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Diphenylammonium salt catalysts for microwave assisted triglyceride transesterification of corn and soybean oil for biodiesel production

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ABSTRACT

Diphenylammonium salts as catalysts for triglyceride transesterification have been investigated. Catalysts studied, such as diphenylammonium mesylate, were able to catalyze the transesterification process. Open atmosphere reactions and microwave-assisted reactions are considered and compared. Additionally, the study helps substantiate the advantage of microwave-assisted technology in organic synthesis.

With the emergence of green chemistry initiatives, the scientific community has been left much of the responsibility to change the way a large amount of science is executed. The global scientific community has worked together in developing new and improved synthetic methods for everyday large-scale processes that people take for granted. The confines of the laboratory have been expanded as contemporary scientists now place themselves as environmental conservators of the future. The scientific community has strived to both introduce and apply alternative resources to replace currently existing resources, such as petroleum-based fuels, which are becoming increasingly scarce in our world. One potential alternative to fossil fuels is biodiesel, an equivalent to diesel, however derived from renewable biological sources.[1] Biodiesel (methyl ester) production from *pongamia pinnata* oil,[2] canola oil,[3] olive oil,[4] and rapeseed oil[5] has already been investigated and shown to be a promising alternative to petroleum-based diesel fuels.

The use of ionic catalysts to promote the transesterification of vegetable oils is currently under investigation. The use of DPA catalysts seems practical for this process especially since they have been used to catalyze various polyesterification reactions.[6] Additionally, diphenylammonium triflate has been shown to be a promising catalyst for the esterification of carboxylic acids and for the transesterification of carboxylic esters.[7] Our work has successfully shown that certain DPA salts can be viable catalysts for microwave-assisted transesterification. Structures of the specific catalysts studied are shown in Figure 1.

Vegetable oil may be converted into methyl esters using both acid and base catalysis. A key complication with the base-catalyzed process is soap formation. Water and free fatty acids can cause soap formation, consume catalyst, and reduce catalyst effectiveness. These all point towards a lower conversion to biofuel.[8] These free fatty acids and water need to be removed prior to a base-catalyzed process, thus causing this process to involve more steps and time. Utilizing an acidic catalyst, however, remedies the issue of soap formation since free fatty acids are additionally converted into methyl esters, leading to an overall higher yield. Thus, investigations into acid-catalyzed transesterification are most appropriate.

First, potential catalysts were synthesized and characterized utilizing ^{1}H NMR spectroscopy. Varying amounts of the catalyst were then added to a fixed amount of a particular vegetable oil (2.00 g) and methanol (5.00 g), which served as the solvent. The contents of each vessel were then subjected to microwave heating. All microwave reactions occurred in sealed GlassChem 20 vessels containing a stir bar, placed onto a turntable, and heated with a programmable CEM corp. Mars® System™ scientific microwave. The microwave was programmed to run at 100% power and hold an entered reaction temperature, typically 140–150 °C for a specific amount of time (10–20 min). Additionally, traditional open atmosphere reactions were performed using a sand bath to provide a constant reflux temperature of 65 °C. Reaction times for reflux varied from 2.5 to 24 h. Scheme 1 illustrates a typical reaction.

Once separated, the product was lastly analyzed using an Anasazi EFT-60 NMR spectrometer equipped with NUTS spectra processing software. To quantitate yields, the following relation[9] was utilized to determine the percent conversion to methyl esters:

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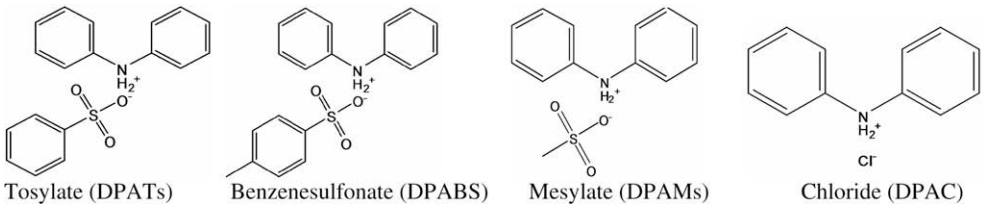
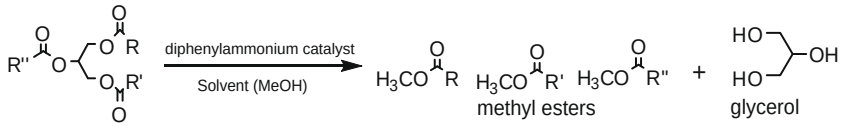


Figure 1. Diphenylammonium (DPA) catalysts considered.



Scheme 1. The general reaction for transesterification of a triglyceride.

$$C_{ME} = \frac{5 * I_{ME}}{(5 * I_{ME}) + (9 * I_{TAG})} * 100$$

where I_{ME} is the integration value of the methyl ester peak and I_{TAG} is the integration value of the triglyceride peak. Thus ideally, that is, for a complete conversion of vegetable oil to biodiesel (methyl ester), one should observe both a strong singlet at approximately 3.6 ppm and the absence of multiplets from 4.0 to 4.4 ppm.

The results indicate that catalysts based on DPA can indeed catalyze the transesterification of corn and soybean oil. Since the work compares microwave technology to traditional heating, an optimal range for all reactions was also approximated. It appeared that 20 min was the optimal microwave reaction time since decreasing the hold time only reduced yields. Both 10 and 15 min microwave reaction times generally proved to be inadequate while 17.5 min seemed to be the threshold, giving an appreciable yield of biodiesel (>80%). With traditional heating, substantial yields of methyl esters were only produced on overnight reflux. Comparing entries 1 and 2 in Table 1 help illustrate the efficiency of microwave-assisted technology compared with traditional reflux. As evidence of this, note that with traditional reflux at 150 min, the yield was only approximately 15% while 20 min under microwave conditions produced approximately 100% yield of methyl ester. Somewhat anomalous results (see entries 17–19 in Table 1) were found using DPAC, with the overnight reflux producing a higher yield than obtained using microwave heating. Earlier research within our group found a similar result using tetraethylammonium iodide as the catalyst, with higher conversion observed with reflux than in the microwave. With the iodide-based catalyst, a purple hue developed in the open atmosphere reaction, signaling the air oxidation of iodide to I_2, which has been shown to be an effective catalyst in transesterification.[10] It is possible that a similar phenomenon is occurring with the chloride counter ion.

Table 1
Representative results using DPA catalysts[a,b]

Entry	Reaction type	Catalyst	Mol %	Oil	Time (min)	Yield (%)
1	Microwave	DPAMs	20	Corn	20	100
2	Reflux	DPAMs	20	Corn	150	15
3	Reflux	DPAMs	20	Corn	1470	100
4	Microwave	DPAMs	10	Corn	20	99
5	Microwave	DPAMs	10	Soybean	20	92
6	Microwave	DPAMs	8	Soybean	20	86
7	Microwave	DPAMs	5	Corn	20	78
8	Microwave	DPAMs	5	Corn	15	53
9	Microwave	DPABS	10	Corn	20	96
10	Microwave	DPABS	9	Soybean	20	97
11	Reflux	DPABS	9	Soybean	1380	95
12	Microwave	DPABS	5	Corn	20	84
13	Microwave	DPATs	10	Corn	20	~100
14	Microwave	DPATs	5	Corn	20	~100
15	Microwave	DPATs	2	Corn	20	43
16	Reflux	DPATs	1	Corn	1440	10
17	Microwave	DPAC	10	Soybean	20	7
18	Microwave	DPAC	8	Soybean	20	5
19	Reflux	DPAC	8	Soybean	1500	43

[a] Both the amount of oil (2.00 g) and amount of methanol (5.00 g) remained fixed.
[b] Microwave reaction temperature 150 °C.

Regarding microwave reactions, noticeable yields of methyl esters were possible only when the temperature was held at approximately 150 °C. Regarding catalyst concentration, appreciable yields were observed when the mol % of the various catalysts was at about 7–8% or greater (Table 1). However, most encouraging results (~100%) were obtained with 5 mol % DPATs. Uncertainty in reported values needs to be considered. It has been estimated that uncertainty associated with the integration software of the spectrometer is believed to cause an approximate standard deviation of ±8–10%. Overall, it is probable that both the electronic nature and the bulkiness of the counter ion play a central role in the catalytic activity of the DPA cation.

Ionic catalysts incorporating DPA as cation are most appropriate due to the weak basicity of diphenylamine. That is, its conjugate acid, DPA cation, is most acidic and was likely the key driving force in the catalysis. Thus, the successes of these DPA ionic catalysts lie primarily in their acidity which assures the triacylglycerol's carbonyl is protonated, which begins the acid-catalyzed transesterification process. Results have indicated that the counter ion does indeed affect catalytic activity. It is likely that the acidity of the DPA proton is the net effect of both the charge–charge interaction and steric hindrance between the ion pair. As shown in Table 1 and Figure 2, the results presented for diphenylammonium chloride (DPAC) show that this particular combination of cation and anion was unable to catalyze the microwave-assisted transesterification process. It can be proposed that having chloride ion as the counter ion greatly enhanced the ion-pairing interaction which suppressed the Bronsted acid properties of the DPA cation. Although this explanation seems practical, this reasoning has yet to be fully investigated.

In conclusion, three diphenylammonium salt catalysts have demonstrated a remarkable ability in catalyzing transesterification of corn and soybean oil into biodiesel. Specifically, DPABS, DPAMs, and DPATs have been identified as suitable Bronsted acid catalysts for this process. Additionally, by utilizing microwave-assisted technology, a more expedient and less wasteful (e.g., water waste typical of reflux) synthesis of methyl ester has been achieved.

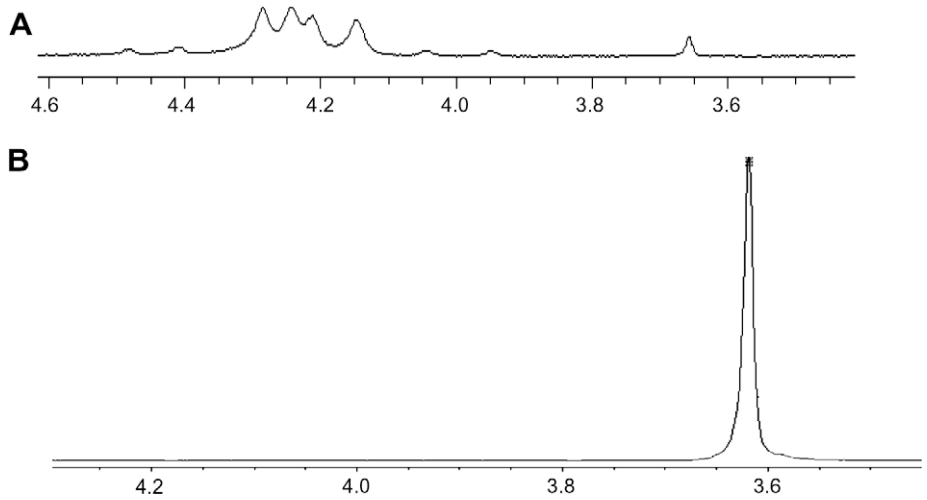


Figure 2. ^{1}H NMR spectra for 10 mol % DPAC (A) and 9 mol % DPABS (B) (δ 3.6 corresponds to methyl ester; δ 4.2 to triglyceride starting material).

Future studies to be performed include the application of these catalysts to other varieties of vegetable oils in addition to waste oils. According to the EPA, restaurants in the United States produce about 300 million gallons of waste oil yearly.[11] Additionally, attempting to recycle the catalysts is necessary to further establish the green aspect of the process. Lastly, quantitatively investigating the effects the counter anion has on the overall transesterification process, more specifically the proton transferring ability of DPA, is also a topic warranting investigation.

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