ORIGINAL PAPER

Catalytic Synthesis of Fatty Acid Methyl Esters from Extremely Low Quality Greases

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Abstract Biodiesel (BD) is a renewable fuel for compression ignition engines that is composed of the simple alkyl esters, usually methyl-, of fatty acids (FAME). It is typically produced via base-catalyzed transesterification between refined vegetable oil or animal fat (e.g., soybean oil, tallow) and an alcohol (e.g., methanol). This process can, however, be marginally cost-effective due to the high feedstock and processing costs. It is thus desirable to develop new catalytic routes that can efficiently convert less expensive feedstocks to BD. We report here on the application of a series of diarylammonium based homogeneous and heterogeneous catalysts for converting a particularly low value, low quality lipid, trap grease, to FAME. In the course of a 1-h reaction at 125 °C these catalysts simultaneously esterified the free fatty acids (>90 wt% of the substrate) and transesterified the acylglycerols (<10 wt%) of the feedstock to FAME with greater than 95% overall conversion.

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Introduction

In recent years, considerable attention has been focused on developing environmentally benign and economically feasible processes to produce alkyl fatty acid methyl esters (FAME) for use as biodiesel (BD). Biodiesel is an alternative to petroleum-based diesel fuel and is most often produced from vegetable oil (i.e., soybean, canola oil) or animal fat in the presence of homogeneous alkali base catalysts (e.g. sodium hydroxide or sodium methoxide). The reaction is typically performed at temperatures from 60 to 80 °C and results in a mixture containing glycerol and FAME. The crude FAME mixture is subsequently separated and purified from glycerol, catalyst and any unreacted materials. Although this technology is currently practiced by multiple producers for the synthesis of approximately 3/4 billion gallons (2.8 billion liters) of BD annually in the United States and substantially greater volumes than this on a global basis, there is continuing interest in improving the efficiency, substrate flexibility, ease of use, and economics of the process. The efficiency of the current technology depends highly on the quality of the feedstocks, reaction temperature, catalyst selectivity, and alcohol to feedstock ratio [1, 2]. In addition, although BD has many advantages over diesel fuel including reduced engine emissions, better biodegradability and lubricity, lower flammability and toxicity and a reduced sulfur content, it is generally not yet cost-competitive with petrodiesel in the absence of federal governmental subsidies [3–5].

Improvements in two areas, namely, reduced raw material cost and improved processing efficiency, can help make BD production cost-competitive with petrodiesel products. Progress in attaining economic competitiveness through feedstock choice has been significant as reflected by the use of less-expensive feedstocks such as greases and animal fats or soapstock [6–8]. In 2006, Haas et al. calculated that the use of refined lipids as feedstocks contributed up to 75% of the overall BD costs [9]. Low cost feedstocks typically contain a high percentage of free fatty acids (FFA), which presents significant technical challenges for BD production by means of alkaline transesterification and negatively affects the quality of the produced BD. To utilize the low-cost feedstocks, an acid catalyzed step (esterification) is required to reduce the FFA content to an acceptable level (<1 wt%) followed by base transesterification to convert the glycerides to FAME [10].

However, if homogeneous acid catalysts (e.g., H_2SO_4) are used in the acid pretreatment step, a neutralization step using base is required in order to remove the acid catalyst. This forms salts and necessitates substantial efforts, sometimes involving large quantities of water, to clean up the BD. The disposal of waste water significantly increases BD production costs. To address this issue, solid catalysts including zirconia oxides [11], modified zeolites [12], and acidic resins [13] have been shown to be effective for the synthesis of FAME from high purity lipids.

We also have recently developed a series of solid (i.e., 'heterogeneous') catalysts based on diarylammonium salts for BD production from inexpensive feedstocks using a two-step reaction protocol [14–16]. In this previous work we demonstrated that the FFA in yellow and brown greases can be converted to FAME in the presence of the acid catalyst diphenylammonium triflate salt (DPAT, Fig. 1, 2) and its immobilized counterparts [i.e., Poly-DVB/PVA-OTf (Fig. 1, 3), SBA-15/PVA-OTf (Fig. 1, 4), and MCM-48/PVA-OTf (Fig. 1, 5)]. After removal of these solid acid catalysts via simple filtration the acylglycerols in the resulting pretreated greases, which contained <2 wt% FFA, could be converted to FAME by conventional base-catalyzed transesterification [14–16]. Reactions performed with solid phase (i.e., heterogeneous) catalysts offer the advantage of a cleaner glycerol obtained with less washing,

since the catalysts can be removed by filtration or centrifugation. The solid catalysts are also potentially reusable, which will further reduce the BD production costs.

To improve the process efficiency further, we wished to combine the acid-catalyzed esterification and the transesterification steps into a single operation. It is known that acids can catalyze the transesterification step, albeit at generally lower rates. In this work, we report the one-step synthesis of BD from trap grease, the lowest quality feedstock, using the acid catalysts based on diarylammonium salts (Fig. 1, 2, 3, 4, 5) which were reported previously to be highly active catalysts for converting FFA to FAME [14–16].

Trap greases are presently waste materials of little value and no significant commercial use. Obtained from lipid interceptors ('grease traps') installed in the waste disposal lines exiting restaurants and other food preparation facilities, they are composed of the lipids contained in food preparation or processing waste streams as well as wastewater, food contaminants, inorganic contaminants, occasional solid organic wastes, and more [17]. Trap greases vary in their FFA contents over time and space, and can exhibit FFA levels as high as 100%. Their conversion to biodiesel is complicated by the need to achieve high levels of conversion of both their FFA and acylglycerol fractions to methyl esters, and to do this in the presence of a myriad of contaminating materials. Although approaches have been reported for the conversion of trap greases to BD, achieving this conversion in an economically affordable manner is a challenge that has prevented general usage of trap greases for biodiesel production to date [18, 19]. We show here that trap greases with >90 wt% FFA and <10 wt% acylglycerols can be converted to FAME at 125 °C in 1 h. The synthesized FAME was analyzed in detail by Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), and Nuclear Magnetic Resonance (NMR).

Materials and Methods

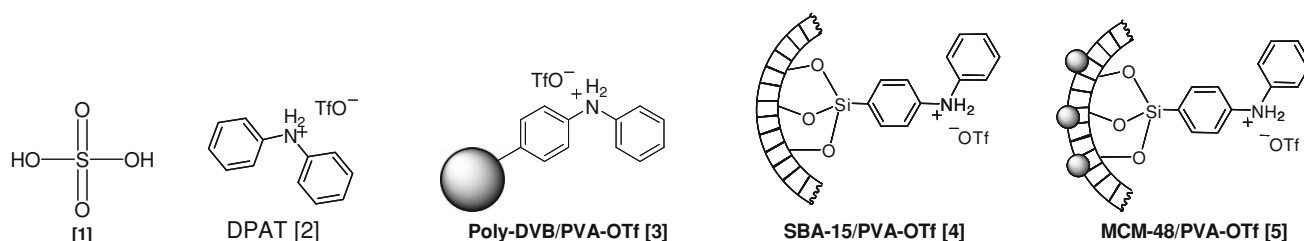4-Bromostyrene was purchased from Alfa Aesar (Ward Hill, MA, USA). Cetyltrimethylammonium bromide,

Fig. 1 Chemical structures of the homogeneous and heterogeneous catalysts

ammonium hydroxide, tetraethyl orthosilicate, 4-(trimethoxysilyl)aniline, sodium *tert*-butoxide, bromobenzene, toluene, methanol, trifluoromethanesulfonic acid, dichloromethane and 1,4-dioxane were purchased from Aldrich Chemical (Milwaukee, WI, USA). Tris[dibenzylideneacetone]dipalladium chloroform and (*R*,*S*)-2,20-bis(diphenylphosphino)-1,10-binaphthalene were obtained from Strem Chemical (Newburyport, MA, USA). These reagents were used to synthesize the catalysts according to detailed protocols previously reported [14–16]. Trap greases from two locations, San Francisco, CA ('SF') and Atlanta, GA ('ATL') were studied here. Both were dewatered before use, and had final water contents of 0.45 and 0.27%, respectively, as determined by automated Karl Fischer Titration (Metrohm, Riverview, FL, USA).

A portion of the ATL material was distilled to remove contaminating material, with the material condensed in the boiling point region between 150 and 250 °C at a distillation pressure of 1,000 microns (designated 'distilled ATL') used in this study. The intention was to remove residual water and minor impurities that could potentially poison the catalysts' activity. The water content of distilled ATL was 0.18% as determined by automated Karl Fischer Titration. Trap greases were gifts from BlackGold Biofuels (Philadelphia, PA, USA). All other reagents used were of the highest purity available from commercial suppliers.

Experimental Procedures

For determination of fatty acid contents, trap grease lipids were converted to fatty acid methyl esters by methanolysis. The mixtures were then analyzed by GC on a Hewlett Packard (HP) Model 5890 GC (currently Agilent Technologies, Santa Clara CA, USA) equipped with Supelco (Bellefonte Park, PA, USA) 24022 capillary column (30 m × 0.25 mm × 0.2μm) and an HP 7673 flame ionization detector. The column was developed with helium carrier gas set at a linear velocity of 22.3 cm/s at 170 °C. The injector and detector temperatures were 220 and 250 °C, respectively. The oven temperature profile was: initial temperature 170 °C, hold for 10 min; ramp at 2.0 °C/min to 200 °C; hold for 10 min.

Conversion of trap greases to FAME with acid catalysts was generally performed according to procedures described previously [14–16]. The catalysts were prepared according to our previously published procedures [14–16], which also included determination of the molar density of active sites on the catalyst. In general, 200 mg of trap grease was incubated with catalyst and methanol, the molar amounts chosen relative to the FFA content of the grease, in conical 4-mL vials with Teflon lined caps. The reactions were magnetically stirred (300 rpm) on a RCT basic IKAMAG®

heating block reactor equipped with a temperature controller (Wilmington, NC, USA). Unless noted, reactions were conducted at 125 °C for 1 h. trap grease (200 mg), methanol (454 mg, 14.2 mmol, 20 equiv relative to FFA), and 2.5 mol% catalyst **3** relative to FFA (0.68 mmol/g of DPAT, 24 mg, 16 mmol) were placed in a conical 4 mL vial with a Teflon cap. The reaction went from dark brown to a light brown/yellow color. Following reaction, the mixtures were allowed to cool to room temperature and transferred with hexane (∼10 mL) into a 50 mL single neck round bottom flask. The solvents were evaporated under reduced pressure while heating at 40 °C. The residue was dried under vacuum for 1/2 h at 45 °C. Then, 3 μL of crude product was pipetted into a 2-mL vial and approximately 1.5 mL of hexane was added. The solution was passed over a 0.45 μm nylon syringe filter (National Scientific, Rockwood, TN, USA) to remove the solid catalyst and the lipid contents of the filtrate were determined.

The contents of FFA, FAME, TG and diacylglycerol (DG) in samples were determined by HPLC using a Chrompack (Raritan, NJ, USA) Spherisorb cyano column (100 × 3.0 mm) eluted by gradients of hexane and methyl *tert*-butyl ether with 0.4% acetic acid in both solvents at a flow rate of 0.43 mL/min [14–16]. Analytes were detected with an evaporative light scattering detector. Data obtained were compared against standard curves.

To determine the isolated yield of the FAME products from these trap greases, the crude FAME products were purified by flash column chromatography. The crude FAME product used was from a reaction performed with 2 mol% catalyst **2**, SF trap grease (200 mg), and 20 equiv of MeOH at 125 °C for 1 h. After esterification/transesterification reaction, the crude product was isolated by simply removing the methanol solvent by evaporation and then dried under vacuum (∼5 Torr) at room temperature for 2 h. 1.37 g of crude product was loaded on a column packed with silica gel, 230–400 Mesh, Grade 60 (Fisher Scientific, Suwanee, GA, USA) that was then developed with hexane:ethyl acetate (90:10 v/v). Three fractions (A, B, C) were obtained from the column. After evaporation of solvents these yielded residues weighing: A (1.11 g), B (0.041 g), and C (0.014 g), with a total weight of 1.165 g and accounting for 94.2% of the material applied to the column. All products were analyzed by HPLC. A 200 MHz NMR was also used to further confirm the FAME products obtained after reactions.

To determine the time course of the conversion of trap grease lipids to FAME, several tubes containing SF grease (449 mg), methanol (410 mg, 12.8 mmol, 20 equiv to FFA), and 5 mol% catalyst **3** relative to FFA (0.68 mmol/g of DPAT 47 mg, 32 mmol) were reacted at 125 °C with stirring for time intervals from 5 to 60 min. The crude products were prepared and characterized by HPLC as described above [14–16].

Results and Discussion

Three types of trap grease (distilled and non-distilled materials collected in Atlanta, GA, USA and non-distilled material originating in San Francisco, CA, USA) were investigated. The fatty acid compositions of trap greases studied here are listed in Table 1. All greases contained high proportions of C_{16} and C_{18} fatty acids, which accounted for 85–91% of the identifiable fatty acids in the samples. Despite their varied geographic origins, they had remarkably similar fatty acid compositions. The ATL substrate underwent distillation with the intention to remove the residual water and minor impurities that could potentially poison the catalysts' activity.

Table 2 lists the results obtained for the esterification/transesterification of distilled ATL trap grease with various acid catalysts at 125 °C for 1 h. The starting distilled ATL trap grease contained 93.7 wt% FFA and 6.3 wt% TG (entry 1). DG was not observed in this feedstock. All reactions were compared to catalysis by liquid sulfuric acid, H_2SO_4 (Fig. 1, 1), as it is a common catalyst for BD synthesis. At 0.5 and 2.0 mol% of catalyst loadings and 20 equiv of MeOH, catalyst 1 simultaneously catalyzed the esterification of FFA and transesterification of TG in the distilled ATL sample to FAME at conversions between 95 and 98%. Interestingly, the results obtained using the diphenylammonium triflate salt (DPAT, Fig. 1, 2), under similar conditions, seemed to give slightly better conversions (Table 2, entries 4–9), but the difference was only about ±2% which is within experimental errors. Similar results were observed with SF grease, as discussed below. Attempts to run the reactions for a longer reaction time (ca. 2 h) with catalyst 2 and 5 equiv of MeOH, however,

did not lead to significant improvements in FAME yields (entry 10). The results obtained with the DPAT catalyst and the distilled substrate are very encouraging.

Similar to H_2SO_4, catalyst 2 is also soluble in the FAME product (i.e., a homogeneous catalyst), and can not be easily removed from the reaction mixture. For this reason we grafted the diphenylammonium salt (PVA-OTf) onto three different supports, i.e., a highly porous highly cross-linked organic polymer (poly-DVB) and two types of mesoporous silicas (SBA-15 and MCM-48) (Fig. 1, 3, 4, 5). These solid catalysts are very effective in simultaneously catalyzing the esterification of FFA and transesterification of glycerides in trap grease materials. As shown in Table 2, entries 11–13, reactions performed with 2.0–3.0 mol% Poly-DVB/PVA-OTf (Fig. 1, 3) and 20 equiv of MeOH, gave a FAME conversion of around 95%. When we increased the catalyst loading to 5.0 mol% and used various amounts of methanol (10 and 20 equiv), the FAME conversion did not improve (Table 2, entries 14 & 15). These results showed that 2.0 mol% catalyst 3 and 20 equiv of MeOH are the best conditions for obtaining a high yield of FAME product. Entries 16–19 in Table 2 list the reactions performed with catalysts SBA-15/PVA-OTf (Fig. 1, 4) & MCM-48/PVA-OTf (Fig. 1, 5). Interestingly, these catalysts gave slightly higher conversions than the polymer supported catalyst 3 and performed as well as the homogeneous catalysts 1 and 2.

The results obtained from the distilled ATL trap grease are extremely encouraging, and we proceeded to test if these catalysts can work effectively with impure substrates. We examined two different types of non-distilled greases, i.e., ATL and SF. Table 3 (entry 1) lists the lipid class compositions of the starting ATL sample, which contained FFA (82.9 wt%), TG (11 wt%), and DG (6.1 wt%). Entries 2–4 list the reactions performed with the homogeneous catalysts 1 and 2. Both systems gave very high catalytic activity, but the FAME conversions were slightly different for catalyst 1 compared to the results obtained with the distilled ATL substrate. However, this difference could be due to experimental errors as they are within ±2%. On the other hand, all three solid catalysts did not work as well as the homogeneous catalysts with these substrates. Higher catalyst loadings were required in order to achieve high FAME conversions. For instance, when the reaction was performed with 2.0 mol% catalyst 3 and 20 equiv of methanol, only 61.2% of the ATL fatty acids were converted to FAME (Table 3, entry 5). However, when the reaction was run with 5.0 mol% of catalyst 3 and 20 equiv of MeOH, a >30% increase in FAME yield was observed (Table 3, entry 6). For catalyst 4, even when the reaction was performed with 5.0 mol% and 20 equiv of methanol, the reaction still did not work well. Only about 70% of the waste grease was converted to FAME (Table 3, entry 7).

Table 1 Fatty acid compositions of trap greases studied here, as determined by gas chromatography

Fatty acid	GC % Compositions		
	Distilled ATL	ATL	SF
C10:0	0.41	0.41	0.34
C12:0	0.30	0.74	0.75
C14:0	1.32	2.82	2.83
C14:1 (c & t)	0.32	0.39	0.64
C16:0	17.9	23.1	31.2
C16:1 (c & t)	1.46	1.84	2.14
C18:0	11.3	10.2	12.7
C18:1 (c & t)	41.1	43.8	32.3
C18:2 (c/t; c/c; t/t)	13.4	11.3	11.5
C18:3 (c/c/c; c/t/c; c/t/t; t/t/t & more)	1.29	0.93	1.03
C20:0	0.19	0.40	1.03
Unknown	11.1	4.07	3.54

Results are expressed as mass% GC response. c = cis; t = trans

Table 2 Conversion of distilled ATL trap grease to FAME using various catalysts

Entry	Catalyst (mol%)	MeOH (equiv)[a]	HPLC wt% Composition			% conv.[b]
			FAME	FFA	TG	
1	No catalyst	–	0	93.7	6.3	–
2	**1** (0.5)	20	94.9	5.1	0	94.6
3	**1** (2.0)	20	98	2	0	97.9
4	**2** (0.5)	5	96.2	3.8	0	95.9
5	**2** (0.5)	10	97.4	2.6	0	97.2
6	**2** (0.5)	20	97.1	2.9	0	96.9
7	**2** (1.0)	20	98.3	1.7	0	98.2
8	**2** (2.0)	5	96.3	3.7	0	96.1
9	**2** (2.0)	20	97.4	2.6	0	97.2
10	**2** (2.0)[c]	5	96.5	3.5	0	96.3
11	**3** (2.0)	20	96.5	3.5	0	96.3
12	**3** (2.5)	20	96.1	3.8	0	95.9
13	**3** (3.0)	20	95.2	4.8	0	94.9
14	**3** (5.0)	10	95.1	4.9	0	94.8
15	**3** (5.0)	20	95.5	4.5	0	95.2
16	**4** (2.5)	20	97.7	2.3	0	97.5
17	**4** (5.0)	20	98	2	0	97.9
18	**5** (2.5)	20	97.5	2.5	0	97.3
19	**5** (5.0)	20	97.6	2.4	0	97.4

All reactions were performed at 125 °C for 1 h. Results were analyzed by HPLC

[a] Number of equivalents relative to the FFA that is present in greases

[b] Percent conversion = $100 \times (FFA^i - FFA^f)/FFA^i$; where FFA^i = initial wt% FFA in the grease and FFA^f = final wt% in the esterified grease

[c] Reaction was performed at 125 °C for 2 h

MeOH methanol, *FAME* fatty acid methyl ester, *FFA* free fatty acid, *TG* triglyceride

When the reaction was performed with 5 mol% catalyst **5** and 20 equiv of methanol, the FAME conversion was 96.4% (Table 3, entry 8).

As for the SF trap grease, its lipid profile (Table 4, entry 1) consisted of FFA (90.3 wt%), TG (6.0 wt%), and DG (3.7 wt%), a slightly higher FFA content and lower concentration of glycerides compared to the ATL material. For this substrate, it is interesting to observe that not all of the TG was converted to FAME, particularly for catalysts **1** and **3**. Entries 2–5 in Table 4 list the results obtained with catalyst **1** at 0.5 and 2.0 mol% loadings and various equivalents of methanol (5–20). The highest FAME synthesis (95.2%) was obtained when the reaction was performed at 2.0 mol% catalyst and 20 equiv of methanol. Entries 5–7 and 12–14 show two sets of triplicate reactions, to examine the reproducibility of the reactions. The results show experimental errors within ±2%. Catalyst **2** also showed high activity with this substrate. As shown in Table 4, entries 8–11, the reactions were performed with 2 mol% of this catalyst and various amounts of methanol (5–20 equiv). High conversion, essentially 97.0%

conversion was obtained with 10 equiv of methanol (Table 4, entry 10). Increasing the methanol content of the reaction to 20 equiv did not increase the conversion (Table 4, entry 11). In addition, when the reaction (i.e., 2 mol% **2** and 5 equiv of MeOH) was conducted for 2 h rather than the standard 1 h, very little additional FAME production was observed (Table 4, entry 8 vs. 9).

Interestingly, we found that when the reaction was carried out using SF trap grease with 2.0 mol% of the solid catalyst **3** and 20 equiv of MeOH, a much higher conversion (92%, Table 4, entry 12) was obtained compared to the 61% conversion achieved with ATL trap grease under similar conditions (Table 3, entry 5). We also examined the SF substrate with 2.5 mol% **3** and 20 equiv of MeOH, but no increase in conversion was obtained (Table 4, entry 15). Thus, higher catalyst loading, i.e., 5.0 mol% catalyst **3,** was used to see whether the reactions could be improved (Table 4, entries 16–19). The best results, greater than 97% conversion, were obtained when the reaction was performed with at least 15 equiv of methanol (Table 4, entries 18, 19). Catalyst **4**, which did not work well with the ATL

Table 3 Conversion of ATL trap grease to FAME using various acid catalysts

Entry	Catalyst (mol%)	MeOH (equiv)[a]	HPLC wt% Composition				% conv.[b]
			FAME	FFA	TG	DG	
1	No catalyst	–	0	82.9	11.0	6.1	–
2	**1** (0.5)	20	94.0	6.0	0	0	92.8
3	**2** (2.0)	5	97.9	2.1	0	0	97.5
4	**2** (2.0)	20	97.7	2.3	0	0	97.2
5	**3** (2.0)	20	67.8	32.2	0	0	61.2
6	**3** (5.0)	20	96.3	3.7	0	0	95.5
7	**4** (5.0)	20	75.9	24.1	0	0	70.9
8	**5** (5.0)	20	97.0	3.0	0	0	96.4

All reactions were performed at 125 °C for 1 h. Results were analyzed by HPLC

[a] Number of equivalents relative to the FFA that is present in greases

[b] Percent conversion $= 100 \times (FFA^i - FFA^f)/FFA^i$; where $FFA^i =$ initial wt% FFA in the grease and $FFA^f =$ final wt% in the esterified grease

MeOH methanol, *FAME* fatty acid methyl ester, *FFA* free fatty acid, *TG* triglyceride, *DG* diglyceride

grease substrate, but did work with its distilled analogue, was also a poor catalyst for the production of FAME from SF grease, failing to achieve greater than 83% FAME production with this substrate (Table 4, entries 20 & 21). We speculate that the impurities in the non-distilled trap greases can block the channels in the SBA-15 system, which run only in one dimension through the carrier, and thus prevent the access of substrate to the catalytic sites. Catalyst **5**, on the other hand, worked extremely well with this feedstock (Table 4, entries 22 & 23), presumably due to its 3-D channel structures.

Overall, the results obtained show that these catalysts are extremely robust and they are not easily deactivated by unknown impurities in the non-distilled substrates. To further determine the level of impurities in the trap greases, the crude FAME product was purified by silica gel chromatography column. This allowed determination of the mass contribution of the lipid products before and after reactions, and determination of the degree of non-lipid materials in the trap greases. From the silica gel column chromatography studies, three fractions (A, B, C) were isolated with a total mass recovery of 94.2%, and analyzed by HPLC. The results showed that fraction A was exclusively the FAME product, B corresponded exclusively to TG, and fraction C contained FFA and DG. These results corresponded to data obtained when the crude FAME product was analyzed by HPLC which also indicated that the main components of the material were FAME, FFA, TG and DG. Fraction A was also analyzed by proton NMR and the NMR spectra confirmed the HPLC results (data not shown). The results confirmed that the trap greases used in this study contained mainly acylglycerol and FFA.

We have also carried out time dependent conversion curves in order to gain more insight into the activities of the different catalysts. Figure 2 shows the conversion curves for FAME production from SF trap grease by four different catalysts, **1**, **2**, **3** and **5**. The time dependent curves were obtained for reactions carried out at 125 °C with 20 equiv of methanol. As expected based on the data shown above, both homogeneous catalysts **1** and **2** gave the best conversions even with only 2 mol% catalyst loading. 5 mol% catalyst loadings were used for both solid catalysts (**3** and **5**). By comparing the two solid catalysts, it appears that in the first 20 min, catalyst **3** gave a much higher conversion than catalyst **5**, but after about 30 min, both catalysts reached >90% conversion. Overall, all catalysts showed very high activities under these conditions as all the reactions were essentially finished in about 30 min.

Despite the high degrees of esterification of the FFA pool that were observed under some reaction conditions, the post-esterification free fatty acid contents exceeded the maximum amount allowed by the acid value specification of ASTM D6751, the accepted standard for biodiesel quality [20]. Further optimization of the use of the new catalysts studied here, a topic beyond the scope of the present work, may achieve acceptably high degrees of esterification of these residual FFAs.

To prevent vaporization of the methanol reactant (boiling point: 64.7 °C) at the 125 °C temperature of the reactions reported here, it was necessary to conduct the work in a pressurized vessel. However, the reaction conditions were not extreme, and fell well within the range routinely practiced in industry. Because of this higher reaction temperature, however, the capital and perhaps operational expenses of biodiesel production with the catalysts described here would probably exceed those of biodiesel production by today's conventional technology, which operates near ambient pressures and temperatures.

Table 4 Conversion of SF trap grease to FAME using various acid catalysts

Entry	Catalyst (mol%)	MeOH (equiv)[a]	HPLC wt% Composition				
			FAME	FFA	TG	DG	% conv.[b]
1	No catalyst	–	0	90.3	6.0	3.7	–
2	**1** (0.5)	20	90.5	9.5	0	0	89.5
3	**1** (2.0)	5	94.1	3.4	2.5	0	96.2
4	**1** (2.0)	10	94.0	3.7	2.3	0	95.9
5	**1** (2.0)[c]	20	95.2	2.1	2.7	0	97.7
6	**1** (2.0)[c]	20	95.2	2.1	2.7	0	97.7
7	**1** (2.0)[c]	20	95.1	2.2	2.7	0	97.6
8	**2** (2.0)	5	94.7	5.3	0	0	94.1
9	**2** (2.0)[d]	5	93.4	3.7	2.9	0	96.0
10	**2** (2.0)	10	94.5	2.7	2.7	0	96.6
11	**2** (2.0)	20	94.8	2.4	2.8	0	97.3
12	**3** (2.0)[e]	20	90.3	7.2	2.5	0	92.0
13	**3** (2.0)[e]	20	92.1	5.6	2.3	0	93.8
14	**3** (2.0)[e]	20	90.3	7.2	2.5	0	92.0
15	**3** (2.5)	20	93.0	7.0	0	0	92.2
16	**3** (5.0)	5	23.5	74	2.2	0	17.7
17	**3** (5.0)	10	75.4	23	1.9	0	74.9
18	**3** (5.0)	15	95.3	2.4	2.3	0	97.3
19	**3** (5.0)	20	95.8	2.0	2.2	0	97.8
20	**4** (5.0)	15	84.3	16	0	0	82.5
21	**4** (5.0)	20	83.0	17	0	0	81.2
22	**5** (5.0)	15	95.2	4.8	0	0	94.7
23	**5** (5.0)	20	98.2	1.8	0	0	98.0

All reactions were performed at 125 °C for 1 h. Results were analyzed by HPLC

[a] Number of equivalents relative to the FFA that is present in greases

[b] Percent conversion = $100 \times (FFA^i - FFA^f)/FFA^i$; where FFA^i = initial wt% FFA in the grease and FFA^f = final wt% in the esterified grease

[c] Mean % conversion is 97.7 ± 0.071 for three replicates

[d] Reaction performed at 125 °C for 2 h. [e]Mean % conversion is 92.6 ± 1.04. For three replicates

MeOH methanol, *FAME* fatty acid methyl ester, *FFA* free fatty acid, *TG* triglyceride, *DG* diglyceride
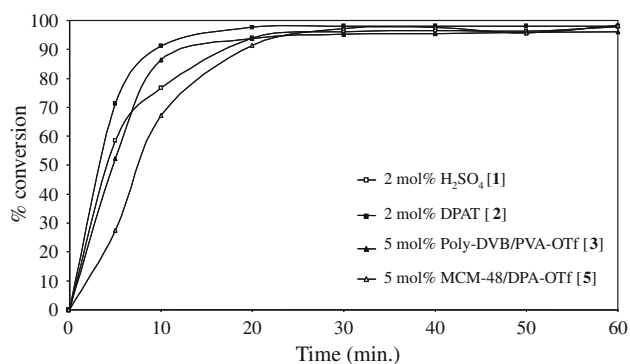

Fig. 2 SF trap grease to FAME conversion curves for different catalyst loading. All reactions were performed with non-distilled SF trap grease and 20 equiv methanol at 125 °C

However, the use of a low cost feedstock, such as those described here, can allow the economical use of somewhat more expensive conversion technologies.

Conclusions

We have successfully demonstrated that homogeneous and heterogeneous catalysts based on diarylammonium salts can convert the FFA and acylglycerols in trap greases to FAME at high degrees of conversion in a single reaction. These catalysts are highly active for esterification of FFA and transesterification of acylglycerols in waste lipids. These results show promising research directions toward the production of BD from inexpensive feedstocks. We will

focus future studies on evaluating the physical properties of the fatty acid methyl ester products derived from these waste materials.

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