Enhancing kinetics of biodiesel production using morpholine

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Abstract

This work illustrates morpholine assisted transesterification of crude canola, corn oil and coffee oil (extracted from spent coffee grounds) using NaOH as a homogeneous base catalyst. Addition of morpholine resulted in a two-fold enhancement in kinetics of transesterification. The properties of the biodiesel final product were evaluated by fuel standard tests and the results were compared with ASTM D6751 standards. Biodiesel produced from canola, coffee and corn oils was found to have a high cetane number (52.5–55.1) and good flash point (140 °C).

Keywords: Biodiesel; Transesterification, Coffee oil;

1. Introduction

Biofuels are increasingly becoming a part of the solution in efforts focused on minimizing the use of fossil fuels. Among these, bioethanol and biodiesel have been chosen by governments to be the best possible substitutes [1]. The processes for production of biodiesel are also well established [2]. Among the methods used for the production of biodiesel from conventional feedstock, alkali based transesterification has advantages of both economy and feasibility, and thus is commonly used for large-scale production of biodiesel worldwide [3].

Recent studies have optimized the catalyst concentrations required in traditional transesterification processes such as [4, 5]. The use of liquid organic amines as a homogenous catalyst along with a co-catalyst in supercritical methanolysis has been previously reported [6]. From published literature, it is evident that addition of organic bases and amines lead to faster transesterification rates and higher conversions [7, 8]. The effect of addition of trace amount of KOH as co-catalyst in an organic amine-catalyzed transesterification using tri-ethylamine, di-ethylamine and tert-butylamine, was investigated. It was concluded that, the side reactions to form acyl amines and fatty acid amides were eliminated after the addition of a trace amount of KOH [9]. Using morpholine as a co-catalyst with NaOH in the transesterification of triglycerides is the main focus of this study. Morpholine is an organic compound that has both amine and ether functional groups [10]. Because of the amine, morpholine functions as a base. Due to its low cost and physical properties, morpholine is considered to be a highly versatile industrial chemical with hundreds of applications [10, 11].

Both NaOH and KOH react with oil in a similar manner but previous studies have also proven that the yield of biodiesel is higher with NaOH than with KOH [12] and catalysts, such as NaOH, and NaOCH₃ exhibit superior catalytic activity than KOH for the transesterification of

soybean oil, sunflower oil, and waste frying oil [13]. So, for the current study, NaOH was preferred over KOH.

In the current research, crude canola oil, oil extracted from spent coffee grounds and corn oil were used as low cost feedstocks for biodiesel synthesis. Also, to the best of our knowledge, no catalytic study that focused on the optimization of reaction kinetics for base-catalyzed transesterification of low free fatty acid (FFA) oils using morpholine has been reported. This study investigates morpholine assisted NaOH catalysis, where morpholine acts as a co-catalyst to NaOH, and presents results from the transesterification of three different oils using NaOH-morpholine mixture. The employment of NaOH-morpholine mixture for biodiesel production also allows for a cost minimization and development of low-waste technology.

2. Materials and Methods

Crude canola oil and corn oil were obtained from Viesel fuel LLC, FL, USA. Spent coffee grounds were obtained from a local store. Coffee oil was extracted using a Soxhlet extractor. Methanol, hexane, phenolphthalein, isopropyl alcohol, NaOH and morpholine used in this study were of analytical or better grade purchased from Sigma Aldrich®.

The reaction parameters were the weight ratio of NaOH over morpholine (1:1), the reaction temperature (65 °C), molar ratio of methanol to oil (6:1), and the catalyst to oil weight ratio (1.5%) and reaction time (3 h). The methyl ester yield values and conversions were determined as a function of time via the collection of 2–3 mL samples from the reaction mixture at 15 min intervals. Following completion of reaction, the mixture was centrifuged and the biodiesel obtained was washed with warm water. An Agilent 6890 Gas Chromatography Mass Spectrometry (GC-MS) system was used to analyse the fatty acids and methyl esters produced.

The Eurofins QTA system method was used to test the in-process biodiesel, heavy phase, B100 biodiesel and feedstock. Fuel properties were analyzed using ASTM testing methodologies.

Total acid number (TAN) indicates the level of free fatty acids present in biodiesel according to Equation (1):

$$\text{TAN} = 1.99 \cdot \text{FFA}\% \quad \dots(1)$$

The FFA of the oils and the biodiesel was analyzed using the AOCS official method Ca 5a-40 [14] and the TAN was calculated.

The percent conversion was calculated using the formula given in Equation (2) [15].

$$\text{Conversion}\% = \frac{\text{acid value (initial)} - \text{acid value (final)}}{\text{acid value (initial)}} \times 100 \quad \dots(2)$$

The yield of biodiesel was calculated using Equation (3) [16].

$$\text{Yield}\% = \frac{\text{Total weight of methyl esters}}{\text{Total weight of oil used}} \times 100 \quad \dots(3)$$

3. Results and Discussion

Crude canola, crude coffee and corn oils were determined to have a TAN of 1.3, 6.8 and 1.2 mg KOH/g respectively. To obtain maximum conversion and yield, the reaction parameters were chosen carefully based on previously published literature [5, 17-18]. Catalyst concentration of 1.5% (w/w) was chosen based on the results obtained from various experiments conducted in the lab previously with different types of catalysts.

Figure 1 represents the time dependent concentration profiles of tri-, di-, and mono-glycerides and the amount of bound glycerin remaining in the biodiesel product and, at the end of 180 min, the bound glycerin values dropped below 0.2.

The FFA reduction over 180 min of reaction time is shown in Figure 2. Almost 100% reduction in FFA was observed at the end of 135 min, 180 min and 165 min for canola, coffee and corn oil respectively.

Further, the identities of individual methyl esters formed was confirmed using GC-MS. The methyl ester compositions of the synthesized biodiesel are shown in Table 1. The FAME composition is the most important factor influencing the corresponding properties of biodiesel. Esters with fatty acids such as C14, C16, C18, C18:1, C18:2, C18:3, C20, C22, C24 were identified as well as esters with the fatty acid C20:1 and some odd-numbered fatty acids such as C17, C19, C21 and C23.

Table 1. Compositions of methyl esters found in biodiesel samples from canola, coffee and corn oils.

Percent% →	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C22:1	Rest
Canola oil biodiesel	-	4.45	2.15	60.5	19.1	10.4	0.8	2.6
Coffee oil biodiesel	0.2	31.1	5.3	8.6	46.7	2.2	0.5	5.4
Corn oil biodiesel	1.15	0.25	15.4	2.9	20.2	55.8	-	4.30

The yield of biodiesel obtained from various experiments is given in Table 2. Although, a number of alternative catalysts are currently available and have been adopted for the production of biodiesel fuel from corn, canola and coffee oils [\[17-22\]](#), they are currently not economically feasible for large scale production.

Table 2. Yield of fatty acid methyl esters at the end of the reaction.

	NaOH		NaOH-morpholine	
Biodiesel Feedstock	Reaction time (min)	Yield%	Reaction time (min)	Yield%
Canola	135	98.1	90	98.4
Coffee	180	98.5	90	97.6
Corn	165	97.4	90	98.6

To speed up transesterification reaction, morpholine was used as a co-catalyst to produce biodiesel. It not only saves time and energy but also lowers the chemical dosage. It offers the potential for shorter reaction times leading to less expensive and smaller chemical plants. The relationship of different glycerides reacted with methanol against the reaction time for crude canola, crude coffee and corn oil, when morpholine was added, is shown in Figure 3. The displayed results indicate the key effect of the addition of morpholine on the transesterification process. It was observed that the optimum conversion of the glycerides was obtained at the end of 90 min and the biodiesel produced was of ASTM D6751 grade. The FFA reduction was also monitored and is shown in Figure 4. ASTM D 664 limits the FFA content in B100 biodiesel to 0.25%. In-spec biodiesel was obtained, at the end of 90 min, when morpholine was used as a co-catalyst in the process. The purpose of the addition of morpholine was due to following benefits; it accelerates chemical reaction, makes process cost effective and is not difficult to separate on completion of process. Morpholine is also a neutralizing amine, which could help reduce the corrosive effects of NaOH, thereby reducing capital cost. The NaOH-morpholine concentration for enhanced biodiesel production was 1.5% (w/w). pH of such a solution of morpholine and NaOH was measured to be 11. So, the alkaline property of the composite catalyst is believed to

be maintained. Most of the reactions using morpholine utilize the secondary amine function due to the inertness of the ether group. In alkaline-catalyzed transesterification, the catalyst activity decreases due to its consumption by side reactions. It is assumed that the NaOH prevents the side reactions due to the addition of amine and thus its catalytic activity is effectively utilized. Also, since the boiling point of morpholine is low, it can be recycled along with the excess methanol through vaporization and condensation. As the rate of methoxy ion formation controls the reaction kinetics, fast ionization of methanol to form methoxide ions in the presence of NaOH is advantageous as amines require higher temperatures for the same. As proved by Yao *et al.*, using trace amount of inorganic base also helps control the metal ion concentration in biodiesel, allowing the sample to pass EN14214 standards [9].

It can be seen from Figure 5 that, 0.5 wt% and 0.75 wt% of morpholine, when added as a co-catalyst reduced the reaction time to 90 min. Although the final FFA was in-spec when 0.5 wt% morpholine was used, higher conversion was observed with 0.75wt% morpholine addition. So, 0.75 wt% was chosen to be the optimum concentration. Also, pure morpholine was found to be less effective than NaOH catalyst itself.

Thus, morpholine enhances the kinetics of NaOH catalysis but does not itself act as a catalyst. This may be due to the fact that pK_b value of morpholine is 5.64 when compared to NaOH whose pK_b value is 0.2. So a combination of weak base – strong base catalyzed system is assumed to have accelerated the reaction proceeding. Ethoxy ethyl amine (EEA), a structurally similar compound, was also employed as a catalyst, and no methyl ester formation was observed; thereby confirming that the ability to catalyze transesterification reactions is limited to morpholine.

Transesterification of triglycerides with morpholine-NaOH catalyst system was a pseudo-irreversible first order reaction, and the following Eq. (5) has been fitted to the concentration-time ($[A]$ vs. t) data so as to obtain the kinetic constant:

$$Rate = k \cdot [A] \quad \dots(5)$$

$$[A] = [A_0] \cdot [1 - X] \quad \dots(6)$$

where $[A]$ is the actual concentration (mol L^{-1}) of triglycerides, k is the reaction rate constant and X is the conversion of triglyceride. The obtained reaction rate constant from these equations were 0.024, 0.033, and 0.026 (min^{-1}) for canola, coffee and corn oil feedstock respectively. If the system methanol-oil-morpholine forms a homogeneous liquid phase, mass transfer limitations between methanol and oil can be overcome [7]. Since the binary systems methanol- morpholine, methanol-NaOH and oil-morpholine are miscible, mass transfer limitations can be assumed to be negligible.

A significant fraction of literature addresses mechanisms of biodiesel formation when homogeneous Brönsted basic catalysts (i.e., NaOH, KOH, Na_2CO_3) are employed. The first step is the formation of an alkoxide ion.

The alkoxide ion then attacks the carbon atom of a carbonyl group in a triglyceride molecule to form a tetrahedral intermediate ion. Based on the above mechanism, a reaction mechanism for a morpholine based system is proposed in Figure 6. After being neutralized by the protonated morpholine, the active species is regenerated and thus diglyceride and pure morpholine is formed. The triglycerides, diglycerides and monoglycerides continue to react, maintaining the catalytic cycle until all the glyceride molecules have been converted to methyl esters and glycerol.

The results for the ASTM testing conducted on the B100 biodiesel (process using morpholine and NaOH) are shown in Table 3. Fuel properties of the biodiesel were found to meet or exceed ASTM standards for use in on-road vehicles.

Table 3. Physico-chemical properties of canola, coffee and corn oil biodiesel.

Method	Test	Canola Bio	Coffee Bio	Corn Bio	Unit	Specification
ASTM D93	Corrected Flash Point	140	140	140	°C	130 Min
ASTM D445	Kinematic Viscosity @140°F/40°C	4.781	4.801	4.782	cSt	1.9 Min - 6.0 Max
ASTM D613	Cetane number	55.1	53.4	52.4		47 Min
ASTM D2500	Cloud Point	-1	1	-1	°C	
ASTM D664	Acid Number	0.04	0.42	0.51	mg KOH/g	0.50 Max
ASTM D6584	Free Glycerin	0.00	0.00	0.00	Wt%	0.02
ASTM D6584	Total Glycerin	0.143	0.05	0.168	Wt%	0.240 Max
ASTM D4951	Phosphorous	<0.0010	<0.0010	<0.0010	Wt%	0.001 Max
EN 14538	Calcium Content	<1.0	<1.0	<1.0	mg/kg	(Ca + Mg) 5 Max
EN 14538	Magnesium Content	<1.0	<1.0	<1.0	mg/kg	
EN 14538	Potassium Content	<1.0	<1.0	<1.0	mg/kg	(K + Na) 5 Max
EN 14538	Sodium Content	<1.0	<1.0	<1.0	mg/kg	
EN 14112	Oxidation Stability	13.4	3.6	8.2	h	3 Min
ASTM D1160	AET @ 90% Recovery	358	357	357	°C	360 Max
ASTM D7501	B100 CSFT Time	120	128	230	sec	360 Max

4. Conclusions

The present work has successfully reported the applicability of morpholine-NaOH mixture as a homogeneous catalyst for the production of biodiesel from canola, corn and coffee oil. Comparison of morpholine assisted method with the conventional method clearly illustrated the role of morpholine in effective conversion and enhancement of the rate of transesterification reaction. The highest yield of biodiesel ~98% was obtained using NaOH-morpholine mixture at

1.5% (w/w) concentration at the end of only 90 min as compared to 180 min that was required in the absence of morpholine. The kinetics of transesterification reaction fitted well with a first order reaction. The properties of the biodiesel were matched with the ASTM standards.

Acknowledgements

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Figure 1. Concentration trajectories at constant temperature for base catalytic transesterification using parameters: NaOH (1.5% (w/w) relative to oil), MeOH: oil molar ratio (6:1), Temperature (65 °C). Initial values – red; Final values – black;

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Figure 5. Effect of varying amounts of morpholine co-catalyst on oil and fats conversion at the end of 90 min. BG-blue; FFA-red.

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Feedstock oils

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Final Biodiesel Samples