Production of FAME from Acid Oil, a By-product of Vegetable Oil Refining

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ABSTRACT: Simple alkyl FA esters have numerous uses, including serving as biodiesel, a fuel for compression ignition (diesel) engines. The use of acid-catalyzed esterification for the synthesis of FAME from acid oil, a by-product of edible vegetable oil refining that is produced from soapstock, was investigated. Soybean acid oil contained 59.3 wt% FFA, 28.0 wt% TAG, 4.4 wt% DAG, and less than 1% MAG. Maximum esterification occurred at 65°C and 26 h reaction at a molar ratio of total FA/methanol/sulfuric acid of 1:15:1.5. Residual unreacted species under these conditions, as a fraction of their content in unesterified acid oil, were FFA, 6.6%; TAG, 5.8%; and DAG, 2.6%. This corresponds to estimated concentrations of FFA, 3.2%; TAG, 1.3%; and DAG, 0.2%, on a mass basis, in the ester product. In an alternative approach, the acylglycerol species in soapstock were saponified prior to acidulation. High-acid (HA) acid oil made from this saponified soapstock had an FFA content of 96.2 wt% and no detectable TAG, DAG, or MAG. Optimal esterification conditions for HA acid oil at 65°C were a mole ratio of FFA/methanol/acid of 1:1.8:0.17, and 14 h incubation. FAME recovery under these conditions was 89% of theoretical, and the residual unesterified FFA content was approximately 20 mg/g. This was reduced to 3.5 mg/g, below the maximum FFA level allowed for biodiesel, by washing with NaCl, $NaHCO_3$, and $Ca(OH)_2$ solutions. Alternatively, by subjecting the unwashed ester layer to a second esterification, the FFA level was reduced to less than 2 mg/g. The acid value of this material exceeded the maximum allowed for biodiesel, but was reduced to an acceptable value by a brief wash with 0.5 N NaOH.

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Within the past three decades, interest in reducing air pollution and in developing domestic energy sources has triggered research in many countries toward developing nonpetroleum fuels for internal combustion engines. For compression ignition (diesel) engines, it has been shown that the simple alcohol esters of FA (biodiesel) are acceptable alternative diesel fuels. Biodiesel has a higher oxygen content than petroleum diesel, and therefore reduces emissions of particulate matter, hydrocarbons, and carbon monoxide while also reducing sulfur emissions due to a low sulfur content (1,2). Because biodiesel is made from agricultural materials, which are produced *via* photosynthetic carbon fixation, its combustion does not contribute to net atmospheric carbon dioxide levels.

Initial efforts at producing, testing, and using biodiesel employed refined edible vegetable oils and animal fats as feedstocks for fuel synthesis. Simple alkali-catalyzed transesterification technology (3) is efficient at esterifying the acylglycerol-linked FA of such feedstocks and is employed in making these fuels. More recently, methods have been developed to produce FAME from cheaper, less refined lipid feedstocks such as spent restaurant grease. In addition to acylglycerols, these can contain substantial levels of FFA and other nonglyceride materials (4–6). Biodiesel synthesis from these feedstocks can be accomplished by alkaline catalysis. In this case, an excess of alkali is required, because the FFA, which are not esterified by this method, are converted to their alkali salts. These can cause difficulties during product washing due to their ready action as emulsifiers. Ultimately, they are removed and discarded. This approach thus involves a loss of potential product, it increases catalyst expenses, and it can entail a disposal cost. Alternatively, a multistep process involving acid-catalyzed esterification of the FFA and alkali-catalyzed transesterification of glyceride-linked FA can be employed to achieve more efficient conversion of heterogenous feedstocks (7). This method can require multiple acid-catalyzed esterification steps to reduce the concentration of FFA to acceptably low levels.

In addition to waste greases, other lipid-rich materials of relatively low value are potential sources of biodiesel. Among these is soapstock (SS), a coproduct of the refining of edible vegetable oils. SS is an alkaline emulsion composed largely of water, acylglycerols, phosphoacylglycerols, and FFA. It is generated at a rate of about 6% of the input of unrefined oil entering a refining operation, amounting to approximately 100 million lb (45 million kg) annually in the United States (Flider, F., personal communication). Although there are some industrial uses for SS, demand fluctuates and the economic return to the producer is not high, leading to interest in developing new uses for this material.

We previously reported methods for producing FAME from soybean SS (8) and established that the performance and emissions properties of the resulting fuel were comparable to those of commercial biodiesel from refined soybean oil (9). This method for FAME synthesis employs sequential alkali-catalyzed saponification, water removal, and acid-catalyzed esterification to produce esters from both the lipid-linked and

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the FFA of SS. The method achieves the efficient production of high-purity biodiesel, but substantial amounts of solid sodium sulfate are generated as a by-product. Disposal of this waste material could be cumbersome and expensive. Therefore, further development of routes for the production of FAME from SS and similar complex lipid mixtures is needed.

Typical industrial processing of SS often involves an operation termed acidulation, wherein sulfuric acid and steam are employed to achieve partial acid hydrolysis and/or removal of the acyl- and phosphoacylglycerol ester bonds of the starting material. The acidic conditions also protonate the FA salts present, greatly reducing their emulsifying properties. The heavy emulsion typical of SS is thereupon destroyed, resulting in spontaneous separation of two phases, an aqueous and an oil layer. The latter contains FFA, acylglycerols, pigments, and other lipophilic materials, and is termed acid oil. It is used as an animal feed ingredient and as a source of industrial FA. Because acid oil is a readily available item of commerce selling for approximately half the price of refined vegetable oil, we have explored its use as a feedstock for biodiesel production.

EXPERIMENTAL PROCEDURES

Chemicals. Triolein, 1,3-diolein, 1-monoolein, and FFA for use as reference standards in HPLC were obtained from Sigma (St. Louis, MO). Palmitic, stearic, oleic, linoleic, and linolenic acids mixed in amounts proportional to their mass abundance in soybean oil (10) served as the FFA standard. A mixture of FAME, whose composition reflected the FA content of soy oil (RM-1), was the product of Matreya, Inc. (Pleasant Gap, PA). Organic solvents were B&J Brand™ High Purity Grade (Burdick & Jackson, Inc., Muskegon, MI). Sulfuric acid (96.3%) was the product of Mallinckrodt Baker (Paris, KY). *t*-Butyl methyl ether (99+%, A.C.S. reagent grade) was from Aldrich (Milwaukee, WI). Hydrated lime, $Ca(OH)_2$, was obtained from Mississippi Lime Co. (Alton, IL).

Soybean acid oil was produced by standard industrial acidulation methods: Concentrated sulfuric acid was added through inlet valves at the bottom of a tank of SS (25,000 gal, 95,000 L), accompanied by the injection of steam, until the pH reached 2. Steam injection was continued for another 2 h, then discontinued, and the resulting phases were allowed to separate by standing. The resulting clear, dark, upper liquid layer (acid oil) was recovered. To produce high-acid (HA) acid oil, the acyl- and phosphoacyl-FA glyceride ester bonds of SS were alkali-hydrolyzed prior to acidulation: Solid NaOH (approx. 800 lb, 364 kg) was added in 50-lb (23-kg) portions to raise the pH of approximately 1100 gal (4170 L) of SS to 11.6. Steam was injected during this process for a total of 2.5 h. The mixture was then acidulated as described above for SS, with the modification that the process was conducted at pH 1.6.

Optimization of esterification. Sulfuric acid-catalyzed methylation of the FFA in acid oil and HA acid oil was conducted in vigorously shaken glass screw-capped containers at 65°C. The esterification of acid oil was conducted in bottles (4.5 × 4.5 × 15 cm) and that of HA acid oil in tubes (2 cm diam. × 180 mm i.d.). A Central Composite Response Surface design (11) was employed to coordinately investigate the effects and interactions of methanol and sulfuric acid concentrations, and reaction time, on the efficiency of esterification of the free and lipid-linked FA. For HA acid oil, this pattern was augmented with reactions chosen on the basis of a Box–Behnken design (11) to gain further information about the effect of the variables under study on the degree of esterification. Preliminary studies (data not shown) were conducted to focus the statistically designed work in the region of variable space giving the highest ester conversions. Reactions contained 5.00 g of lipid substrate. In the esterification of acid oil, the amounts of methanol tested were 3.0, 4.8, 7.5, 10.2, and 12.0 mL; the amounts of sulfuric acid were 0.03, 0.25, 0.5, 0.80, and 1.0 mL; and reaction times were 15, 18, 22.5, 27, and 30 h. For the esterification of HA acid oil, the amounts of methanol were 0.71, 0.85, 1.07, 1.28, and 1.42 mL; the amounts of sulfuric acid were 0.1, 0.12, 0.15, 0.18, and 0.2 mL; and reaction times were 5, 8, 12.5, 17, and 20 h. Following reaction, amounts of unreacted FFA and acylglycerols were quantitated by HPLC, and are expressed as a percentage of their amounts in acid oil or HA acid oil prior to esterification.

To confirm the identification of reaction conditions optimal for the production of FAME from HA acid oil, we conducted reactions at these conditions using 20.0 g of HA acid oil. The yield of FAME and content of unreacted lipid in the resulting product were determined.

Residual unesterified FFA were removed from the ester product resulting from a single esterfication of HA acid oil by gentle washing (McCormick, R., personal communication) with (i) two sequential 28 vol% batches of 5% (wt/vol) NaCl in tap water, (ii) 20 vol% of 11% (wt/vol) $NaHCO_3$ in tap water, and (iii) 20 vol% of 4.5 M $Ca(OH)_2$ in tap water. After each wash the ester layer was recovered by centrifugation (20 min, 4600 × *g*).

Analytical methods. Acid value was determined according to an AOCS Official Method (12) following the protocol for colored samples and using NaOH rather than KOH as titrant.

Levels of FFA, acylglycerols, and FAME were determined by HPLC using an IB-Sil 5-m CN-BD cyanopropyl-silica column (250 × 4.6 mm; Phenomenex, Torrance, CA) essentially as described (13). Peaks were eluted by a gradient of *t*-butyl methyl ether in hexane/0.4% (vol/vol) acetic acid, detected by ELSD, and quantitated by reference to response curves generated with standards. For the esterifications conducted here, containing roughly 5000 mg of substrate, the minimum detectable levels of TAG, DAG, and MAG were 15–20 mg for each species. Most analytes of interest were detected and quantitated using an HPLC method in which the three eluting liquids were mixed from individual reservoir bottles just prior to entering the column. Retention times (min) were FAME, 4.3–5.0; TAG, 11.0–12.0; FFA, 12.0–12.8; DAG and phytosterols, 15.5–16.3; and MAG, 27.4–28.0. This method gave baseline separation for all species except DAG and phytosterols, which coeluted. To quantify DAG, the glacial acetic acid component was added to 0.4% (vol/vol) to the ether and hexane components before addition to the solvent reservoir bottles. With this solvent system, retention times (min) were FAME, 4.3–5.0; FFA, 5.0–5.2; TAG, 6.7–7.2; phytosterol, 13.8; DAG, 15.0; MAG, 28.8. This method could not be used for all analyses because the differences between the mobilities of FFA and FAME were insufficient to resolve small amounts of the former in the presence of the large amounts of the latter that were present following successful esterification.

With multiple potential reactants (TAG, DAG, etc.) being present, determination of the degree of esterification of each of these species, rather than simple measurement of the amount of ester produced, was judged to be the most informative manner of stating the efficiency of any set of reaction conditions in converting each of the FA-bearing species in acid oil into methyl esters. Thus, the amount of each lipid species remaining unreacted following an esterification reaction was quantitated, with results expressed as the amount of remaining unreacted species, as a percentage of that originally present. A low residual level of unreacted material indicates efficient esterification. The esterification efficiency for any species, expressed as the percentage of material converted to ester, would be [100 – amount, as a percentage of that originally present, of that species that remained unreacted after esterification reaction].

HPLC/MS-EI. During esterification under optimal reaction conditions, the FFA content was reduced so greatly that an unidentified minor constituent that coeluted with FFA in cyanopropyl-silica HPLC substantially interfered with the measurement of FFA. To quantitate FFA in such ester preparations, LC was performed with a Waters HPLC 2690 Separation Module (Waters Co., Milford, MA) connected in series to a Waters Thermabeam Mass Detector (Integrity System). The HPLC portion used a Luna 3-µm C8 column (2 × 100 mm) (Phenomenex, Torrance, CA). Gradient elution, at a flow rate of 0.25 mL/min, was as follows (all concentrations expressed as vol%): water 40%/formic acid 0.1%/acetonitrile 59.9% held for 5 min, raised to formic acid 0.1%/acetonitrile 99.9% at 30 min by a linear acetonitrile gradient and held for 10 min, then brought to water 40%/formic acid 0.1%/acetonitrile 59.9% over 5 min and held for 10 min. The MS–EI detector was set to scan in the mass range of *m/z* 50–600 at 1 scan/s with an ionization energy of 70 eV. Ionization source temperature was 200°C, nebulizer temperature was 63°C, and expansion region temperature was 75°C. The mass of material detected was determined by reference to a linoleic acid standard.

RESULTS AND DISCUSSION

Production of FAME from acid oil. Acid oil is an established item of commerce and a potentially attractive source of FA for biodiesel synthesis. Because alkaline transesterification is ineffective at esterifying FFA, it is by itself an inappropriate method for the high-efficiency production of FAME from acid oil and other high-FFA feedstocks. Both free- and acylglycerol-linked FA are esterified under acidic conditions, though the latter react much more slowly than during alkaline transesterification (3). We therefore investigated the utility of acid catalysis in the synthesis of FAME from acid oil, which contains both FFA and acylglycerols. As received, acid oil contained (by wt) FFA, 59.3%; TAG, 28.0%; DAG, 4.4%; and MAG, less than 1%. Statistical design methods were employed to determine the effects of the methanol and sulfuric acid concentrations and of length of incubation at 65°C on the degree of esterification of the free- and glyceride-linked FA in acid oil. Reaction times were limited to a maximum of 24–26 h because this was felt to be the longest duration suited to an industrial operation. Equations 1–3 present the equations of the best-fit second-order response surfaces describing the relationships between the reaction variables examined and the percentages of remaining unesterified FFA, TAG, and DAG. MAG were not detected following esterification.

$$\mathrm{FFA} = 40.80 - 2.98\,M - 4.35\,A - 1.88\,T + 0.16\,MA + 0.06\,AT + 0.18\,M^2 + 0.48\,A^2 + 0.04\,T^2 \quad [1]$$

$$\mathrm{TAG} = 193.3 - 11.25\,M - 134.2\,A - 7.00\,T + 7.73\,MA + 0.03\,MT + 0.87\,AT + 0.27\,M^2 + 30.06\,A^2 + 0.12\,T^2 \quad [2]$$

$$\mathrm{DAG} = 209.7 - 18.43\,M - 107.9\,A - 6.8\,T + 7.46\,MA + 0.13\,MT + 0.69\,AT + 0.56\,M^2 + 14.33\,A^2 + 0.10\,T^2 \quad [3]$$

where all acylglycerol terms are expressed as wt% of their mass in the unreacted starting material and where M = methanol (mL/5.00 g input acid oil); A = sulfuric acid (mL/5.00 g input acid oil); T = incubation time (h). The R^2 values for these equations were 0.91–0.92, indicating acceptable fits to the experimental data.

Figure 1 shows the dependence of the amounts of residual unesterified FFA, DAG, and TAG on reaction conditions in the esterification of acid oil, derived from Equations 1–3. The data in Figure 1 correspond to a reaction time of 26 h, chosen as a probable maximum practical limit for a reaction of this type on an industrial scale. Seven to 8 mL of methanol/5.00 g acid oil was indicated as giving optimal FFA esterification, with higher residual FFA levels above and below this amount (Fig. 1A). Unreacted FFA levels were lower at the higher sulfuric acid concentrations used (Fig. 1A). A similar optimal methanol level existed for DAG esterification, and was also achieved at the higher sulfuric acid levels used (Fig. 1B). Residual DAG increased noticeably at low methanol concentrations, particularly when accompanied by low sulfuric acid levels (Fig. 1B). For TAG (Fig. 1C), the lowest residual levels were seen in reactions containing the maximum amounts of methanol tested (12 mL/5.00 g acid oil) and between 0.3–0.5 mL of sulfuric acid. Higher amounts of sulfuric acid (1 mL) reduced the amount of methanol at maximum TAG transesterification to 7.5 mL (Fig. 1C).

By combined analysis of Equations 1–3, the reaction conditions 5.00 g acid oil, 7.5 mL methanol, and 1.0 mL sulfuric acid were identified as those giving the minimum combined amount of unreacted acylglycerols and FFA in a 26 h reaction at 65°C. This corresponds to a mole ratio of total FA/methanol/acid of 1:15:1.5. The predicted residual amounts of FFA, TAG, and DAG under these conditions were 6.6, 5.8, and 2.6% of input, respectively. Based on the initial amounts of these materials, this corresponds to concentrations of 3.2, 1.3, and 0.2% (wt basis), respectively, for FFA, TAG, and DAG in the ester product. Relatively long reaction times were required to achieve these levels of unreacted species, and reaction rates were low at the longer incubation times. For example, after 15 h of incubation at optimal conditions, the amount of remaining DAG was about 15% of input (corresponding to a concentration of 1%, mass basis). A further 5 h incubation reduced this value by only one-half. Similar low esterification rates were seen for FFA and TAG at the longer incubation times. This requirement for relatively long incubations is most likely because (i) sulfuric acid is a poor catalyst for the transesterification of acylglycerols (3), and (ii) the process was inhibited by accumulated water released during the esterification of FFA. The requirement for relatively long incubations suggests that this method would be of little value industrially.

Production of FAME from HA acid oil. Despite the use of a 15-fold molar excess of methanol and relatively long incubations, acid-catalyzed esterification was unable to completely eliminate the TAG and DAG in acid oil (above). As an alternative approach, we investigated the possibility that, by completely hydrolyzing the acylglycerols of SS prior to acidulation, an acid oil readily and completely esterified by acid-catalysis could be prepared.

Injection of steam at pH values exceeding 11 quickly and completely saponified SS (data not shown). Acidulation of the resulting material produced an acid oil with an FFA content of 96.2 wt% and no detectable TAG, DAG, or MAG. This resulting HA acid oil was readily esterified by acid catalysis. Through statistical design methods, the relationships between the degree of esterification, the composition of the reaction mixture, and the length of incubation at 65°C were determined. The best-fit second-order response surface to describe the results is given by Equation 4 (terms are as defined above for Eqs. 1–3):

$$\mathrm{FFA} = 37.88 - 38.01\,M - 62.69\,A - 0.42\,T + 15.35\,MA + 0.10\,MT + 0.72\,AT + 12.99\,M^2 + 96.22\,A^2 + 0.01\,T^2 \qquad [4]$$

This equation fit the experimental data well: $R^2 = 0.96$. It can be used to predict that the earliest minimum in remaining unreacted FFA occurs at approximately 12.5 h of reaction. A plot of the relationship of methanol and sulfuric acid concentrations to the level of FFA remaining after 12.5 h esterification, derived from Equation 4, is shown in Figure 2. This response surface indicates the large impact of changes in methanol concentration, and the smaller role of variations in

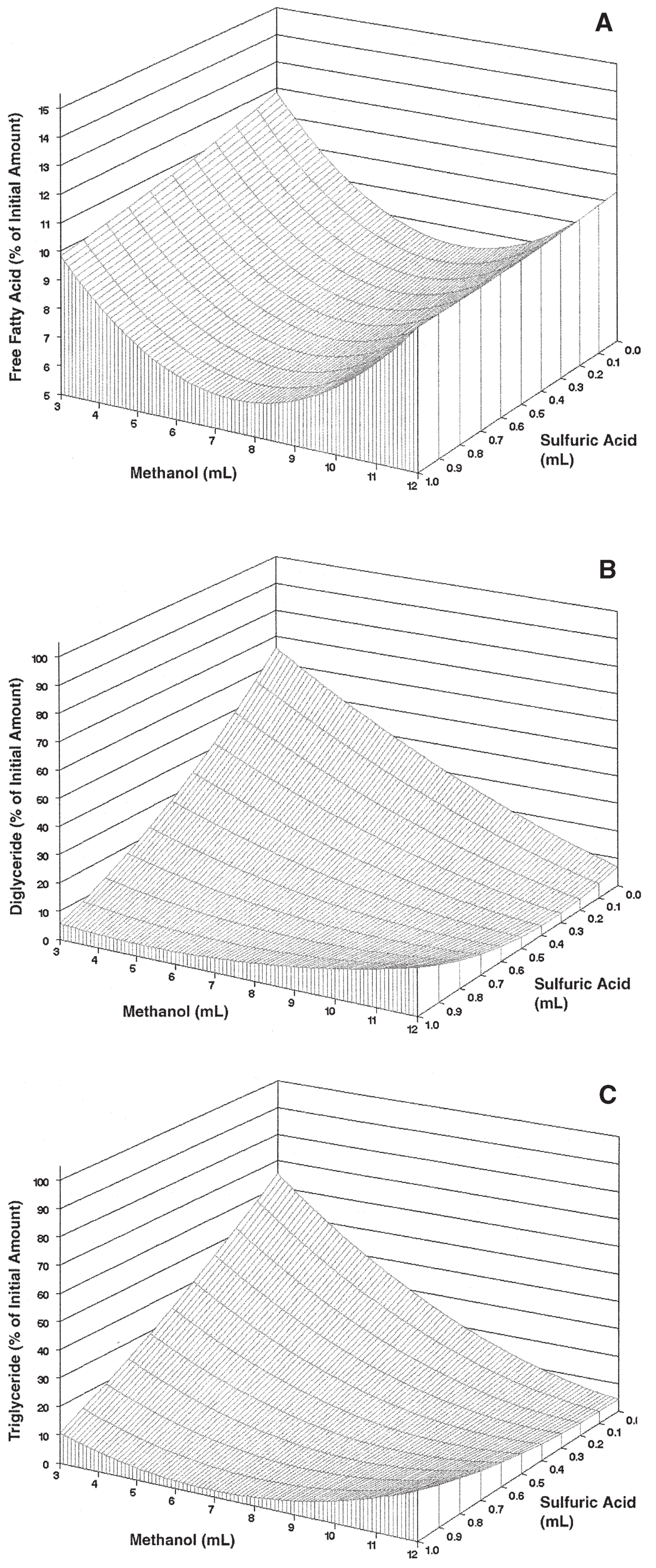

FIG. 1. Predicted response surfaces, calculated from Equations 1–3, for the reduction in substrate lipids during the acid-catalyzed methyl esterification of 5.00 g soybean acid oil for 26 h at 65°C, as a function of the amounts of methanol and sulfuric acid. Extents of esterification are expressed as the percentages of unesterified species remaining relative to their content in unreacted acid oil. (A) FFA, (B) DAG, (C) TAG.

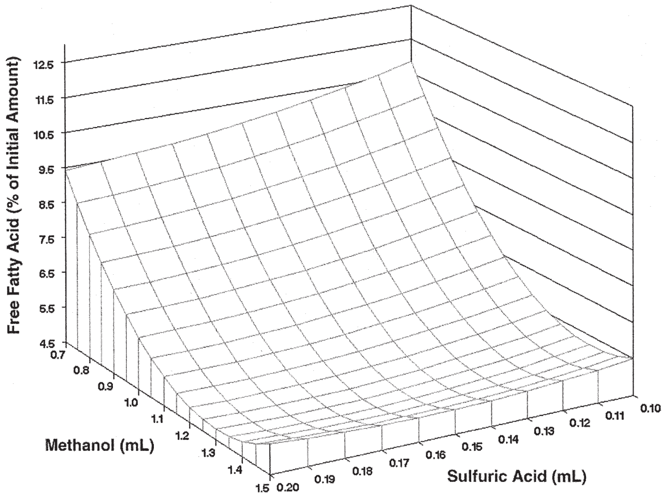

FIG. 2. Response surface, predicted unreacted FFA following the esterification of 5.00 g soybean high-acid acid oil at 65°C and 12.5 h, as a function of the inputs of methanol and sulfuric acid. Calculated from Equation 4.

sulfuric acid concentration, in achieving high-level esterification. The esterification of HA acid oil was initially rapid, with FFA levels quickly falling to less than 10% of original (data not shown). Further reduction proceeded slowly, requiring more than 5 h incubation to reach a minimum. Nonetheless, the length of reaction was substantially shorter than the 26 h required to achieve the same degree of esterification with regular acid oil (above).

A canonical analysis of Equation 4 identified 5.00 g HA acid oil, 1.31 mL methanol, 0.17 mL sulfuric acid, and a reaction time of 14 h at 65°C as the reaction conditions predicted to yield the highest degree of FFA esterification. This represents a molar reactants ratio of FFA/methanol/sulfuric acid of 1:1.8:0.17, superior to the 1:15:1.5 ratio required (above) for the esterification of conventional acid oil. The predicted unreacted FFA level was approximately 5% of input (corresponding to a concentration of approximately 5 wt%, or 50 mg FFA/g). When 20 g of HA acid oil were incubated under these conditions, the yield of FAME was 89% of theoretical. The FFA content of the FAME product was determined by HPLC to be 17 mg/g FAME. This is in acceptable agreement with the approximately 50 mg/g predicted by Equation 4. The FAME product lacked detectable TAG, DAG, and MAG. Phytosterols, water, and unidentified materials made up the remaining matter.

The level of remaining unreacted FFA and acylglycerol is of interest in the context of the use of FAME preparations as engine fuels because these materials affect engine performance and fuel storage stability. For this reason, maximum acceptable levels of these have been established. The Standard Specification for Biodiesel Fuel (14) expresses the maximum FFA level in terms of acid number, with a maximum permissible acid number of 0.80 mg KOH/g of biodiesel. (This corresponds to a maximum allowable acid number of 0.57 mg/g when using NaOH as titrant, as was done here.) Assuming 1:1 stoichiometry in the neutralization of FFA by KOH, this corresponds to an FFA content of 3.91 mg FFA/g soy-derived FAME.

The ester preparation synthesized here from HA acid oil under optimum reaction conditions, containing 17 mg FFA/g, exceeded the maximum allowed FFA levels. A simple protocol involving sequential washing with aqueous solutions of NaCl, $NaHCO_3$, and $Ca(OH)_2$ was implemented to convert the FFA to their calcium salts, which were removed with the aqueous phase of the wash. The resultant washed FAME had 3.5 mg/g FFA, less than the maximum allowed by the acid value specification for biodiesel. The amount of potential FAME lost by such removal (approximately 5% of input) may be acceptable in an industrial-scale esterification operation. In addition, FAME produced from HA acid oil lacked TAG, DAG, and MAG, substances also subject to maximum tolerance specifications in biodiesel (14). The washing protocol has not been optimized; a considerably simpler process might also suffice to reduce the FFA levels in the ester product.

As an alternative to the use of multiple washing steps to remove unreacted FFA from the FAME product, a second esterification reaction was investigated. Water, produced during esterification, is known to inhibit further reaction. After the initial esterification of HA acid oil under optimal reaction conditions, the sample was centrifuged (6000 × *g*). The resulting lower and middle layers, which were water soluble and constituted 15% of the total volume, were removed. The remaining (upper) layer was again subjected to esterification under the optimal conditions for HA acid oil. The product was centrifuged and the water-soluble lower and middle layers removed. Analysis of the resulting FAME by HPLC/MS–EI indicated a maximum FFA content of 0.4 mg/g sample, substantially less than the 3.91 mg/g allowed based on the acid value specifications for biodiesel (14). The acid value of this material was 2.2, exceeding the 0.57 value (NaOH titrant) allowed for biodiesel. This could be due to the presence in the FAME of trace amounts of the sulfuric acid esterification catalyst. By washing for 1 h with one volume of 0.5 N NaOH, the acid value (NaOH) was reduced to 0.36, an acceptable value. Neither the conditions of the second esterification reaction nor of the subsequent NaOH wash were fully optimized. It is possible that an acceptable FFA level could be achieved with substantially smaller amounts of acid and alcohol, and/or with an optimized wash protocol.

HA acid oil is superior to regular acid oil as a feedstock for FAME production because its optimal esterification requires only approximately one-eighth the amount of alcohol and one-ninth the amount of acid, and yields a product acceptably low in FFA and lacking residual acylglycerols.

The approach of saponifying SS to free all glyceride-bound FA for subsequent esterification was also taken in our previous method for FAME synthesis from this feedstock (8). The present method is superior to that procedure in that it does not require an expensive, time-consuming drying of the SS, and does not produce a solid sodium sulfate waste stream. Sodium sulfate is produced in the current method during acidulation of the saponified SS. However, it dissolves readily in the water phase formed during acidulation, and is removed with that phase. Additional attractive features of the method described here are that it can be conducted at ambient pressure and at relatively low temperatures. (In an industrial setting, conducting the reaction at the boiling point, with reflux condensation and recovery of methanol, may be advantageous from an engineering standpoint. This should not compromise the speed and efficiency of the process or the quality of the product.) The method described here may also be effective for the production of FAME from other high-FFA feedstocks.

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REFERENCES

1. Sheehan, J., V. Camobreco, J. Duffield, M. Graboski, and H. Shapouri, Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus, National Renewable Energy Laboratory, Report NREL/SR-580-24089, Golden, CO, 1998.
2. Graboski, M.S., and R.L. McCormick, Combustion of Fat and Vegetable Oil Derived Fuels in Diesel Engines, *Prog. Energy Combust. Sci. 24*:125–164 (1998).
3. Freedman, B., E.H. Pryde, and T.L. Mounts, Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils, *J. Am. Oil Chem. Soc. 61*:1638–1643 (1984).
4. Mittelbach, M., and P. Tritthart, Diesel Fuel Derived from Vegetable Oils, III. Emission Tests Using Methyl Esters of Used Frying Oil, *Ibid. 65*:1185–1187 (1988).
5. McCormick, R.L., M.S. Graboski, T.L. Alleman, and A.M. Herring, Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine, *Environ. Sci. Technol. 35*:1743–1747 (2001).
6. Haas, M.J., G.J. Piazza, and T.A. Foglia, Enzymatic Approaches to the Production of Biodiesel Fuels, in *Lipid Biotechnology*, edited by T.M. Kuo and H.W. Gardner, Marcel Dekker, New York, 2002, pp. 587–598.
7. Canakci, M., and J. Van Gerpen, Biodiesel Production from Oils and Fats with High Free Fatty Acids, *Trans. Am. Soc. Automotive Eng. 44*:1429–1436 (2001).
8. Haas, M. J., S. Bloomer, and K. Scott, Simple, High-Efficiency Synthesis of Fatty Acid Methyl Esters from Soapstock, *J. Am. Oil Chem. Soc. 77*:373–379 (2000).
9. Haas, M.J., K.M. Scott, T.L. Alleman, and R.L. McCormick, Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock, *Energy Fuels, 15*:1207–1212 (2001).
10. Fritz, E., and R.W. Johnson, Raw Materials for Fatty Acids, in *Fatty Acids in Industry. Processes, Properties, Derivatives, Applications,* edited by R.W. Johnson and E. Fritz, Marcel Dekker, New York, 1989, pp. 1–20.
11. Box, G.E.P., W.G. Hunter, and J.S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978.
12. Acid Value, AOCS Official Method Cd 3d-63, Revision of 1999, in *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 5th edn., AOCS Press, Champaign, 1998.
13. Foglia, T.A., and K.C. Jones, Quantitation of Neutral Lipid Mixtures Using High Performance Liquid Chromatography with Light Scattering Detection, *J. Liq. Chromatogr. Rel. Technol. 20*:1829–1838 (1997).
14. Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, Designation D 6751-02, American Society for Testing and Materials, West Conshohocken, PA, 2002.

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