Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks†

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Recyclable and reusable heterogeneous diarylammonium catalysts are highly effective in catalyzing the esterification of the free fatty acid (FFA) present in greases to methyl esters to reduce the FFA content from 12–40 wt% to 0.5–1 wt%; the resulting ester–glyceride mixture (pretreated grease) could then be readily converted to methyl esters by base-catalyzed transesterification.

Biodiesel (BD) is defined as the simple alkyl esters of fatty acids derived from vegetable oils and animal fats. BD is biodegradable and environmentally benign and is used as an alternative fuel in diesel engines and heating systems. In contrast to fossil fuels, BD does not cause a significant net carbon dioxide increase because the carbon sources are photosynthetically-derived.[1] BD also reduces carbon monoxide and hydrocarbon particulates from diesel engine emissions.[2] In comparison to fuel ethanol, BD production results in a lower release of nitrogen, phosphorus, and pesticide pollutants per net energy gain and is estimated to have a higher energy yield (93%).[1]

Most BD is currently made by alkali-catalyzed transesterification of an oil or fat.[3] The major cost of BD production comes from that of the feedstock.[4] High fatty acid-containing feedstocks such as yellow and brown greases are readily available, inexpensive, and renewable resources and hence are attractive feedstocks for the production of BD.[5] The high free fatty acid (FFA) content of these feedstocks, however, makes it difficult to produce BD using base-catalyzed transesterification.[6] Although grease feedstocks can be used for BD production, an acid pretreatment step is used to reduce the FFA content in the greases to $<$ 1 wt% prior to alkali transesterification. Thus a large amount of base is required to neutralize the acid catalyst remaining in the pretreated greases using this two-step process, which increases the production cost of BD from greases.[7] There thus is a need to develop efficient catalysts that can reduce the FFA content in greases (to $<$ 2 wt%) and be readily removed from the treated greases.[8]

We report here the development of a series of diarylammonium catalysts that are highly effective in catalyzing the esterification of the FFA present in greases (12–40 wt% FFA) to fatty acid methyl esters (FAME). At a catalyst loading of 1–3 mol%, high conversions of FFA to FAME (95–99%) were achieved by treating the greases with 5–20 equiv. of methanol at 95 °C for 2 h. The treated greases had a final FFA content of 0.5–1 wt%. We also demonstrated that the heterogeneous catalysts could be readily recycled and re-used for the esterification of FFA in greases. The resulting ester–glyceride mixture could then be readily converted to esters by base-catalyzed transesterification.

Intrigued by recent reports of diphenylammonium triflate (DPAT) catalyzed esterification reactions,[9] we examined the esterification of oleic acid (OLA) to methyl oleate (MO) in the presence of various diphenylammonium salts as a model reaction for converting the FFA in greases to FAME.§ After 2 h of reactions at 95 °C in the presence of 2 equiv. of MeOH, DPAT (0.5 mol%), diphenylammonium tosylate (0.5 mol%), and diphenylammonium camphorsulfonate (0.5 mol%) gave an OLA to MO conversion of 99%, 93%, and 87%, respectively. Sulfuric acid (**1**) gave a modest OLA to MO conversion of 65% under the same conditions. Since DPAT gave the highest OLA to MO conversion, subsequent work focuses on diarylammonium salts with triflate counterions. Time-dependent conversion curves as shown in Fig. 1 clearly indicated that DPAT not only gives a higher conversion but also is a much more active catalyst than sulfuric acid in esterifying OLA to MO.

We proceeded to examine the efficacy of DPAT in converting the FFA in greases to FAME. Esterification experiments were carried out with greases containing 12, 21, and 40 wt% FFA. As shown in Table 1, for the grease containing 12 wt% FFA, a 2.5 mol% loading of DPAT gave a conversion of FFA to FAME of 94% (in the presence of 10 equiv. of MeOH relative to FFA)

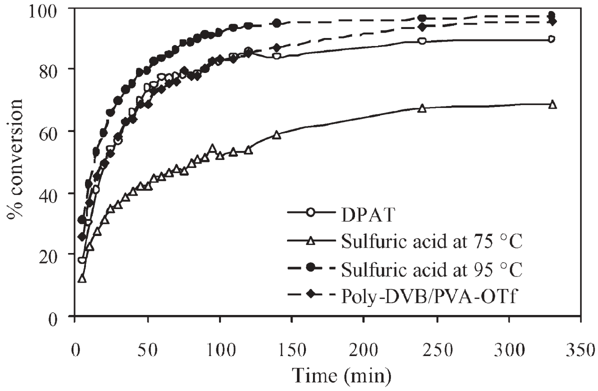

Fig. 1 Time-dependent OLA to MO conversion curves for different catalysts at 1 mol% loading. DPAT and sulfuric acid shown in solid lines were obtained by reacting 1 : 1 molar ratio of OLA and MeOH at 75 °C, while Poly-DVB/PVA-OTf and sulfuric acid shown in dashed lines were obtained by reacting 1 : 10 molar ratio of OLA and MeOH at 95 °C.

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Table 1 Esterification of FFA in greases with sulfuric acid (**1**), DPAT, and Poly-DVB/PVA-OTf (**2**)[a]

Catalyst (mol%)	MeOH (equiv.)[b]	Percent composition by HPLC					% conv. of FFA[c]
		FAME	FFA	TG	DG	MG	
Grease	—	0	12.0	66.0	20.4	1.6	—
1 (2.5)	10	18.3	0.9	54.8	22.4	3.6	93
DPAT (2.5)	10	20.1	0.7	55.7	19.4	4.1	94
2 (2.5)	20	20.3	0.4	52.9	22.6	3.8	97
Grease	—	0	21.4	40.3	30.2	8.9	—
1 (2.5)	10	28.5	2.2	35	27.8	6.5	90
DPAT (2.5)	10	32.3	1.3	32.3	23.9	10.2	94
2 (5)	20	29.3	0.7	39.9	24.3	5.8	97
Grease	—	0	40	31.6	25	3.4	—
1 (3)	20	49.1	1.0	17.5	24.6	7.8	98
DPAT (3)	20	44.8	0.7	28.6	22.1	3.8	98
2 (5)	20	50.6	1.2	24.6	19.2	4.4	97
2 (7.5)	20	63.8	< 0.1	15	15.6	5.5	> 99

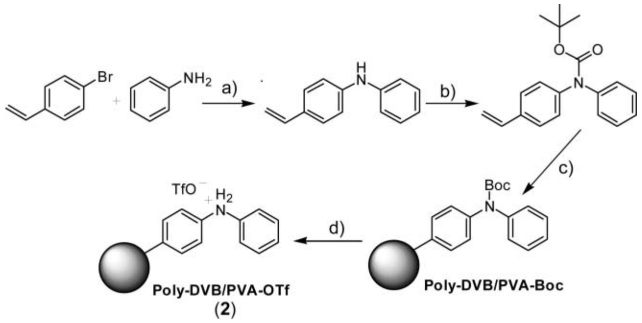
[a] All reactions were performed at 95 °C for 2 h. [b] Number of equivalents relative to FFA that is present in greases. [c] % conversion = 100 × $(FFA^i - FFA^f)/FFA^i$ [i = initial; f = final].

with a reaction time of 2 h at 95 °C.¶ The conversion obtained for DPAT is comparable to the results obtained using **1** under similar conditions (Table 1). A catalyst loading of 2 to 3 mol% was needed to reduce the FFA content down to < 1 wt%. We also examined the esterification of FFA to FAME in the grease that contains 21 wt% FFA using DPAT. With 2.5 mol% of catalyst DPAT, a FFA to FAME conversion of 94% (with 1.3 wt% FFA remaining) was obtained in the presence of 10 equiv. of methanol. As shown in Table 1, excellent conversions of FFA in brown grease (40 wt% FFA) to FAME were obtained at 3 mol% catalyst loading of DPAT and 20 equiv. of MeOH (with 0.7 wt% FFA remaining). These results clearly show the utility of diarylammonium salts in catalyzing the conversion of FFA to FAME in high FFA content greases.

One of the major drawbacks associated with homogeneous catalysts is the difficulty with their recovery and reuse after the catalytic reactions. This becomes a problem when the homogeneous acid catalysts are used for pretreatment of greases because the remaining acid catalysts have to be neutralized with bases before the reaction mixture can be used in subsequent base-catalyzed transesterification reactions. To overcome this drawback, we immobilized the diarylammonium salts onto a porous highly crosslinked organic polymer.

Pd-catalyzed *N*-arylation of aniline with 4-bromostyrene under microwave reaction conditions afforded *N*-phenyl-4-vinylaniline,[10] which was protected with the bulky ^{t}Boc group (Scheme 1). The ^{t}Boc-protected *N*-phenyl-4-vinylaniline was readily co-polymerized with DVB in a 1 : 4 (w/w) ratio with the AIBN free radical initiator in toluene at 80 °C to afford Poly-DVB/PVA-^{t}Boc in a quantitative yield. After Soxhlet extraction of the polymer solid with methanol, the resin was treated with dilute triflic acid (TfOH) to simultaneously remove the ^{t}Boc protecting group and activate the diarylamine to generate the heterogeneous catalyst Poly-DVB/PVA-OTf, **2** (Scheme 1).

The use of toluene porogen and rigid diarylamine comonomer allowed the synthesis of highly porous crosslinked copolymers.[11] Nitrogen sorption isotherms were taken on the porous copolymers to estimate their surface areas and pore sizes. Interestingly, an increase in surface area was observed as the Poly-DVB/PVA-^{t}Boc underwent deprotection and activation steps. Poly-DVB/PVA-^{t}Boc and **2** had surface areas of 850 $m^2 g^{-1}$ and 1000 $m^2 g^{-1}$, respectively (Fig. 2). This result is consistent with a slightly larger size of the ^{t}Boc protection group over the triflate anion. Both Poly-DVB/PVA-^{t}Boc and **2** have wide pore size distributions as they contain micropores, mesopores, and macropores. Given the high porosity and large pore size of the copolymer, the diarylammonium active sites were expected to be readily accessible to the substrates in heterogeneously catalyzed esterification reactions.



Conditions: a) Pd(OAc)$_2$, NaO*t*Bu, BINAP, PhCH$_3$, MW (140 °C); b)Boc$_2$O, DMAP, CH$_3$CN, reflux; c) DVB, AIBN, PhCH$_3$, 80°C; d) 10 equiv TfOH in DCM and dioxane

Scheme 1

With only a 0.5 mol% loading of catalyst **2**, we were able to completely convert OLA to MO by reaction with 5 equiv. of MeOH. The time-dependent OLA to MO conversion curve showed that catalyst **2** is slightly less active than sulfuric acid under the same conditions, presumably owing to slower diffusion of reactants and products through the polymer matrix (see Fig. 1).[12] For the grease containing 12 wt% FFA, only 2.5 mol% catalyst **2** was needed to attain a 97% conversion of FFA to FAME (with the final FFA content of 0.4%) (Table 1). As for the greases with 21 wt% and 40 wt% FFA, 5 mol% catalyst **2** gave an FFA to FAME conversion of 97% in both cases. The results indicate that the porous copolymer catalysts are very effective in converting FFA to FAME in the high FFA content greases.

Since the FFA in greases could be converted to FAME with the heterogeneous diarylammonium catalysts, it was important to show that the pretreated greases could be directly used for FAME

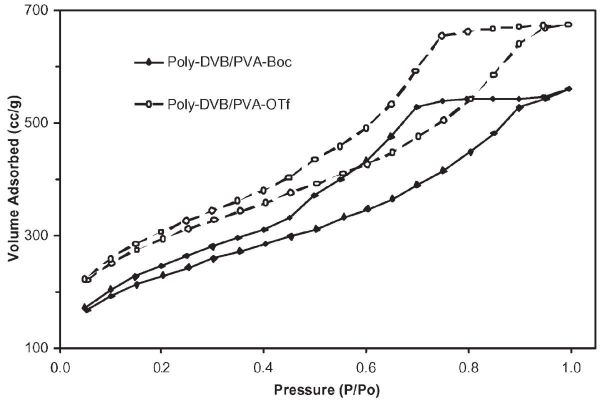


Fig. 2 Nitrogen sorption isotherms of porous copolymers after 6 h of heating at 100 °C.

Table 2 Transesterification of pretreated greases[a]

Sample	MeOH (equiv.)[b]	HPLC wt%				
		FAME	FFA	TG	DG	MG
Pretreated[c]		20.5	0.9	52.4	22.1	4.1
After trans.	4.4	95.9	1.5	2.6	0	0
After trans.	8.5	98.1	1.9	0	0	0
Pretreated[d]		18.4	0.9	57.1	20.2	3.4
After trans.	7.2	90.6	1.3	6.1	2.0	0
After trans.	11.2	98.6	1.4	0	0	0
Pretreated[e]		24.2	0.7	54.9	15.6	4.6
After trans.[e]	3	99.0	1.0	0	0	0

[a] All the transesterification reactions were run with 0.3 wt% NaOMe catalyst at 50 °C for 2 h. [b] Numbers of equiv. of MeOH were calculated relative to the equivalent moles of FFA in pretreated greases. [c] The pretreated grease was vacuum dried to remove water and MeOH from the pretreatment (esterification) step. [d] Catalyst **2** was removed from the pretreated greases by centrifugation, *i.e.*, methanol and water carried over from the esterification step were not removed from the pretreated greases. [e] Reaction was performed at 50 g scale and catalyst **2** was removed from the pretreated greases by centrifugation and the liquid was transferred into a separatory funnel. Two phases were observed and the bottom layer was drained and used for transesterification reaction.

production *via* well-established base-catalyzed transesterification processes. As shown in Table 2, catalyst **2** reduced the FFA content of the grease from 12 wt% (initial) to 0.9 wt% (after pretreatment). After removal of the solid catalyst **2** by simple filtration (and removal of volatile solvents), this pretreated grease was subjected to base-catalyzed transesterification. In the presence of 0.3 wt% sodium methoxide catalyst, between 4.4 and 8.5 equiv. of methanol (relative to FFA equivalents in the grease) were needed to completely convert all of the glycerides in the grease to FAME at 50 °C for 2 h. The final mixture contained > 98 wt% FAME and < 2 wt% FFA. About half of the residual FFA is carried over from the pretreated grease. We also examined the transesterification reactions using pretreated greases containing methanol and water from the pretreatment (esterification) step. In these experiments, the solid catalyst **2** was removed from the pretreated grease by centrifugation. For the pretreated grease with 1.0 wt% final FFA content, transesterification with 11.2 equiv. of MeOH (relative to FFA equivalents in the grease) in the presence of 0.3 wt% sodium methoxide catalyst gave the final FAME content of 98.6 wt% (with a final FFA content of 1.4 wt% and no residual glycerides). Interestingly, when the lipid mixture was separated from the methanol/water layer (by decantation), only 3 additional equiv. of MeOH were needed to achieve complete conversion of the glycerides to FAME.

The solid catalyst **2** recovered from the esterification reaction was no longer active for subsequent reactions, presumably as a result of deactivation by impurities present in the greases. Interestingly, the recovered solid could be re-activated by treating with 0.1 M TfOH in dioxane (5 equiv.). After reactivation with TfOH, **2** was active for at least three rounds of esterification reactions, reducing the FFA content to 1.4 wt%, 1.0 wt%, and 1.6 wt% from the 12 wt% FFA containing grease.

In summary, we have successfully demonstrated the utility of diarylammonium catalysts in esterifying the FFA in greases to FAME and in reducing the FFA content in greases to < 1%. We have also incorporated these diarylammonium catalysts into insoluble porous polymers *via* free radical initiated polymerization. The immobilized diphenylammonium triflate catalysts were nearly as effective as their homogeneous counterparts in reducing the FFA content in greases. The heterogeneous diarylammonium catalysts were readily removed from the treated greases, and re-activated for subsequent reactions. The pretreated greases were converted to FAME in up to 99% yield in subsequent base-catalyzed transesterification reactions. The two step process represents a promising alternative approach for the production of BD from readily available, low-cost, high FFA-containing feedstocks.

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Notes and references

§ *Esterification of oleic acid.* A mixture of OLA (90%, 100 mg, 0.35 mmol), methanol (230 mg, 7.1 mmol), and DPAT (1.1 mg, 3.5 μmol) was mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2 h. The reaction mixture went from colorless to a dark red color. The mixture was allowed to cool to r.t. and ~ 5 mL of hexane were added to transfer the mixture into a 25 mL one neck round bottom flask. The solvents were evaporated under reduced pressure and the crude product analyzed by GC and HPLC. For time-dependent conversion studies, a small aliquot of reaction mixture was removed from the reaction vessel after a set period of time and analyzed by GC to determine the percent conversion.

¶ *Esterification of FFA in greases using diarylammonium catalysts.* A mixture of grease (12 wt% FFA, 1 g, 0.43 mmol based on the FFA content), methanol (180 mg, 5.6 mmol), and DPAT (1.8 mg, 5.8 μmol) was mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2 h. The reaction went from light yellow to a dark brown color. The mixture was allowed to cool to r.t. and transferred with hexane (~ 5 mL) into a 25 mL one neck round bottom flask. The solvents were evaporated under reduced pressure. 10 μL of crude product were pipetted into a 2 mL vial and ~ 1.5 mL of hexane were added. The mixture was passed through a syringe filter and analyzed by HPLC using a published procedure.[13]

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