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Short communication

Enhancing kinetics of biodiesel production using morpholine

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ABSTRACT

This work illustrates morpholine assisted transesterification of crude canola oil, 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).

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, diethylamine 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 $NaOCH_3$ 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

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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 Eq. (1):

$$TAN = 1.99 \cdot FFA\%. \quad (1)$$

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 Eq. (2) [15].

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

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

$$Yield\% = \frac{Totalweightofmethylesters}{Totalweightofoilused}\ x\ 100 \quad (3)$$

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.

Fig. 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 Fig. 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 were 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.

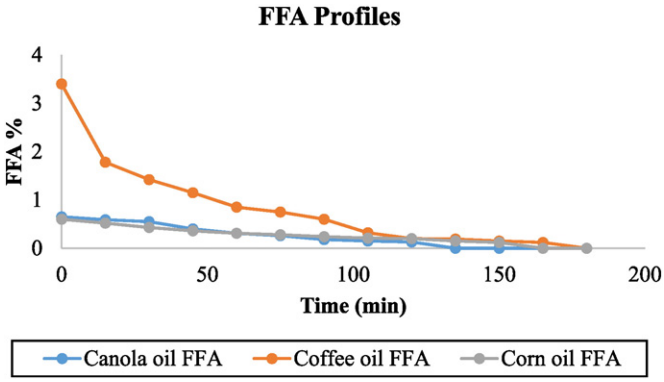

Fig. 2. Reduction in FFA observed at NaOH concentration of 1.5% (w/w), 65 °C, 180 min and 225 rpm. The FFA concentration gradually reduced to zero indicating 100% conversion.

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.

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 Fig. 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 Fig. 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,

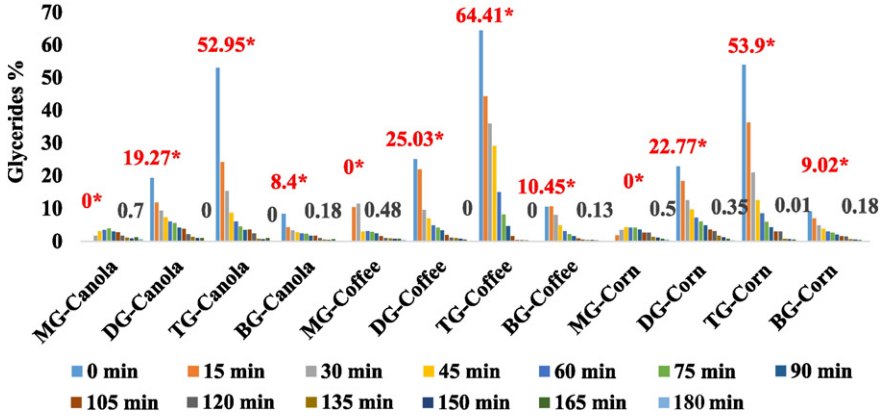

Fig. 1. Concentration trajectories at constant temperature for base catalytic transesterification using parameters: NaOH (1.5% (w/w) relative to oil), MeOH: oil molar ratio (6:1), Temperature (65 °C). Initial values – red with asterisk; Final values – black without asterisk.