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Short Communication

A comparative investigation of palmitic acid esterification over *p*-sulfonic acid calix[4]arene and sulfuric acid catalysts via ^{1}H NMR spectroscopy

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ABSTRACT

This work reports the novel results of *p*-sulfonic acid calix[4]arene-catalyzed esterification reactions of palmitic acid with deuterated methanol. The *p*-sulfonic acid calix[4]arene organocatalyst is easily obtained and handled, and is significantly less corrosive than mineral acids commonly used in esterification reactions. Although used in homogeneous conditions, *p*-sulfonic acid calix[4]arene catalyst can be recovered and reused without losing its activity and may therefore be potentially useful in biodiesel production. A comparative study by use of in situ ^{1}H NMR spectroscopy between the kinetic and thermodynamic parameters obtained from the palmitic acid esterification reaction, showed that at 0.5 mol% concentration the activation energy of the *p*-sulfonic acid calix[4]arene-catalyzed reaction is lower than that measured for sulfuric acid. However, a higher dependence in relation to sulfuric acid concentration was observed. Conversely, ΔG values obtained suggested that this reaction becomes more spontaneous with an increase in temperature than calix[4]arene catalyzed esterification reactions.

1. Introduction

Esterification is one of the most fundamental and important reactions in organic synthesis [1,2]. Organic esters are important fine chemicals used widely in the manufacturing of flavors, pharmaceuticals, plasticizers, polymerization monomers, emulsifiers in the food and cosmetic industries, and biodiesel [3–5]. Specifically, biodiesel is a renewable fuel comprised of monoalkyl esters of fatty acids. Interest in biodiesel as an alternative fuel has accelerated tremendously due to depletion of fossil fuels [6,7]. Biodiesel is now recognized as a “green fuel” that has several advantages over conventional diesel [8]. Non-edible oils make up a sustainable feedstock for biodiesel production; however, these oils contain large amounts of free fatty acids (FFA), which complicate the use of conventional alkaline catalysts due to undesirable saponification reactions [9].

The most commonly used methodology for ester synthesis is direct esterification of carboxylic acids with alcohols in the presence of acid-catalysts. Although efficient, homogeneous catalysts such as mineral acids are toxic, non-reusable, corrosive and often hard to remove from the products [10–11]. Organocatalysts are an attractive alternative, however, their use is still scarce in ester synthesis as well as in biofuel production [12–15].

Calix[*n*]arene macrocycles are formed from the condensation of *para*-substituted phenols with formaldehyde in basic medium and have been widely used as ligands in organometallic catalysis [16]. On the other hand, examples of calix[*n*]arenes as organocatalysts have been even less explored [17–19]. Currently, the use of calix[*n*]arenes still remains little explored for esterification reactions [14,15].

Thus, this paper describes the data obtained from kinetic study of palmitic acid esterification with deuterated methanol, in the presence of the *p*-sulfonic acid calix[4]arene and sulfuric acid, using in situ ^{1}H NMR spectroscopy. It was possible to determine the main thermodynamic properties such as activation energy (ΔE), entropy variation (ΔS), enthalpy variation (ΔH) and Gibbs free energy variation (ΔG). From this data, an accurate discussion was conducted on the catalytic activity of *p*-sulfonic acid calix[4]arene and sulfuric acid.

2. Experimental section

2.1. Chemicals

Palmitic acid (95% wt) was purchased from General Purpose Reagent. This fatty acid (FA) was selected due to it being commonly present in several biodiesel feedstocks. Deuterated methanol (99.75% w/w) and deuterated chloroform (99.8% w/w) were purchased from Sigma Aldrich. Toluene (99% w/w) and sulfuric acid (98.5% w/w) were acquired from Quimica Moderna and Sigma Aldrich, respectively, and used as received. All other reagents were of analytical grade and used without prior purification.

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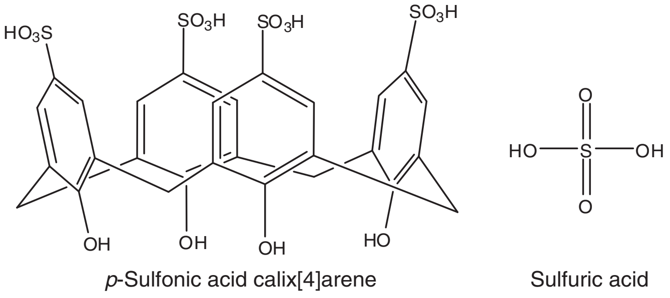

Fig. 1. Structure of palmitic acid (FA model), *p*-sulfonic acid calix[4]arene and sulfuric acid catalysts.

2.2. Catalyst synthesis

The *p*-sulfonic acid calix[4]arene was synthesized in our laboratory according to literature procedures. First, *p-tert*-butylcalix[4]arene was prepared by the Gutsche and Iqbal method [20]. Secondly, the *p-tert*-butylcalix[4]arene was dealkylated by treatment with aluminum chloride in the presence of toluene and phenol according to the method described by Ungaro and co-works [21]. Preparation of the *p*-sulfonic acid calix[4]arene was performed by treatment of calix[4]arene with concentrated sulfuric acid (98.5% w/w) [22]. The reaction mixture was agitated under a nitrogen environment and the temperature was maintained at 353 K. The reaction was followed by taking samples, which were then washed in a minimum amount of water to test their solubility. Complete solubility of the sample indicated complete sulfonation and then the reaction stopped. In total this took about 4 h.

2.3. Methods

2.3.1. General procedure of the kinetic measurements

The reactions were performed in a NMR tube, where 0.08 mmol of palmitic acid (FA) was dissolved in 0.6 mL of the deuterated methanol and heated to reaction temperature in the presence of the catalyst. Kinetic data was obtained from ^{1}H NMR spectra acquired during 5 minute time intervals in a NMR spectrometer (Mercury-300 Varian Spectrometer) which were processed using the Varian "software". The operation frequency was 300.069 MHz for ^{1}H (64 k data points), 30° excitation pulse duration of 2.2 µs, spectral width of 6 kHz, acquisition time of 3.3 s and relaxation delay of 10 ms and 32 scans in a 5 mm probe with direct detection.

In general, the methylenic group neighboring the carbonyl groups of palmitic acid or methyl palmitate (R-$\mathbf{CH_2}$-CO_2R'(H) show ^{1}H NMR signals (triplet) in the chemical shift (δ) range of 2.4–2.2 ppm. Thus, reaction progress was monitored according to the resonance signal intensity (triplet) of these methylenic groups along the reactions. Intensity of the two signals to the right of each triplet provides an adequate parameter to quantify substrate conversion [23]. Acid conversion can be estimated by comparing the areas of these signals because of R-$\mathbf{CH_2}$-CO_2R'(H), as defined by the equation given below: (Eq. (1)):

$$\text{Fatty acid conversion}\,(\%) = \frac{\mathrm{R}\mathbf{CH_2}\mathrm{CO_2CD_3}}{\mathrm{R}\mathbf{CH_2}\mathrm{CO_2H}} \times 100 \qquad (1)$$

3. Results and discussion

3.1. General aspects

Acid-catalyzed esterification is an equilibrium limited reaction. Palmitic acid reacts with deuterated methanol in the presence of *p*-sulfonic acid calix[4]arene or sulfuric acid catalysts to produce deuterated methyl palmitate and water. The catalyst initiates the esterification reaction by donating a proton to the carboxylic acid molecule. Carboxylic acid is then subjected to nucleophilic attack by the hydroxyl group of alcohol (CD_3OD), and the reaction continues with water elimination. Here kinetic and thermodynamic parameters are obtained related to the performance of two acid catalysts: *p*-sulfonic acid calix[4]arene and sulfuric acid (Fig. 1). Moreover, when directly comparing experimental data a more accurate discussion regarding catalytic activity is possible.

3.2. Kinetic studies

Palmitic acid esterification with deuterated methanol was evaluated via in situ ^{1}H NMR spectroscopy (Fig. 2) in the presence of *p*-sulfonic acid calix[4]arene or sulfuric acid catalysts. NMR spectroscopy showed to be an efficient monitoring method and allowed for obtaining precise reaction kinetic data for the two catalysts [23]. Good correlations ($R^2 \geq 0.996$) were obtained for both catalysts (Fig. 2).

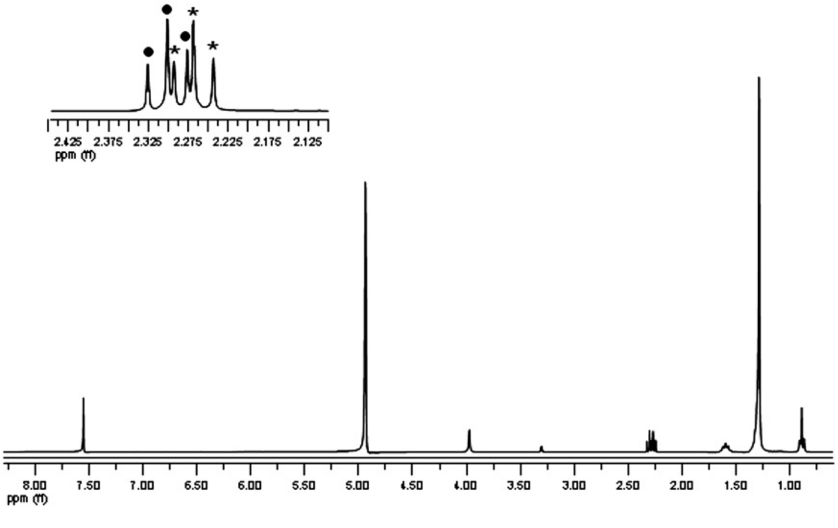

Fig. 2. Representative ^{1}H NMR spectra (300.069, CD_3OD, 318 K) obtained after partial esterification of palmitic acid. Legend: R$\mathbf{CH_2}$$CO_2H$ (palmitic acid) (*); R$\mathbf{CH_2}$$CO_2CD_3$ (deuterated methyl palmitate) (•).

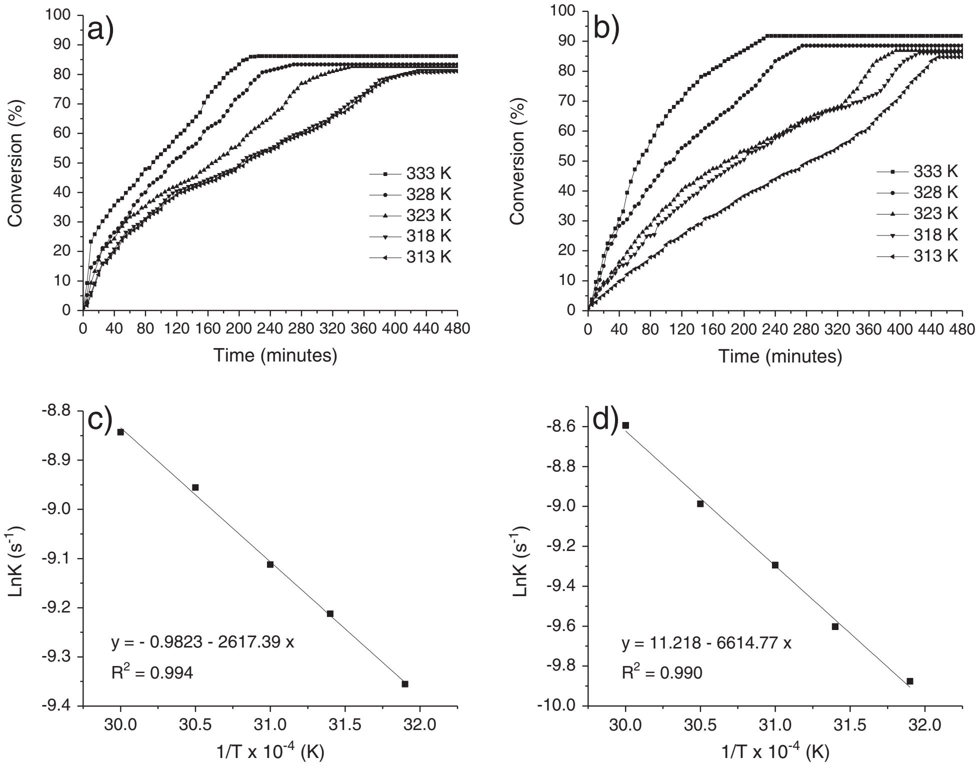

Fig. 3. Kinetic studies of palmitic acid esterification with deuterated methanol at temperatures from 313 to 333 K over the catalysts a) *p*-sulfonic acid calix[4]arene and b) sulfuric acid, and their respective Arrhenius plots: c) *p*-sulfonic acid calix[4]arene and d) sulfuric acid.

Table 1
Kinetic parameters for palmitic acid esterification with deuterated methanol over *p*-sulfonic acid calix[4]arene and sulfuric acid catalysts[a].

p-Sulfonic acid calix[4]arene catalyst				Sulfuric acid catalyst			
T	k (×10^{-5})	TOF[a]	E_a	*T*	k (×10^{-5})	TOF[a]	E_a
(K)	(L mol^{-1} s^{-1})	(mol s^{-1})	(kJ mol^{-1})	(K)	(L mol^{-1} s^{-1})	(mol s^{-1})	(kJ mol^{-1})
313	8.7	162		313	6.6	170	
318	10.0	162		318	6.6	172	
323	12.1	166	22.0	323	9.1	174	54.6
328	12.9	168		328	12.8	178	
333	19.9	172		333	18.1	184	

[a] The turnover frequency (TOF, mol s^{-1}) is moles of palmitic acid converted per mole of acid sites (H$^+$) on the catalyst per second (i.e. four to calix[4]arene and two to sulfuric acid catalyst).

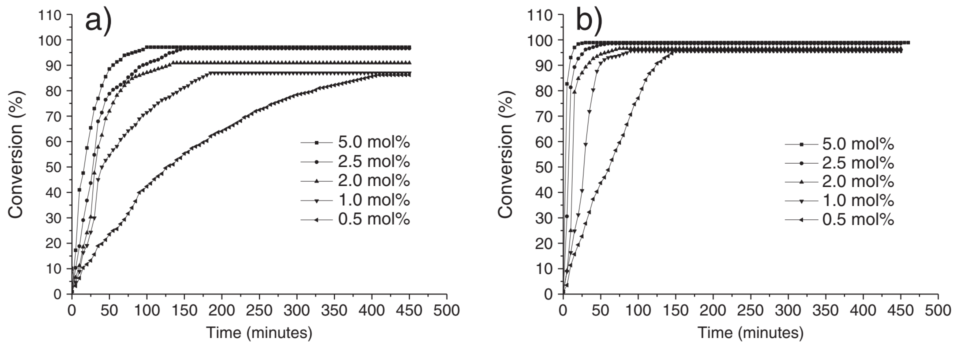

Fig. 4. Effects of catalyst concentrations on palmitic acid esterification with deuterated methanol: a) *p*-sulfonic acid calix[4]arene and b) sulfuric acid.

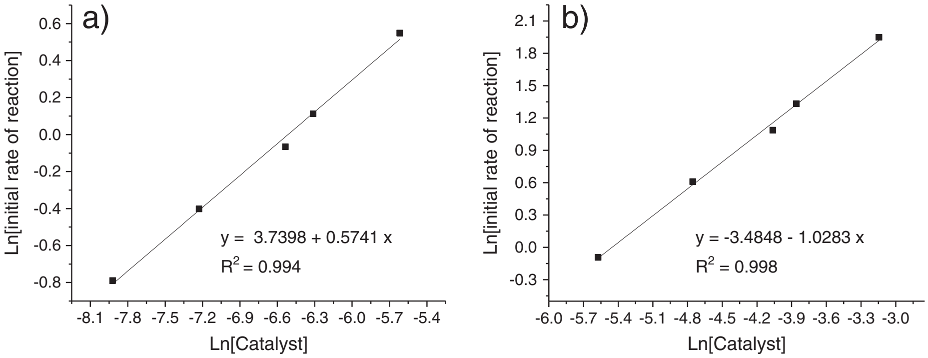

Fig. 5. Order of reaction with respect to catalyst concentration: a) *p*-sulfonic acid calix[4]arene and b) sulfuric acid.

The kinetic parameters were determined by carrying out the esterification reactions at similar conversion levels (ca. 85–95%). All catalysts were used at the same hydrogenionic concentration (molar ratio of fatty acid:H^+ equal to 800:1). All experimental data points collected over 8 h were fitted to a curve passing through the origin. From this curve (conversion versus time), initial rates were determined. Only the rates obtained during the initial period of the reactions were taken into account (first 30 min).

As seen in Fig. 3a and b, the reaction rate strongly depends on temperature. Note that the reaction conversion increases steadily, reaches maximum values (ca. 90%) after a reaction time of ca. 450 min and remains almost invariable afterwards. Furthermore, observe that the two acidic catalysts, although bearing significantly different structures, displayed quite similar activities as can be confirmed by the comparable final conversion at the end of the reaction (Fig. 1).

However, it should be highlighted that only the initial rate will be used for obtaining kinetic parameters. This data was then used to calculate the rate constant (k) using the pseudo-first order rate law. Employing the Arrhenius equation and the k values determined at different temperatures, activation energy values (ΔE) were then determined. According to Table 1, we can see that for all temperatures the rate constants (k) of *p*-sulfonic acid calix[4]arene-catalyzed esterification were higher than those observed in sulfuric acid-catalyzed esterification reaction. Consequently, the observed activation energy value (22.0 kJ mol^{-1}) for esterification of palmitic acid with deuterated methanol over *p*-sulfonic acid calix[4]arene is much lower than the activation energy obtained by using the traditional sulfuric acid catalyst (54.6 kJ mol^{-1}). This result suggests that temperature more drastically affects the initial rate of reaction for the sulfuric acid catalyst; however during the firsts 13 min, the initial rate of calix[*n*]arene-catalyzed reactions was higher than that of sulfuric acid at all temperatures.

Fig. 3 displays the kinetic curves obtained from measuring the conversion of palmitic acid in deuterated methyl palmitate in the presence of *p*-sulfonic acid calix[4]arene or sulfuric acid at different temperatures (313–333 K) via in situ ^1H NMR spectroscopy (Eq (1)).

3.3. Dependence of reaction rate in relation to catalyst concentration

Identical reaction conditions as those described above were employed with the exception of the amounts of the *p*-sulfonic acid calix[4]arene or sulfuric acid catalysts, which varied from 0.5 to 5.0 mol% (Fig. 4). Again, only the rate obtained during the initial period of the reaction was taken in account. All the experimental data points collected were fit to a curve that should be passing through the origin. However, a time interval of 3 min (NMR signal adjust) was required prior to performing the measurements. From this curve (conversion versus time plot), initial rates were determined.

From the data shown in Fig. 4, a linear plot of ln (reaction rate) calculated in terms of mmol palmitic acid consumed/1800 s of reaction versus ln [catalyst concentration], expressed in mmol of the catalysts, the order of reaction was determined with regard to catalyst concentration (Fig. 5).

The slope of the curve for the initial reaction rate versus concentration, which was approximately 0.57 ($R^2 = 0.994$) for the *p*-sulfonic acid calix[4]arene, and 1.0 for sulfuric acid, confirms the higher efficiency of sulfuric acid (Fig. 5). It should be emphasized that the measured ΔE values should not necessarily agree with the order of catalyst concentration; this observed dependence suggests that in the range concentration studied, reactions in the presence of calix[4]arene are less sensible to high catalyst loadings. Contrarily, when utilizing sulfuric acid as the catalyst, an increase in its concentration more significantly increases the initial reaction. This effect can be attributed to the absence of diffusion problems, which are caused by higher steric volume of *p*-sulfonic acid calix[4]arene.

3.3. Thermodynamic studies

When writing the equilibrium constant for the palmitic acid esterification reaction with deuterated methanol (K_{eq}) some considerations must be made. Firstly, it should be considered that it does not depend on methanol concentration (due to its excess), and secondly that both water and deuterated methyl palmitate concentrations are equal. Thus, Eq. (2) can be defined as:

$$K_{eq} = [\text{deuterated methyl palmitate}]^2/[\text{palmitic acid}] \qquad (2)$$

Table 2
Values of Gibbs free energy for the *p*-sulfonic acid calix[4]arene and sulfuric acid-catalyzed palmitic acid esterification reactions with deuterated methanol.

Temperature (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})
p-Sulfonic acid calix[4]arene catalyst			
313	−2.0		
318	−3.0		
323	−4.0	+60.6	+0.2
328	−5.0		
333	−6.0		
Sulfuric acid catalyst			
313	−5.9		
318	−6.4		
323	−6.9	+25.4	+0.1
328	−7.4		
333	−7.9		

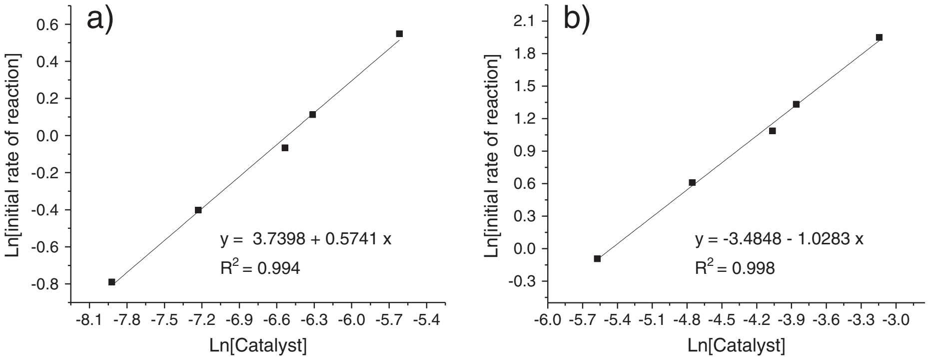

Fig. 6. Linear plots of ln Keq versus 1/T for the palmitic acid esterification reaction with deuterated methanol: a) *p*-sulfonic acid calix[4]arene and b) sulfuric acid.

The initial concentration of palmitic acid was equal to 0.13 mol L^{-1}. Table 2 shows the equilibrium constants calculated for each reaction at the different temperatures studied.

Eq (3) is valid if the enthalpy change of the reaction is assumed to be constant with temperature, and was obtained from the second law of thermodynamic and definition of Gibbs free energy ($\Delta G = -RT \ln Keq$):

$$lnKeq = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \lim_{x \to \infty}. \tag{3}$$

From the data shown in Table 2, it was possible to build the linear plots of ln K_{eq} versus ln 1/T which is presented in Fig. 6, and by using Eq. (3) the respective values of ΔS and ΔH were calculated and displayed in Table 2.

The slope of the curve provides the value of ΔH and the Y axis intercept indicates ΔS. Thus, enthalpy and entropy variations were found to be equal to 60.6 and 0.2 kJ mol^{-1} for *p*-sulfonic acid calix[4]arene-catalyzed reactions, and 25.4 and 0.1 kJ mol^{-1} for sulfuric acid-catalyzed reactions, respectively. Table 2 shows these values as well as the Gibbs free energy obtained for each reaction at the specific reaction temperatures. It is important to note that although entropy variation may be affected by solvent presence, calculations were made taken into account the CD_3OD concentration but only negligible differences were encountered. These kinetic and thermodynamic results suggest that the esterification reactions studied herein are not controlled by the number of protons dissociable present in the catalysts only. Actually the catalyst structure noticeably affected catalyst performance when the reaction parameters of catalyst concentration and reaction temperature are varied.

4. Conclusions

Kinetic studies utilizing in situ ^{1}H NMR spectroscopy showed that the catalysts studied here (i.e. *p*-sulfonic acid calix[4]arene and sulfuric acid) presented a different behavior in the palmitic acid esterification reaction. These catalysts were differently affected when main reaction parameters such as temperature and catalyst concentration are varied. It was found that the activation energy of the *p*-sulfonic acid calix[4]arene-catalyzed esterification reaction is lower than that observed in reactions in the presence of sulfuric acid at catalyst concentrations equal to 0.5 mol%. On the other hand, the dependence of reaction rate on sulfuric acid concentration is higher than on that of *p*-sulfonic acid calix[4]arene (1.0 against 0.57 respectively), in the concentration range of 0.5 to 5.0 mol%. Conversely, ΔG values obtained suggested that this reaction catalyzed by sulfuric acid becomes more spontaneous with increases in temperature than those performed in the presence of the *p*-sulfonic acid calix[4]arene catalyst. Hence, the *p*-sulfonic acid calix[4]arene can be recovered and reused without losing catalytic activity and can be potentially employed as an efficient and environmentally benign catalyst in biodiesel production from FFA esterification reactions.

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