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ORIGINAL PAPER

Esterification of Fatty Acids in Greases to Fatty Acid Methyl Esters with Highly Active Diphenylamine Salts

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Abstract Diphenylamine sulfate (DPAS) and diphenylamine hydrochloride (DPACl) salts were found to be highly active catalysts for esterification and substantial transesterification of inexpensive greases to fatty acid methyl esters (FAME). In the presence of catalytic amounts of DPAS or DPACl and excess methanol, the free fatty acids as well as the acylglycerols in waste greases were converted to FAME at 125 °C within 1 h. Although the DPAS and DPACl catalysts were found to have similar catalytic activities to their parent liquid acids (i.e., sulfuric and hydrochloric acids) the diphenylammonium salts are much easier to work with than concentrated liquid acids.

Keywords Biodiesel · Diphenylamine hydrochloride · Diphenylamine sulfate · Esterification · Fatty acid methyl esters · Transesterification · Trap grease · Yellow grease

Introduction

For over a century, society has been strongly dependant on petroleum products. Chemical technologies have thus been designed and optimized to operate on petroleum-based fossil fuels and chemical feedstocks. For the past decade, the consequences of this societal choice have become increasingly clear and raised concerns regarding undesirable impacts on the environment. It is therefore important to develop alternate sources for the energy and chemical feedstocks that are presently obtained from petroleum products.

Efforts here targeted the development of alternative catalysts that enable commercially-preferred processes for the production of biodiesel, i.e., fatty acid methyl esters (FAME), from available, low-cost feedstocks. These feedstocks, however, contain free fatty acids (FFA) that can form soaps when used as a feedstock with the base catalysts typically employed in biodiesel production via triacylglycerol transesterification. This problem can be eliminated if acid catalysts are used to esterify the FFA. For instance, Banavali et al. [1] reported the esterification of FFA with polymeric heterogeneous catalysts that could convert the FFA (from 1 to 100 wt% in the feedstock) to their corresponding methyl esters in quantitative yields. Kim et al. [2] reported a class of zirconia supported metal oxide catalysts that could achieve high degrees of conversion of the FFA in yellow and trap greases to FAME. More recently, Corro et al. [3] reported an interesting process in which the FFA in *Jatropha curcas* crude oil was esterified to FAME in the presence of ZnO/SiO_2 photocatalyst and methanol under UV irradiation. Other interesting acid catalytic systems for the synthesis of biodiesel, including zeolite catalysts such as H-ZSM5 and H-Y [4], lignin-derived carbonaceous material [5], stannic chloride [6], and pumice, a natural volcanic material [7] have also been reported. Our group has also identified a family of homogeneous (Fig. 1a) and heterogeneous catalysts such as diarylammonium triflate salts that are effective at reducing the 12–40 wt% FFA content of waste greases to <1.0 wt% [8–10]. The acylglycerols in the treated greases were then efficiently transesterified by alkali to FAME in a two-step

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sequence. Although these salts are highly effective in converting the FFA in greases to FAME, the triflic acid that they contain is not only expensive but also difficult to work with. To improve the economics of this family of catalysts we have therefore explored the use of alternate acidic catalysts, and describe here FFA esterification with diphenylamine hydrochloride (DPACl) and diphenylamine sulfate (DPAS) (Fig. 1b, c). These salts are commercially available and have been examined by Curtis-Palmer et al. [11] for the transesterification of soybean oil to form FAME using microwave heating. Under these conditions, the yields of FAME were 5–7 % of maximum theoretical [11]. Interestingly, when the reaction was performed under reflux conditions, 43 % conversion was obtained [11]. The objective of our work was to utilize the acidity of these salts to convert the waste greases to FAME products. Although DPAS and DPACl are commercially available, there is very little information reported in the literature on their synthesis, purification and characterization. Therefore we report here the synthesis and characterization of these compounds along with their catalytic properties in FAME production.

Materials and Methods

Materials

Oleic acid (technical grade, 90 %) was purchased from Aldrich Chemical (Milwaukee, WI, USA). The trap grease (93 % FFA), and brown (22 wt%) and yellow (8.6 % FFA) grease were gifts from Blackgold Biofuels (San Francisco, CA, USA) and Kaluzny Bros. Inc. (Joliet, IL, USA), respectively. Methanol, ethyl acetate (EA), hexanes, and methyl *tert*-butyl ether were obtained from Fisher Chemical (Fair Lawn, NJ, USA) and ethanol from Warner-Graham Co. (Cockeysville, MD, USA). Diphenylamine (DPA) and 1.25 M hydrochloric acid (HCl) in methanol were obtained from Sigma Aldrich (St. Louis, MO, USA). Sulfuric acid (H_2SO_4) was acquired from J. T. Baker (Phillipsburg, NJ, USA) and aqueous HCl (12.1 M) from Fisher Chemical (Fair Lawn, NJ, USA). Deuterated dimethyl sulfoxide ($(CD_3)_2SO$) and deuterated methanol (CD_3OD) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). DPACl and DPAS were purchased from City Chemical LLC (West Haven, CT, USA). All materials were used as received.

Analytical Methods

The FAME products were analyzed by high performance liquid chromatography (HPLC) utilizing a Waters Spherisorb S3 CN (Milford, MA, USA) column (150 × 2.0 mm, 3 μm) using a previously reported solvent system with slight modifications[12]. The eluent flow rate was 0.21 mL min^{-1} with a solvent mixture of hexanes (solvent A) and methyl *tert*-butyl ether (solvent B), each with 0.4 % glacial acetic acid. The solvent profile began at 100 % solvent A, changed to 60 % A:40 % B over a period of 6 min, then to 30 % A:70 % B over 4 min with a 2.1 min hold, and returned to 100 % A with a 9.9 min equilibration period for a total run time of 22 min. Previously reported evaporative light scattering detection and calibration methods were used [12].

DPACl and DPAS were characterized by various analytical techniques, including acid number (AV), melting point (MP), nuclear magnetic resonance (NMR), and attenuated total reflectance infrared spectroscopy (ATR-IR). NMR experiments were recorded at 9.4 T using a Varian (Palo Alto, CA, USA) INOVA or at 4.7 T, using a Varian Gemini NMR Spectrometer. All experiments were performed at 25 °C; those acquired at 9.4 T utilized a 5-mm dual broad-band probe, while those at 4.7 T utilized a direct-detect probe. The proton (^1H) spectra were obtained with a 90-degree pulse angle and a 2.5-s relaxation delay. The carbon (^{13}C) spectra had sweep-widths equivalent to ~250 ppm for both spectrometers (30,000 Hz at 100 MHz) and were acquired with a 45-degree pulse angle and a 2-s

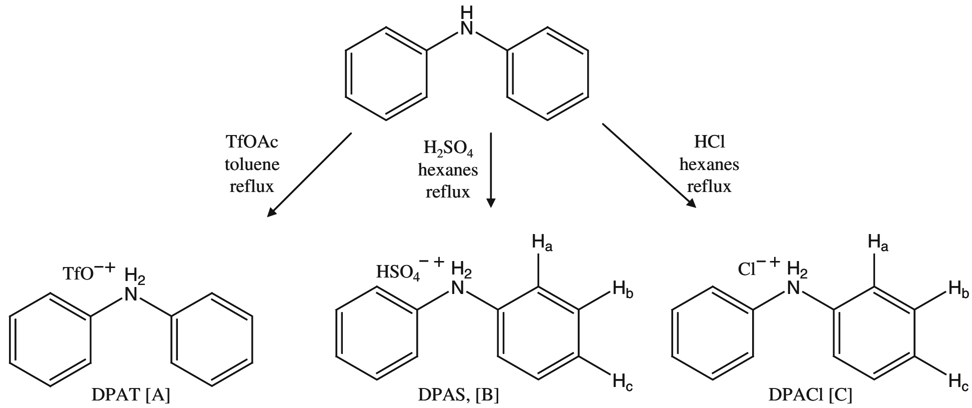

Fig. 1 Synthesis of diphenylamine salts: structure A is diphenylamine triflate (DPAT), structure B is diphenylamine sulfate (DPAS), and structure C is diphenylamine hydrochloride (DPACl)

relaxation delay. The ^{1}H-NMR spectra were referenced to the proton resonance resulting from incomplete deuteration of $(CD_3)_2SO$ (δ 2.50) with TMS (δ 0.00), while the ^{13}C-NMR spectra were similarly referenced to $(CD_3)_2SO$ (δ 39.51). The assignments of the exchangeable protons of the NH and $>NH_2^+$ groups were determined and assigned by addition of small quantities of D_2O. NMR samples were prepared using a freeze–pump–thaw procedure. The liquid was frozen in an acetone/dry ice bath, the air was removed under vacuum, nitrogen was introduced, and the sample was brought to room temperature (RT). This freeze–pump–thaw process was repeated a total of three times for each sample. Infrared spectroscopic analysis was conducted with a Bruker IR equipped with an ATR platinum diamond crystal. The absorbance of each sample (10 mg) was taken at wavelength ranges of 4,000–500 cm^{-1}. Twenty-four scans were collected at a resolution of 4 cm^{-1}.

Synthesis of Diphenylamine Sulfate

In a nitrogen atmosphere, DPA (10 g, 59 mmol) was dissolved in hexanes (200 mL) in a three-neck round-bottom flask fitted with an addition funnel containing H_2SO_4 (6.5 mL, 115 mmol). At RT, H_2SO_4 was added dropwise from the addition funnel to the DPA solution while stirring. The mixture was allowed to react at RT for 48 h. Upon completion, the hexanes were decanted off, and the remaining yellow emulsion was rinsed with EA (~125 mL) to produce a fine off-white solid crude product (DPAS). The solid was vacuum filtered using a Büchner funnel with a 90-mm Grade 2 Whatman filter paper (Maidstone, England) to remove EA. The solid was ground using a mortar and pestle and dried in vacuo, resulting in a 91 % yield of crude off-white DPAS. Since the H_2SO_4 used to make this salt complex could also catalyze FFA esterification, the crude DPAS salt was thoroughly purified to ensure that it was free from liquid acid. Crude DPAS was transferred to a 125-mL centrifuge flask with 80 mL EA and stirred for 30 min. The suspension was centrifuged at RT at $4{,}000\times g$ for 10 min, and the liquid phase was decanted. The solid was then mixed for 30 min with 80 mL EA, centrifuged, and drained. This washing process was repeated eight more times followed by one final vacuum filtration with EA wash. This procedure resulted in grey DPAS in 52 % yield. While this method probably removed residual liquid H_2SO_4, we were still concerned that there could be residual acid trapped in the salt. Thus, we developed a recrystallization procedure to purify the crude DPAS. We first dissolved the salt (300 mg, 1.12 mmol) in methanol (0.6 mL) in an 85 °C oil bath. The solution was allowed to cool to RT, after which EA (10 mL) was slowly added to form two distinct layers. The mixture was then placed in a −15 °C freezer for 5 days. The crystals which formed were ground and dried in vacuo to afford purified pale blue DPAS in 65 % yield. ^{1}H NMR ($(CD_3)_2SO$, δ ppm, Fig. 1b): 11.09 (s, $–NH_2^+–$), 7.20 (t, $–CH_b=$), 7.07 (d, $=CH_a–C–N$), and 6.79 (t, $=CH_c–$). ^{13}C NMR ($(CD_3)_2SO$, δ ppm, Fig. 1b): 143.54 (=C–N), 129.34 ($–CH_b=$), 119.82 ($=CH_c–$), and 116.87 ($=CH_a–C–N$).

Synthesis of Diphenylamine Hydrochloride

DPA (1 g, 5.9 mmol) was dissolved in hexanes (20 mL) in a round-bottom flask fitted with an addition funnel containing 12 M aqueous HCl (0.65 mL, 7.8 mmol). At RT, the HCl was added dropwise from the addition funnel to the DPA solution while stirring. The mixture was stirred under nitrogen at RT for ~48 h. As the reaction proceeded, solids precipitated from the hexanes solvent. The solids were then vacuum filtered to remove the liquid and provided 88 % yield of light pink solid, crude DPACl. Crude DPACl was then purified by recrystallization: DPACl (2 g, 9.7 mmol) was dissolved in ethanol (30 mL) in a 60 °C oil bath and, after cooling, EA was slowly added. White solids were formed after chilling for 4 days at −15 °C. The solids were gravity filtered and washed with cold ethanol to afford pale light green pure DPACl in 50 % yield. ^{1}H-NMR ($(CD_3)_2SO$, δ ppm, Fig. 1c): 11.06 (s, $–NH_2^+–$), 7.20 (t, $–CH_b=$), 7.09 (d,$=CH_a–$), and 6.80 (t,$=CH_c–$). ^{13}C NMR ($(CD_3)_2SO$, δ ppm, Fig. 1c): 143.38 (=C–), 129.19 ($–CH_b=$), 119.83 ($=CH_c–$), and 116.90 ($=CH_a–C–N$).

Transesterification and/or Esterification of Fatty Acids

A typical reaction was performed as follows. Pure oil (oleic acid, 2 g, 6.4 mmol) or used grease (yellow and brown greases, 2 g, 0.6 mmol or trap grease, 0.5 g, 1.6 mmol) was reacted with methanol (20 equiv. to FFA in the oil) and catalyst (0.5 mol% to FFA in the oil) in a tightly capped conical vial sealed with Teflon tape with heating and stirring at 125 °C for 1 h. After the reaction, the solution was transferred with hexanes (~2 mL) and dried in vacuo at RT. The resultant oil was filtered with a glass syringe fitted with a 0.45 μm Millipore PTFE filter (Billerica, MA, USA). A small aliquot was diluted with hexanes (1.5 mL) and analyzed by HPLC.

Results and Discussion

Two homogeneous diphenylammonium salts, DPAS and DPACl, were investigated for FAME synthesis. The structures of the salts are shown in Fig. 1b, c. Although the salts are commercially available, there is very little information available regarding their synthesis and characterization. We therefore decided to carry out their synthesis and characterization. As shown in Fig. 1b, DPAS was synthesized in >90 % yields by simply mixing diphenylamine and H_2SO_4 in hexanes for ~48 h. It was found that DPAS could also be synthesized in methanol, but the yields of the desired product were low (~30 %). That the reaction in hexanes resulted in high yields could be due to the low solubility of the product salt in hexanes. As the reaction proceeds, the salt precipitates from the solvent, which helps drive the reaction to afford products. DPACl catalyst could also be made in high yields using a similar procedure (Fig. 1c). It is imperative that the liquid acids are completely removed from the salts, because they can also catalyze esterification of FFA to form the FAME product. Several attempts were made to purify the salts and the most efficient approach involved recrystallization from alcohol. For example, DPAS was first dissolved in hot methanol, followed by the addition of EA to precipitate pure DPAS. The purified salts were characterized thoroughly with analytical techniques including AV, MP, NMR and ATR-IR.

As shown in Table 1, HCl and DPACl gave the expected AV results (Entries 1–2). H_2SO_4 and DPAS on the other hand could be doubly deprotonated, so they gave AVs twice as high as the expected results (Entries 3 and 4). The melting points of DPACl and DPAS corresponded to the results obtained with the commercial products (Entries 2 and 4). These MP are very different from the starting material (DPA), which ranged from 41 to 44 °C (Entry 5).

Figure 2 shows the ATR-IR spectra of DPA, DPAS, and DPACl. As shown in Fig. 2a, the peak at 3381 cm^{-1} corresponded to the strong N–H stretch of DPA. Upon protonation that stretch was no longer observed in the DPAS and DPACl spectra (Fig. 2b, c), which indicated the formation of the salts. New peaks for the DPAS and DPACl salts were observed between 3,000 and 2,000 cm^{-1}.

Table 1 Selected properties of the acid catalysts employed and synthesized

Entry	Material	AV (mg KOH/g)	MP (°C)
1	HCl	560[a]	–
		574[b]	
2	DPACl	277[a]	135–146
		272[b]	133–144[c]
3	H_2SO_4	1,058[a]	–
		572[b]	
4	DPAS	428[a]	135–137
		210[b]	138–141[c]
5	DPA	–	41–44

AV acid value, *MP* melting point, *DPA* diphenylamine, *DPACl* diphenylamine hydrochloride, *DPAS* diphenylamine sulfate

[a] Experimentally determined

[b] Calculated, assuming stoichiometric titration with KOH

[c] For commercial material purchased from City Chemical LLC, West Haven, CT

The NMR spectra for the precursor and salts produced the expected resonances. A broad peak assigned as $>NH_2^+$ was observed in the NMR spectra of the salts and was further downfield when compared to the NH peak in DPA. This is consistent with salt formation.

The activity of DPAS as an esterification and transesterification catalyst using real-world low quality feedstocks was next investigated. Table 2 (Entries 1, 7 and 15) lists the substrate compositions obtained by HPLC. The other entries list the product distributions for DPAS-catalyzed FAME production from oleic acid, yellow, and trap greases, during 1 h reactions at 125 °C. Oleic acid was used as a model feedstock to demonstrate esterification activity of this homogeneous catalyst. A control reaction containing oleic acid, 0.1 mol% H_2SO_4 and 20 equiv. of methanol gave 99 % conversion of oleic acid to methyl oleate (Entry 2). Under similar conditions, the DPAS salt gave only 91 % conversion of oleic acid to methyl oleate (Entry 3). This reaction was repeated to ensure its reproducibility and the standard deviation was ± 0.7 % (Entry 4). However, when the DPAS catalyst loading was increased to 0.5 mol%, a 99 % conversion was obtained (Entry 5). This result is similar to the results obtained with the commercial DPAS (Entry 6). We then carried out experiments with the low-cost feedstocks. Entries 7–17 showed the catalytic activities of H_2SO_4 and DPAS in the esterification and transesterification of yellow grease

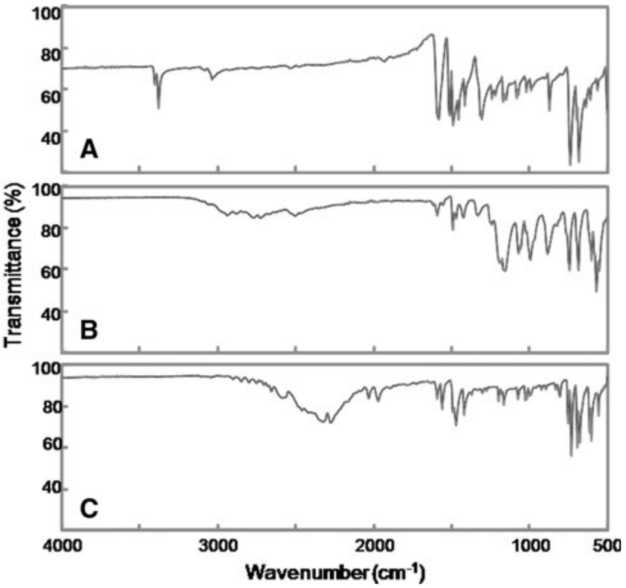

Fig. 2 ATR-IR spectra of diphenylamine salts: spectrum A is diphenylamine, spectrum B is diphenylamine sulfate, and spectrum C is diphenylamine hydrochloride

Table 2 Esterification and/or transesterification of fatty acids with sulfuric acid and diphenylamine sulfate salt

Entry	Catalyst (mol% loading to FFA in oil)	MeOH (equiv. to FFA in oil)[a]	HPLC wt%					FFA conv.[b] (%)
			FAME	FFA	TG	DG	MG	
1	Starting FA—oleic acid	–	–	100	0	0	0	–
2	H_2SO_4 (0.1)	20	99	1.0	0	0	0	99
3	DPAS (0.1)	20	91	9.0	0	0	0	91
4[c]	DPAS (0.1)	20	90	10	0	0	0	90
5	DPAS (0.5)	20	99	1.0	0	0	0	99
6[d]	DPAS (0.5)	20	99	1.0	0	0	0	99
7	Starting FA—yellow grease	–	–	8.6	80	11	0.4	–
8	H_2SO_4 (1.0)	20	21	2.3	52	22	2.7	73
9	H_2SO_4 (2.5)	20	34	0	37	22	7.0	100
10	DPAS (1.0)	20	21	2.6	43	29	4.4	70
11	DPAS (2.5)	20	21	0.8	53	21	4.2	91
12	DPAS (5.0)	20	32	1.0	41	20	7.0	88
13	DPAS (7.5)	20	36	0.1	36	20	7.9	99
14	DPAS (10)	20	39	1.4	35	18	6.6	84
15	Starting FA—trap grease	–	–	93	5.8	1.2	0	–
16	H_2SO_4 (2.5)	20	99	1.0	0	0	0	99
17	DPAS (2.5)	20	99	1.0	0	0	0	99

All reactions were performed at 125 °C for 1 h

FAME fatty acid methyl ester, *FFA* free fatty acid, *TG* triacylglycerol, *DG* diacylglycerol, *MG* monoacylglycerol, *equiv.* equivalent, *DPAS* diphenylamine sulfate

[a] Equivalent to feedstocks

[b] % FFA conversion = $(FFA^i - FFA^f/FFA^i) \times 100$

[c] Replicate of entry 3

[d] DPAS was purchased from City Chemical LLC

containing a mixture of FFA (8.6 wt%) and acylglycerols (91.4 wt%) and trap grease containing a mixture of FFA (93 wt%) and acylglycerols (7.0 wt%). We also evaluated the potassium, sodium, and water content of these waste greases as we were concerned that these metals and water content could poison the catalysts. The analyses showed there were <0.05 % of all these contaminants in the grease. Such low level of these contaminants should not affect the catalysis results. In the presence of 1.0 mol% of H_2SO_4, the FFA content of yellow grease was successfully reduced to 2.3 wt% while the acylglycerols remained high (Entry 8). When the catalyst loading was increased to 2.5 mol%, the FFA level dropped to 0 wt%, however, the acylglycerols level did not seem to change much (Entry 9). Note that we report only the % FFA conversion in all the Tables because we could not simply show the % TG conversion, as the diacylglycerol (DG) and monoacylglycerol (MG) could also be transesterified to FAME. Thus to simplify the information, we only show the glyceride results in terms of before and after reactions. Interestingly, when we performed the reactions with the DPAS catalyst using similar reaction conditions to the sulfuric acid, we obtained very similar results to those using the liquid acid (Entries 10 and 11). We also attempted to completely convert the acylglycerols to FAME with higher catalyst loading; unfortunately, the results showed that only moderate amounts of acylglycerols in yellow grease were converted to FAME (Entries 10–14).

The results with trap grease showed that a FFA conversion of 99 % could be achieved with only 2.5 mol% of H_2SO_4 or DPAS catalyst (Entries 16 and 17). These results are not surprising as the trap grease contained a majority of FFA. These catalysts could thus successfully catalyze both esterification of FFA and transesterification of acylglycerols in a sample composed predominantly of FFA.

Table 3 shows optimization of the amount of methanol needed for this chemistry. Entries 2–5 show that at least 10 equiv. of methanol were needed in order to achieve 99 % esterification of oleic acid. As for the yellow grease, at 2.5 mol% of DPAS, about 10 equiv. of methanol were also needed in order to decrease the FFA and glyceride levels from 8.6 to 1.7 wt% and 91.4 to 75.3 wt %, respectively (Entries 7–9). Increasing the methanol level to 15 equivalents further decreased the FFA level to about 0.7 wt% while the acylglycerols still remained high (Entry 10). As for the trap grease feedstock, similar behaviors were observed (Entries 12–16) although 99 % conversion was not achieved at methanol levels less than a 20-fold molar excess over FFA.

We also examined the performance of the DPACl salt in reactions performed at 125 °C for 1 h (Table 4). The DPACl catalytic activities were compared to 1.25 M methanolic HCl, 3 M methanolic HCl and 12 M aqueous HCl. We chose to compare the DPACl with methanolic HCl because we felt that this acidic solution would give the most appropriate comparison. The results obtained with the

Table 3 Esterification and/or transesterification of fatty acids with diphenylamine sulfate salt with various amounts of methanol

Entry	Catalyst (mol% loading to FFA in oil)	MeOH (equiv. to FFA in oil)^a	HPLC wt%					FFA conv.^{b} (%)
			FAME	FFA	TG	DG	MG	
1	Starting FA—oleic acid	–	–	100	0	0	0	–
2	DPAS (0.5)	1	88	12	0	0	0	88
3	DPAS (0.5)	5	95	5.0	0	0	0	95
4	DPAS (0.5)	7.5	95	5.0	0	0	0	95
5	DPAS (0.5)	10	99	1.0	0	0	0	99
6	Starting FA—yellow grease	–	–	8.6	80	11	0.4	–
7	DPAS (2.5)	1	12	15	41	30	2.0	0
8	DPAS (2.5)	5	20	2.7	51	22	4.3	69
9	DPAS (2.5)	10	23	1.7	49	21	5.3	80
10	DPAS (2.5)	15	25	0.7	46	22	6.3	92
11	Starting FA—trap grease	–	–	93	5.8	1.2	0	–
12	DPAS (2.5)	1	78	22	0	0	0	76
13	DPAS (2.5)	5	91	9.0	0	0	0	90
14	DPAS (2.5)	10	95	5.0	0	0	0	94
15	DPAS (2.5)	15	96	4.0	0	0	0	95
16	DPAS (2.5)	20	99	1.0	0	0	0	99

All reactions were performed at 125 °C for 1 h

FAME fatty acid methyl ester, *FFA* free fatty acid, *TG* triacylglycerol, *DG* diacylglycerol, *MG* monoacylglycerol, *equiv.* equivalent, *DPAS* diphenylamine sulfate

[a] Equivalent to FFA in oils

[b] % FFA conversion = $((\mathrm{FFA}^i - \mathrm{FFA}^f)/\mathrm{FFA}^i) \times 100$

Table 4 Esterification and/or transesterification of fatty acids with hydrochloric acid and diphenylamine hydrochloride salt

Entry	Catalyst (mol% loading to FFA in oil)	MeOH (equiv. to FFA in oil)^a	HPLC wt%					FFA conv.^{b} (%)
			FAME	FFA	TG	DG	MG	
1	Starting FA—oleic acid	–	–	100	0	0	0	–
2	1.25 M HCl (methanolic) (0.5)	20	88	12	0	0	0	88
3	3 M HCl (methanolic) (0.5)	20	89	11	0	0	0	89
4	12 M HCl (aqueous) (0.5)	20	93	7.0	0	0	0	93
5	DPACl (0.5)	20	98	2.0	0	0	0	98
6^c	DPACl (0.5)	20	93	7.0	0	0	0	93
7	Starting FA—brown grease	–	–	22	41	33	4.0	–
8	12 M HCl (aqueous) (5)	20	23	2.3	33	34	7.7	90
9	12 M HCl (aqueous) (10)	20	27	2.0	29	31	11	91
10	DPACl (5)	20	24	2.0	31	34	9.0	91
11	DPACl (10)	20	30	1.0	30	25	14	95
12	Starting FA—trap grease	–	–	93	5.8	1.2	0	–
13	DPACl (0.5)	20	6.9	90	0	0	0	3.0
14	DPACl (2.0)	20	95	5.0	0	0	0	95
15	DPACl (5.0)	20	99	1.0	0	0	0	99

All reactions were performed at 125 °C for 1 h

FAME fatty acid methyl ester, *FFA* free fatty acid, *TG* triacylglycerol, *DG* diacylglycerol, *MG* monoacylglycerol, *equiv.* equivalent, *DPACl* diphenylamine hydrochloride

[a] Equivalent to feedstocks

[b] %conversion = $((\mathrm{FFA}^i - \mathrm{FFA}^f)/\mathrm{FFA}^i) \times 100$

[c] DPACl was purchased from City Chemical LLC

methanolic HCl solution were quite interesting in and of themselves (Entries 2 and 3). We were expecting the results for methanolic HCl to be similar to the results for aqueous HCl (Entry 4). However, in contrast, a reduction in the degree of FAME production from about 93 % to about 88 % was observed with methanolic HCl (these experiments were repeated three times to ensure that these results were real). This could be due to the instability of HCl in methanol, as it has been reported that HCl can react nucleophilicly with methanol to produce chloromethane and water [13]. At any rate, the synthesized DPACl was shown to be as active as aqueous HCl in the esterification of a high quality, free acid feedstock (Entry 5), and of higher activity than methanolic HCl. We also compared our synthesized DPACl with the commercial DPACl. Interestingly, we found that our DPACl (Entry 5) performed better than the commercial DPACl (Entry 6) in the esterification of pure oleic acid and it is difficult to reason why this is the case as we don't know how the commercial DPACl was prepared and purified. We also examined the activity of synthesized DPACl on brown and trap greases. Entries 8–11 show that in reactions performed with brown grease, a mixture of FFA (22 wt%) and acylglycerols (88 wt%), in the presence of 5.0–10 mol% aqueous HCl or DPACl catalyst and 20 equiv. of methanol, the FFA in the brown grease was reduced to as low as 1 wt% while the acylglycerols level remained high. It is worth noting that although the aqueous HCl and DPACl gave similar activities, it is much easier to work with the DPACl solid salt than the liquid HCl. Note that we also examined the reactions with 0.5 and 2.5 mol% DPACl and 20 equiv. of methanol, unfortunately under these conditions the catalyst gave extremely low yields (data not shown).

We found that our DPACl also worked well with trap grease and the results were comparable to the aqueous HCl (data not shown). When that reaction was performed with 0.5 mol% of DPACl and 20 equiv. of methanol, it gave an FFA conversion of only about 3 % (Entry 13). Interestingly, the acylglycerols in this grease were all converted to FAME (Entry 13). Increasing the catalyst loading to 2.0 mol% substantially increased the extent of conversion (Entry 14) and when we used about 5.0 mol% of DPACl, the conversion increased to 99 % (Entry 15). These results indicate that DPACl catalysts are also effective in converting FFA to FAME, and demonstrate some effectiveness in the transesterification of acylglycerols (Table 4, data with trap grease substrate).

We examined the time-dependence of the esterification of oleic acid to methyl oleate using the catalysts. As shown in Fig. 3, the DPAS and DPACl catalysts have esterification activities similar to liquid sulfuric and hydrochloric acid, respectively.

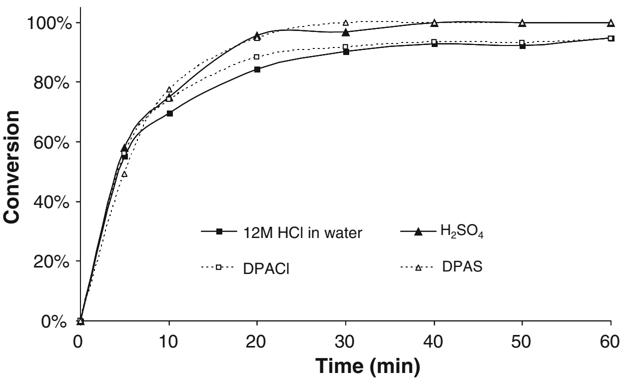

Fig. 3 Time-dependent oleic acid to methyl oleate conversion curves for different catalysts at 0.5 mol% loading. All reactions were performed with 1:20 molar ratio of oleic acid to methanol at 125 °C

Conclusion

Diphenylamine sulfate and diphenylamine hydrochloride salts were found to be active catalysts for both the esterification of free fatty acids and the transesterification of acylglycerols to some extent. They are capable of converting the FFA in the low-cost greases to fatty acid methyl esters in very high yields using a simple one-step reaction. These salts are much easier to handle and thus represent improved catalysts over traditional liquid acids. Future work will focus on immobilizing these salts onto polymer supports to generate heterogeneous systems for FAME production.

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