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Kinetic modeling and optimization of biodiesel production from white mustard (*Sinapis alba* L.) seed oil by quicklime-catalyzed transesterification

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ABSTRACT

The biodiesel production from white mustard (*Sinapis alba* L.) seed oil (WMSO) by transesterification with methanol over the quicklime powder was investigated in a batch stirred reactor. Two independent first-order models with respect to triacylglycerols (TAGs) or a more complex model that combined the changing mechanism and the first-order rate law with respect to TAGs and fatty acid methyl esters (FAMEs), respectively described successfully the kinetics of this transesterification reaction. Besides that, the response surface methodology coupled with a full factorial design with replication was applied to model and optimize esters content with methanol-to-WMSO molar ratio, catalyst amount and reaction time (X_1, X_2 and X_3, respectively). The analysis of variance indicated that all individual process factors, the interactions X_1–X_2 and X_2–X_3 and the quadratic term X_2^2 influenced significantly FAME content at the 95% confidence level. According to the reduced quadratic model, complete conversion could be achieved with the catalyst loading of 9.8%–10% and the methanol-to-WMSO molar ratio in the range between 6.1:1 and 11.6:1 in 50 min. WMSO was transesterified even faster than sunflower oil in the presence of both quicklime and KOH, due to higher total content of unsaturated fatty acids.

1. Introduction

Tremendous attention has been paid to biodiesel by governments, business sectors and scientific institutions all over the world in recent years because of many positive technical characteristics and important economic, environmental, social and political impacts [1]. Despite these benefits, the main barrier to biodiesel commercialization is the high price of its production, caused by the high cost of currently used oily feedstocks (mainly edible vegetable oils), which makes 70–95% of the total biodiesel cost [2]. Furthermore, even if the whole amount of available edible oils is used for the biodiesel production, current diesel requirements will not be satisfied [3]. Thus, other seed crops that could grow on marginal lands and produce non-edible oils should be looked for. Additional possibilities for the improvement of biodiesel production are to use the heterogeneous catalysts, to optimize transesterification reactions, to use more effective reactors and to upgrade each production stage.

White mustard (*Sinapis alba* L.), an annual plant of the family Brassicaceae, is cultivated worldwide because of its numerous uses. The aboveground parts are used in agriculture as a green manure and a fodder crop as tasty young seedlings are edible [4]. White mustard seed (WMS) has the largest agronomic value because of high oil and protein contents and low starch content [5]. WMS oil (WMSO) contains mainly oleic, linoleic, linolenic and erucic acid [6]. It is used in industry for lightning and as lubricant [7] or diesel fuel additive [8], in traditional medicine as anti-tumor, antiviral and analgesic agent [9], as well as in food preparation as a condiment [10,11] and a preservative [12]. WMSO is usually extracted from ground seeds by the Soxhlet extraction apparatus using *n*-hexane or petroleum ether, water or supercritical CO_2 extraction and cold pressing or expelling [13]. Press cake, a by-product of oil recovery, can be used in poultry production [14].

WMSO is currently seen as a promising biodiesel resource [15,16]. Low quality WMSO has already been employed for biodiesel production [17,18]. An overview of the previous studies of biodiesel production from WMSO is given in Table 1. Mainly methanol and alkali hydroxides were used in the biodiesel production from WMSO. NaOH was more active than KOH as higher esters yield (92%) was achieved with the former than with the latter (84%) [19]. The catalyst amount was in the range between 0.3% and 1.8%, mostly about 1% of the oil weight while the methanol-to-oil molar ratio was from 2:1 to 12:1, most frequently

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Table 1
The review of the transesterification of *Sinapis alba* oil.

Feed stock	Type, volume of reactor/ agitation speed, rpm	Type of alcohol	Alcohol-to-oil molar ratio	Catalyst/loading,%	Temperature, °C	Optimal conditions		Remark/objective of study	Reference
						Reaction conditions	Yield (purity), %/time		
Extracted mustard oil	–	Methanol	6:1, 7:1 and 8:1	–	–	8:1	(85%)/–	Esters synthesis and properties	[27]
Commercial mustard oil	Stirred reactor, –/600 rpm	Methanol	6:1	KOH/ 1% of oil	40–60	60	–	Reaction kinetics	[22]
Extracted mustard oil	Stirred reactor, 500 mL/–	Methanol	6:1	CH_3OK/0.2:1 catalyst-to-oil molar ratio	60	–	(> 98)/1.5 h; (99)/4h	Esters yield and properties	[15]
Extracted mustard oil	Stirred reactor, 2 L/–	Methanol	6:1	NaOH/0.8% of oil	70	–	(82)/2	Esters properties	[28]
Extracted mustard oil	Stirred reactor, 500 mL/ 600 rpm	Methanol	2:1–10:1 6:1	NaOH/0.1–0.9% of oil KOH/0.5% of oil	50–75 65	6:1, 0.5%, 65 °C –	92/75 min 84/75 min	Reaction optimization, esters properties	[19]
Dehydrated oil/THF miscella	Stirred reactor, 200 mL/ magnetic	Methanol + THF (1:1 mL/ mL)	14:1	NaOH/1.2% of oil	Room	–	(99.3)/10 min	Miscella and biodiesel production	[21]
Extracted mustard oil	–	Methanol	12 wt% of KOH/ -	KOH/0.5% of oil	22	–	–	Fuel performances	[25]
Commercial mustard oil	Erlenmeyer flask/magnetic/ 300 rpm	Methanol	25:6 mL/mL	KOH/1.8% of oil	65	–	96.56/2h	Viscometric analysis of biodiesel	[24]
Mustard oil	–	Methanol	6:1	KOH/0.3% of oil	60	–	–/2h	Emission characteristics of blends	[26]
Commercial mustard oil	Stirred reactor, –/600 rpm	Methanol Ethanol, propanol, 1-butanol	6:1	KOH/ 1% of oil	60	–	64.75/1.5 h	Properties as diesel additive	[8]
Commercial mustard oil	Glass container/–	Methanol	–	NaOH (150 mL, 1 M)	55	–	–/5 min	Fuel performances	[23]

6:1. The reaction temperature was usually close to the boiling point of methanol (60–65 °C). Methyl esters content lower than the prescribed limit for biodiesel (96.5%) was most likely because of the use of crude (unrefined) oil as feedstock. Exceptionally, Tabtabaei et al. [20,21] used the dewatered WMSO/water/tetrahydrofuran emulsion and methanol in the presence of NaOH to produce biodiesel while Issariyakul et al. [8] reported the production of biodiesel from WMSO by KOH-catalyzed transesterification with methanol, ethanol, propanol and butanol. A few studies are related to the process optimization using the traditional "one-factor-at-a-time" method [19] and the kinetic modeling [22]. Table 1 indicates that no solid catalyst has been applied to accelerate the WMSO transesterification. A number of recent studies are related to fuel properties, performances and exhaust gas emission of WMSO biodiesel and its blends with diesel fuel [11,16,23–26].

CaO is frequently employed as a catalyst for transesterification of various feedstocks because of its high basicity, mild reaction condition, high esters yield, possible recycling, low cost and easy preparation from natural or waste sources [29–31]. Since this reaction can be mass transfer- or reaction rate-controlled, two independent first-order models with respect to triacylglycerols (TAGs) [32] or a more complex model that combines the changing mechanism and the first-order rate law with respect to TAGs and fatty acid methyl esters (FAMEs) [33], respectively have been employed so far for describing the kinetics of transesterification over CaO-based catalysts.

The biodiesel production from non-edible WMSO by transesterification with methanol over low-cost quicklime was investigated in a batch stirred reactor. The main goal was to select the better model between the two above-mentioned models of Veljković et al. [32] and Miladinović et al. [33] and to make it simpler and easier for application. In addition, the transesterification reaction was optimized using a full factorial design with replication in combination with the response surface methodology in order to select the best reaction conditions (methanol-to-WMSO molar ratio, catalyst amount and reaction time) ensuring the maximum FAME content.

2. Theoretical background

Both kinetic modeling and statistical modeling and optimization of the transesterification of WMSO with methanol in the presence of quicklime powder were applied in this study.

2.1. Kinetic modeling

For modeling the kinetics of the WMSO transesterification with methanol over quicklime powder in a batch stirred reactor, two different reaction mechanisms were supposed: (1) the pseudo first-order reaction in the heterogeneous and pseudo-homogeneous regimes and (2) the changing mechanism combined with the TAG mass transfer limitation. In both cases, the transesterification reaction presents the stepwise conversion of TAGs *via* di- and monoacylglycerols (DAGs and MAGs, respectively) to FAMEs and glycerol. Since the consumption of DAGs and MAGs is faster than TAGs, the intermediates will not be considered, so the WMSO transesterification is shown as the following overall reversible reaction:

$$A + 3B \leftrightarrows 3R + S \quad (1)$$

where A, B, R and S present TAGs, methanol, FAMEs and glycerol, respectively.

Further assumptions were as follows:

a) The WMSO transesterification occurs via the initial heterogeneous and later pseudo-homogeneous regimes where the mass transfer resistance and chemical reaction, respectively control the overall reaction. As a consequence, the variation of FAME content with time is sigmoidal as it has been observed for the sunflower oil transesterification catalyzed by quicklime [33] or CaO [32].