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Esterification of oleic acid to biodiesel using magnetic ionic liquid: Multi-objective optimization and kinetic study

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HIGHLIGHTS

- Esterification of oleic acid using magnetic ionic liquid.
- Multi-objective optimization was performed for two responses.
- Both predicted yield and conversion were 83.4% at optimum conditions.
- Recycled ionic liquid can be used repeatedly without significant activity loss.
- Low activation energy and pre-exponential factor for esterification of oleic acid.

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ABSTRACT

The esterification of oleic acid in the presence of magnetic ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][$FeCl_4$]) at reaction temperature of 65 °C has been investigated. Artificial neural network-genetic algorithm (ANN-GA) was used to simultaneously optimized methyl oleate yield and oleic acid conversion for the reaction. It was found that optimum responses for both yield and conversion were 83.4%, which can be achieved using molar ratio methanol–oleic acid of 22:1, catalyst loading of 0.003 mol and reaction time at 3.6 h. Esterification of oleic acid at optimum condition using recycled [BMIM][$FeCl_4$] registered not much loss in catalytic activity after six successive runs. Kinetic study indicated that the reaction followed a pseudo-first order reaction, with activation energy and pre-activation energy of 17.97 kJ/mol and 181.62 min^{-1}, respectively. These values were relatively low compared to homogeneous or heterogeneous catalysts for esterification of oleic acid. Thus, [BMIM][$FeCl_4$] is a promising new type of catalyst for conversion of high free fatty acid (FFA) feeds to biodiesel.

1. Introduction

In the wake of today's environmental concerns and limited fossil fuel resources, biodiesel has stepped up to be a viable solution to both problems. Biodiesel can be obtained via transesterification of triglycerides or esterification of free fatty acids (FFAs), where these reactions require the presence of alcohol to produce fatty acid alkyl esters (FAAEs) [1]. Triglycerides occur naturally in vegetable oils and animal fats, thus reducing the dependency on fossil fuel for energy. Some biodiesel properties are even superior to petroleum diesel. Its higher flashpoint ensures safety of biodiesel during transportation or distribution, while higher cetane number indicates that biodiesel has a higher combustion efficiency [2]. Generally, carbon monoxide, carbon dioxide, oxides of nitrogen and sulfur oxides are reduced for exhaust emissions from biodiesel combustion [3]. The reductions are beneficial for the environment, especially carbon dioxide as it is one of the main greenhouse gases that contributes to global warming phenomena.

Different range of materials can be used for biodiesel synthesis. These include vegetable oils such as soybean, rapeseed, canola, and palm [1]. In order to avoid competition with food sector, non-edible sources are utilized. Examples of these types of feedstock are waste cooking oil (WCO), and *Jatropha curcas*. However, they usually have higher FFAs content, which is not preferable for alkali-catalyzed process. A significant amount of FFAs in the feedstock can reduce the efficiency of the alkaline catalyst, where FFAs react with the catalyst and leads to the formation of soap and water through the saponification process [2]. This reaction is undesirable as it complicates the separation of products further downstream, and also consumes alkali catalysts. Consequently, a longer production process is required due to the loss of catalyst activity, and further resulted in higher operating cost.

Acid catalysts are preferable for conversion of FFAs to alkyl esters. The catalysts are able to tolerate high FFAs content in the feedstock. Sulfuric acid (H_2SO_4) is usually used as the conventional

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catalyst in esterification of FFAs. Aranda et al. [4] explained that the higher H_2SO_4 catalytic activity in the esterification of palm fatty acids was due to its ability to protonate the carboxylic moiety of the fatty acid and also accelerate the formation of the tetrahedral intermediate. Although the catalyst effectively converts FFAs to biodiesel, there are some concerns regarding its utilization, which includes corrosion to the equipments and also its effluent is hazardous to the environment [5]. Since then, different types of catalysts have been developed and studied in order to obtain higher biodiesel yield. Heterogeneous catalysts allows easier separation from products after reaction and can be further recycled, thus eliminating dangerous acidic wastewater. Sulfated zirconia [6], tungsten oxide zirconia [7], and heteropoly acid [8] are heterogeneous catalyst that have been previously used for biodiesel synthesis.

In recent years, there have been growing interests in using ionic liquids (ILs) as catalysts in biodiesel synthesis. Among attractive characteristics offered by ILs are virtually negligible vapor pressure, high thermal stability, excellent solubility and miscibility with reactants, and also the acidity and basicity of ILs that can be tuned or controlled [9]. Ionic liquids with acidity nature are preferred for biodiesel production. Most ionic liquids involved in biodiesel synthesis can be categorized as Brønsted acidic ILs [5,10,11], while Lewis acid IL [12] and basic IL catalyst [13] have also been applied for the synthesis. The use of ionic liquid to catalyze transesterification and esterification reactions for biodiesel production has been reviewed recently [9,14].

In the pursuit of searching for an ionic liquid catalyst that can improve biodiesel synthesis, the magnetic property can facilitate the separation of IL from the homogeneous reactants. Hayashi and Hamaguchi [15] discovered a new type of IL that response to an externally applied magnetic field, and demonstrated that the IL showed a strong response towards a magnet placed nearby. The magnetic ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][$FeCl_4$]) contains tetrachloroferrate anion ([$FeCl_4$]$^-$), which is said to exhibit paramagnetic properties, thus displays magnetic behavior under the influence of magnetic field. This property is potentially beneficial for the recovery of the catalyst and eliminates the generation of wastewater for removing the catalyst from the biodiesel product. The same type of IL has been employed as catalysts in several reactions. The IL was employed for catalyzing the synthesis of 3,4-dihydropyrimidin-2(1H)-ones via Bignelli condensation, where high product yields were obtained even for low catalyst loading (i.e. 0.5–1 mmol of [BMIM][$FeCl_4$]) [16]. In another process, Wang et al. [17] successfully utilized the Lewis acidic [BMIM][$FeCl_4$] to catalyze acetylation of alcohols and phenols and also conversion of aldehydes, with the recycled IL can be reused in six successive runs without significant drop in the product yield. With similar characteristics suitable for catalyzing esterification reaction, the catalyst, which has not been used in any prior studies concerning biodiesel production, is tested in this work.

In this study, artificial neural network coupled with genetic algorithm was employed to simultaneously optimize two responses for oleic acid esterification. It is essential to understand that the single- and multi-objective optimization processes are theoretically different. Baños et al. [18] explained that single response optimization provides only a single solution with a single optimized solution as the outcome, while multiple responses optimization gives a set of optimal solutions, particularly Pareto-based optimization method that is based on the Pareto-dominance relationships containing non-dominated solutions. A set of non-dominated solutions is known as Pareto front, where it is not possible to improve one objective without worsening any other objective for any of the solution [19]. Multi-objective optimization have been successfully applied in chemical reaction processes involving simultaneous responses, including oxidative coupling of methane for hydrocarbons production [20], alkali-catalyzed transesterification of waste cooking oil for biodiesel production [21], and non-catalytic combined reforming for synthesis gas formation [22].

Kinetic studies for esterification reaction have been conducted using both homogeneous and heterogeneous catalysts [23–27]. Activation energy (E_a) is often reported to determine the minimum amount of energy required for the esterification reaction to occur. Esterification of free fatty acids in sunflower oil was catalyzed by H_2SO_4, followed by the development of kinetic model [23]. In the report, they determined that the higher H_2SO_4 concentration employed resulted in higher activation energy, plus the activation energy for the forward reaction was larger than for the reversed reaction in the equilibrium system. Song and co-workers [24] determined the kinetic parameters for esterification of oleic acid in subcritical methanol and zinc acetate ($Zn(CH_3COO)_2$) as the catalyst. They found that the reaction order was 2.2, while E_a was 32.6 kJ/mol. The presence of methanol in subcritical form resulted in reasonably low activation energy compared to other reaction using heterogeneous catalyst. Esterification of oleic acid was carried out in the presence of 12-tungstophosphoric ($H_3PW_{12}O_{40}$) acid with methanol [25]. The process followed first order reaction, and the activation energy was determined to be 51.0 kJ/mol. Although biodiesel synthesis via esterification reaction have been conducted using ionic liquids as catalysts [5,10], however the kinetic study of the reaction has been scarce.

In this paper, magnetic ionic liquid (MIL), 1-butyl-3-methylimidazolium tetrachloroferrite ([BMIM][$FeCl_4$]) was utilized to catalyze the esterification of oleic acid to biodiesel. Oleic acid was chosen as the model compound for feeds with high free fatty acid contents such as microalgae, *J. curcas*, and waste cooking oil. Table 1 lists feedstocks and their respective free fatty acid contents [28–32]. Multi-objective optimization was conducted to simultaneously determine the optimal value of two responses: methyl oleate yield and oleic acid conversion. Next, the performance of the recycled MIL in the process was observed and evaluated. Finally, kinetic study of oleic acid esterification using MIL was performed to determine the kinetic parameters, including the reaction rate constants at different temperatures, the activation energy of the reaction, as well as the pre-exponential factor.

2. Methods

2.1. Materials

All chemicals were commercially available and used without further purification. Oleic acid of high purity was purchased from QReC, New Zealand while methanol was obtained from Merck, Germany. Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were also acquired from Merck (Germany) and were used for the preparation of magnetic ionic liquid.

2.2. Catalyst preparation

The catalyst, 1-butyl-3-methylimidazolium tetrachloroferrite ([BMIM][$FeCl_4$]) was prepared following the method suggested

Table 1
Free fatty acids content in biodiesel feedstocks.

Feedstocks	FFAs content (%)	References
Chlorella oil	5.1	[28]
Waste cooking oil	8.7	[29]
Coconut oil	12.8	[30]
Animal fats	4.9–13.5	[31]
Jatropha curcas oil	14.0	[32]
Karanja oil	18.0	[32]