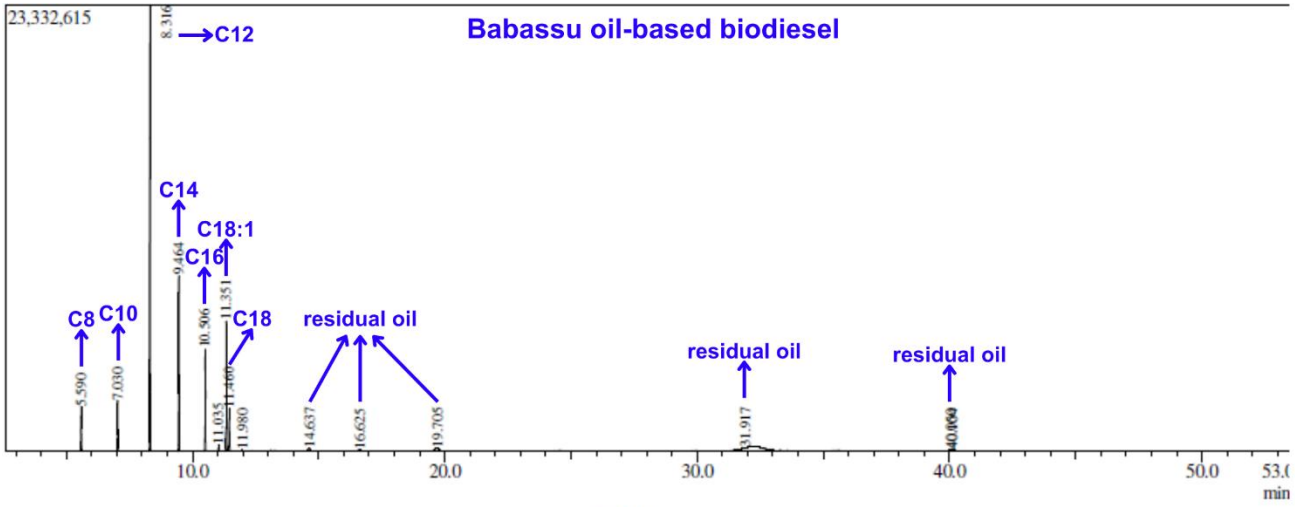
T[a] (℃)	Density, ρ (g cm^{-3})				Refractive index, n				Dynamic viscosity, η (mPa s)			
	BO[b]	BO BD[b]	CSO[b]	CSO BD[b]	BO	BO BD	CSO	CSO BD	BO	BO BD	CSO	CSO BD
25	0.9176	0.8631	0.9160	0.8870	1.4582	1.4381	1.4741	1.4595	41.67	3.03	52.49	17.52
30	0.9136	0.8593	0.9126	0.8834	1.4572	1.4370	1.4732	1.4584	35.25	2.66	43.97	15.25
35	0.9105	0.8554	0.9092	0.8798	1.4564	1.4359	1.4725	1.4574	28.04	2.35	36.72	13.31
40	0.9070	0.8516	0.9058	0.8762	1.4555	1.4349	1.4716	1.4565	24.30	2.12	30.93	11.50
45	0.9034	0.8478	0.9024	0.8726	1.4547	1.4338	1.4708	1.4557	20.05	1.89	26.54	10.13
50	0.9000	0.8439	0.8991	0.8690	1.4537	1.4328	1.4701	1.4549	17.91	1.70	22.81	9.01
55	0.8964	0.8401	0.8957	0.8654	1.4531	1.4318	1.4693	1.4540	15.12	1.65	20.31	8.12
60	0.8931	0.8363	0.8924	0.8618	1.4522	1.4303	1.4685	1.4533	13.67	1.51	17.81	7.21
65	0.8894	0.8324	0.8890	0.8581	1.4516	1.4286	1.4678	1.4525	11.82	1.34	15.75	6.45

[a] Measurement temperature in ℃.
[b] BO, BO BD, CSO, and CSO BD stands for babassu oil, babassu oil-based biodiesel, cottonseed oil, and cottonseed oil-based biodiesel, respectively.

Independent variables and the set of levels previously defined by laboratory groups to generate the DOE-based statistical model are presented in Table SI-3.

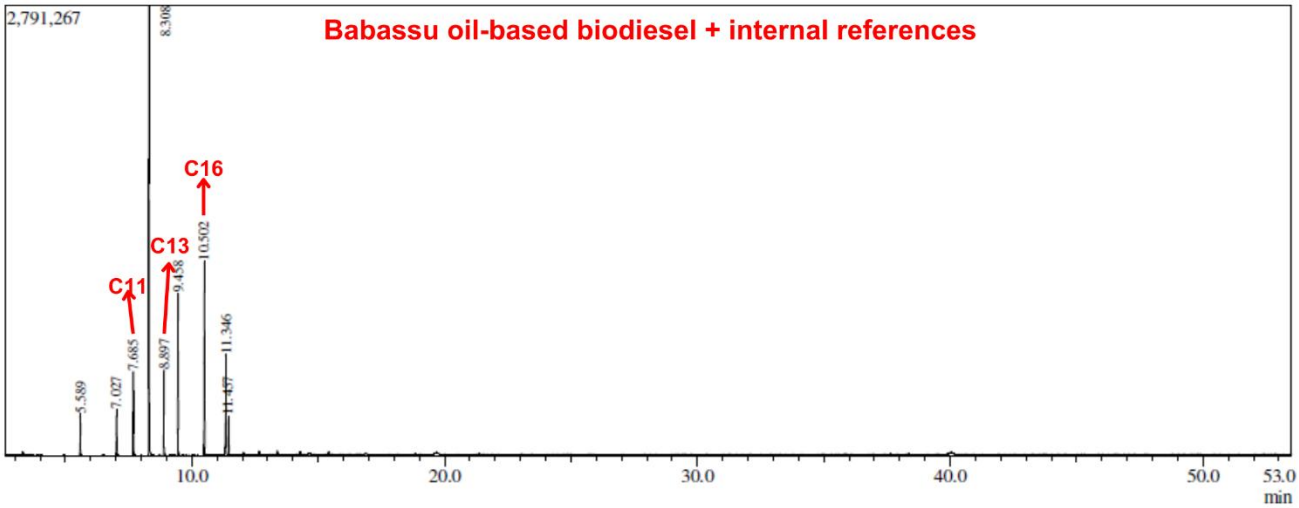
Table SI-3. Independent Levels and Variables defined by G1-G8 groups for factorial design for biodiesel synthesis

Laboratory Groups	Independent variables (Factors)	Levels set		
		-1	0	1
G1-G4	Ethanol/babassu oil molar ratio ($\chi_{EtOH/babassu\ oil}$)	6	9	12
	Reaction time (min)	60	90	120
G5-G8	Ethanol/cottonseed oil molar ratio ($\chi_{EtOH/cottonseed\ oil}$)	6	9	12
	Reaction time (min)	60	90	120



Peak Report

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.590	5.558	5.683	3108489	4.09	2321890	4.40	1.34		Octanoic acid, ethyl ester
2	7.030	6.992	7.117	3762413	4.95	2656083	5.03	1.42		Decanoic acid, ethyl ester
3	8.316	8.275	8.408	31319718	41.17	23330026	44.18	1.34		Dodecanoic acid, ethyl ester
4	9.464	9.425	9.533	12671001	16.66	9180392	17.38	1.38		Tetradecanoic acid, ethyl ester
5	10.506	10.475	10.575	7154875	9.41	5327111	10.09	1.34		Hexadecanoic acid, ethyl ester
6	11.035	11.008	11.092	554348	0.73	335836	0.64	1.65	V	Dodecanoic acid, 2,3-dihydroxypropyl este
7	11.351	11.292	11.417	10366782	13.63	6810169	12.90	1.52		(E)-9-Octadecenoic acid ethyl ester
8	11.460	11.417	11.525	2983608	3.92	2229626	4.22	1.34	V	Octadecanoic acid, ethyl ester
9	11.980	11.950	12.025	126162	0.17	76338	0.14	1.65		Tetradecanoic acid, 2-hydroxy-1-(hydroxyı
10	14.637	14.525	14.725	852472	1.12	158027	0.30	5.39		1-Hydroxy-3-(octanoyloxy)propan-2-yl de
11	16.625	16.525	16.750	475130	0.62	68069	0.13	6.98		Hexadecanoic acid, 1-[[[(2-aminoethoxy)h
12	19.705	19.517	19.867	1710844	2.25	163438	0.31	10.47		Dodecanoic acid, 1-(hydroxymethyl)-1,2-e
13	31.917	31.875	32.025	71842	0.09	13194	0.02	5.45		Dodecanoic acid, 1,2,3-propanetriyl ester
14	40.050	39.942	40.067	273610	0.36	59097	0.11	4.63		Dodecanoic acid, 1,2,3-propanetriyl ester
15	40.104	40.067	40.308	643259	0.85	78455	0.15	8.20	V	Dodecanoic acid, 1,2,3-propanetriyl ester
				76074553	100.00	52807751	100.00			



Peak Report

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.589	5.558	5.633	368263	3.67	260244	3.49	1.42		Octanoic acid, ethyl ester
2	7.027	7.000	7.067	384351	3.83	284351	3.82	1.35		Decanoic acid, ethyl ester
3	7.685	7.658	7.733	690519	6.88	517114	6.94	1.34		Undecanoic acid, ethyl ester
4	8.308	8.275	8.392	3628018	36.14	2788531	37.44	1.30		Dodecanoic acid, ethyl ester
5	8.897	8.867	8.942	730357	7.28	527702	7.08	1.38		Ethyl tridecanoate
6	9.458	9.425	9.508	1308565	13.03	1003632	13.47	1.30		Tetradecanoic acid, ethyl ester
7	10.502	10.475	10.550	1623125	16.17	1198288	16.09	1.35		Hexadecanoic acid, ethyl ester
8	11.346	11.292	11.400	980276	9.76	626417	8.41	1.56		(E)-9-Octadecenoic acid ethyl ester
9	11.457	11.400	11.500	325551	3.24	241923	3.25	1.35	V	Octadecanoic acid, ethyl ester
				10039025	100.00	7448202	100.00			

Figure SI-1. Gas chromatograms of babassu oil-based biodiesel (blue) and the latter with ethyl undecanoate (C_{11}), ethyl tridecanoate (C_{13}), and ethyl hexadecanoate (C_{16}) internal references (red)

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