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Article

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Continuous catalyst-free biodiesel synthesis from rice bran oil fatty acid distillate in a microreactor

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Abstract

This work proposed the catalyst-free biodiesel synthesis from the low-grade feedstock. Rice bran oil fatty acid distillate (RBOFAD) containing 65.5% of free fatty acids and ethanol were applied as a feedstock. The influence of operating parameters including residence time, reaction temperature, and ethanol-to-oil molar ratio on the biodiesel content (%Ester) were investigated. The experiments were carried out in a microreactor under the supercritical conditions. It was found that all parameters were important for achieving high %Ester. The optimal conditions for obtaining high biodiesel content (75%) were as follows: reaction temperature of 300 ° C, ethanol-to-oil molar ratio of 5:1, and residence time of 24 min. The potential enhancement of this synthesis was studied through the addition of either iso-propanol or acetic acid which acted as a co-reactant. Unfortunately, both additives did not increase the %Ester further over the range of operating conditions studied.
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Keywords: Biodiesel; Supercritical; Rice bran oil fatty acid distillate; Microreactor; Additive

1. Introduction

Nowadays, one of the critical issues confronted by biodiesel industry is the net cost of biodiesel production, conveying to the unattractiveness of using biodiesel as a substitute for petroleum-based diesel. The cost of refined vegetable oil constitutes over 80% of the total biodiesel production [1]. Using the low-cost feedstocks (high free fatty acid (FFA) and water content) is one of the promising solutions to improve the economic viability. Unfortunately, the conventional method for biodiesel production (transesterification using alkaline catalyst) is not appropriate for the use of these materials due to the low purity and yield of biodiesel. To overcome this issue, the modification of biodiesel production has been explored. Recently, supercritical technology has emerged as a promising technique

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for this purpose. The successes of biodiesel synthesis from low-grade materials under supercritical conditions were reported [2,3] with several key features such as non-catalytic, high tolerance for water and FFA, and compatible with low-grade feedstocks.

Rice bran oil fatty acid distillate (RBOFAD) obtained from rice bran oil refining process is one of the attractive materials for biodiesel production due to the nature of non-food-based feedstock as well as its availability and inexpensiveness [4]. Biodiesel production from RBOFAD under supercritical conditions has hardly been investigated and carried out in a continuous process. Only a few batch processes have been examined [5,6]. Therefore, the continuous biodiesel process from RBOFAD was new and interesting to explore.

Microreactor is one of the efficient types of chemical reactor that can be used for high productivity and large-scale production. High performance of biodiesel production in the microreactors compared to those of batch reactors has been reported [7]. Hence, in our work, the microreactor was used for developing biodiesel synthesis from RBOFAD.

The highlight of this research was to continuously synthesize biodiesel from low-value feedstock (RBOFAD) which was conducted in a microreactor under supercritical conditions. The influence of main operating variables including the reaction temperature, residence time, and alcohol-to-oil molar ratio on the biodiesel content was investigated. The potential enhancement of biodiesel production through the addition of several additives, iso-propanol and acetic acid, was also studied in this work.

2. Materials and methods

Semi-solid RBOFAD was supplied from Surin Bran Oil company. AR grade ethanol, iso-propanol and acetic acid were purchased from Merck. Acetone and acetonitrile for product analysis were obtained from RCI Labscan and Honeywell, respectively. The continuous supercritical biodiesel synthesis in this work was carried out in a microtube reactor (ID: 0.8 mm, volume: 4.8 mL). The experimental setup was followed according to our previous work [8]. Briefly, the liquefied RBOFAD and ethanol were separately fed into the T-shaped micromixer at different volumetric flow rates depending on the residence time and ethanol-to-oil molar ratio. After exiting the mixer, the mixture entered the microreactor where the reaction took place. The desired reaction temperature and constant pressure of 85 bar were provided via a convection oven and a back-pressure regulator, respectively. After that, the effluent stream was quenched by passing through the cooling water bath. The sample was collected for purification step after threefold of the residence time has elapsed. DI water was used to purify the biodiesel which was separated by using the microcentrifuge. The sample was then analyzed for biodiesel content (%Ester) by HPLC-RI technique which was based on the report of Chueluecha et al. [9]. The viscosity and density of RBOFAD were measured by a viscometer and pycnometer, respectively. The acid value of RBOFAD was determined using titration method with 1 mol/L KOH. The saponification value was determined via the reaction with 0.5 mol/L of KOH, followed by the back titration of 0.5 mol/L HCl. The composition of RBOFAD including free fatty acids; and mono-, di-, and triacylglycerides was determined under the same method as reported by Akkarawatkhoosith et al. [8].

3. Results and discussion

3.1. RBOFAD properties

The properties of RBOFAD were summarized in Table 1. The results indicated that the main component of RBOFAD was the free fatty acids, according to the high acid value, followed by the diacylglycerides and

Table 1. Physicochemical properties of RBOFAD.

Properties	RBOFAD
Density (kg/m^3)	920
Viscosity (cSt)	35.6
Acid value (mg$_{KOH}$/g)	135
Saponification value (mg$_{KOH}$/g)	170
Free fatty acids (wt%)	65.5
Monoacylglycerides (wt%)	4.9
Diacylglycerides (wt%)	16.2
Triacylglycerides (wt%)	11.3

triacylglycerides. Therefore, RBOFAD was not suitable as a feedstock for the conventional biodiesel production due to the high FFA content.

3.2. Influence of process variables on biodiesel content

The influence of main biodiesel processing variables including the reaction temperature, residence time, and ethanol-to-oil molar ratio on the biodiesel content was investigated under various operating conditions. The effect of ethanol-to-oil molar ratio (1:1 to 25:1) on the biodiesel content was firstly considered at the reaction temperature of 280 °C with varying residence times in the range of 12 to 40 min. The results as shown in Fig. 1(a) indicated that the intensification of ethanol-to-oil molar ratio (from 1:1 to 5:1) could shift the reaction toward the formation of biodiesel and offered high content of biodiesel (%Ester). Further increase of ethanol-to-oil molar ratio did not significantly improve the biodiesel content, i.e., at 30 min of residence time, the %Ester was slightly altered (71.1% to 69.8%) when the ethanol-to-oil molar ratio increased from 5:1 to 11:1. Moreover, the surplus ethanol in the system negatively affected the biodiesel content due to the dilution effect [10]. These phenomena were in accordance with the results of Zhang et al. [6] who used the crude rice bran oil for acid-catalyzed biodiesel synthesis. Hence, operating under the ethanol-to-oil molar ratio of 5:1 was possible to obtain the high yield while improving economic viability of the process. In addition, the residence time of 30 min was required to reach the equilibrium state for all ethanol-to-oil molar ratios investigated..

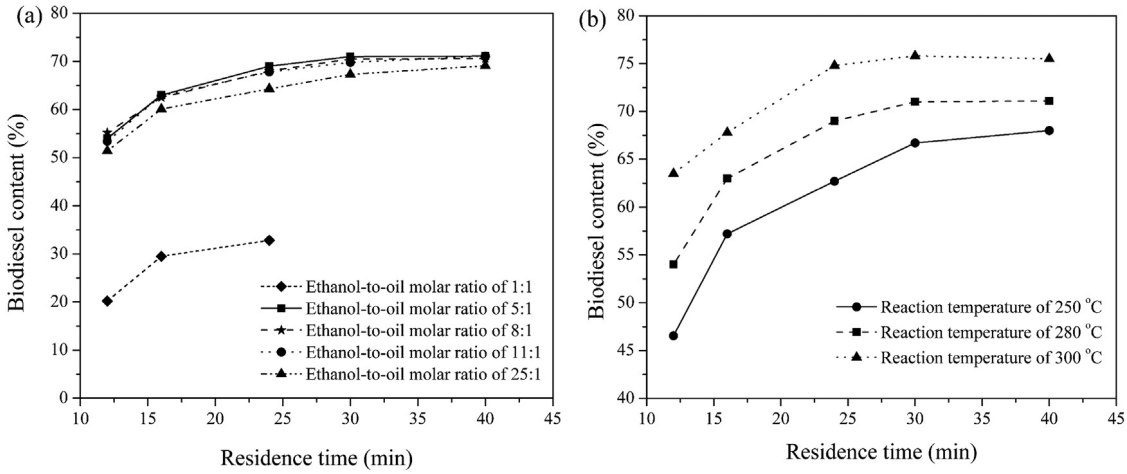

Fig. 1. Effect of operating variables on the biodiesel content; (a) effect of ethanol-to-oil molar ratio (reaction temperature of 280 °C) and (b) effect of reaction temperature (ethanol-to-oil molar ratio of 5:1).

Next, the effect of reaction temperature on the %Ester was studied in the range of 250 to 300 °C. The experiments were carried out at the constant ethanol-to-oil molar ratio of 5:1 with various residence times. The reaction temperature exceeding 300 °C might not be suitable for biodiesel synthesis due to the decomposition of fatty acid chains [11]. As shown in Fig. 1(b), the strong effect of reaction temperature was demonstrated. The increase of reaction temperature could further increase the biodiesel content (at the same ethanol-to-oil molar ratio). The %Ester of 66.7% increased to 75.8% when the reaction temperature rose from 250 °C to 300 °C at the residence time of 30 min, due to the growth of kinetic constant. Since the biodiesel content of 75% was achieved at the reaction temperature of 300 °C, ethanol-to-oil molar ratio of 5:1, and residence time of 24 min, the potential for further improvement of this process would be addressed to reach the %Ester standard (≥96.5%).

3.3. Influence of additive

The enhancement of our biodiesel synthesis from RBOFAD and ethanol was studied through the addition of several additives which acted as a co-reactant. Iso-propanol and acetic acid have been applied to improve the transesterification of biodiesel as reported in literature [8,12]. However, using these additives for the enhancement

of FFA esterification has not been undertaken. Hence, iso-propanol and acetic acid were selected in this work. All experiments were conducted at several reaction temperatures (250, 280, and 300 °C) and residence times (12, 16, and 24 min), while the alcohol-to-oil molar ratio was kept constant at 5:1. The results for the addition of iso-propanol (10 and 30 wt% based on oil), as presented in Fig. 2, indicated that the addition of iso-propanol could not improve the %Ester over the entire range of alcohol content studied. Nevertheless, the presence of isopropyl esters in the fuel could help improve the fuel properties particularly the cold-flow properties [8].

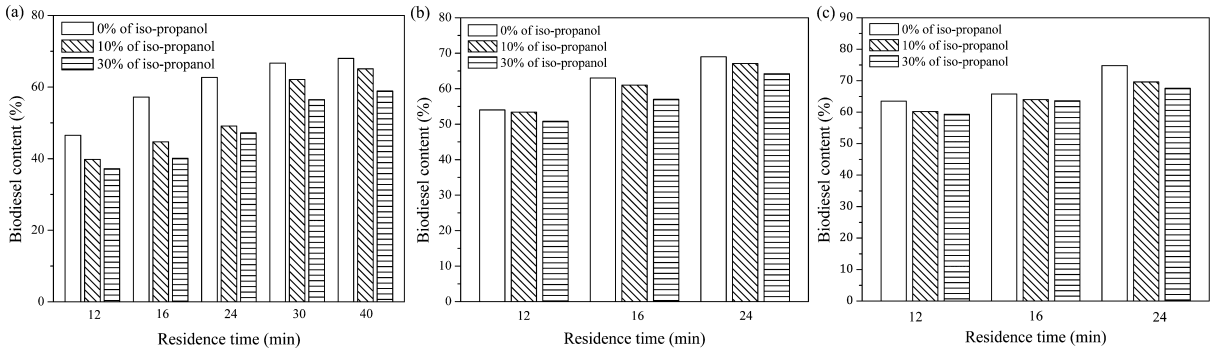

Fig. 2. Influence of iso-propanol addition at various reaction temperatures; (a) 250 °C, (b) 280 °C, and (c) 300 °C.

The influence of acetic acid addition (5, 10, 25 wt% based on oil) was presented in Fig. 3. The negative effect of adding acetic acid on the biodiesel content was observed. This might be caused by the esterification of ethanol and acetic acid, leading to the decrease of ethanol concentration in the system. Note that, although further increasing the content of acetic acid beyond 25% appeared to reverse this effect, the net production cost might be the next barrier to encounter.

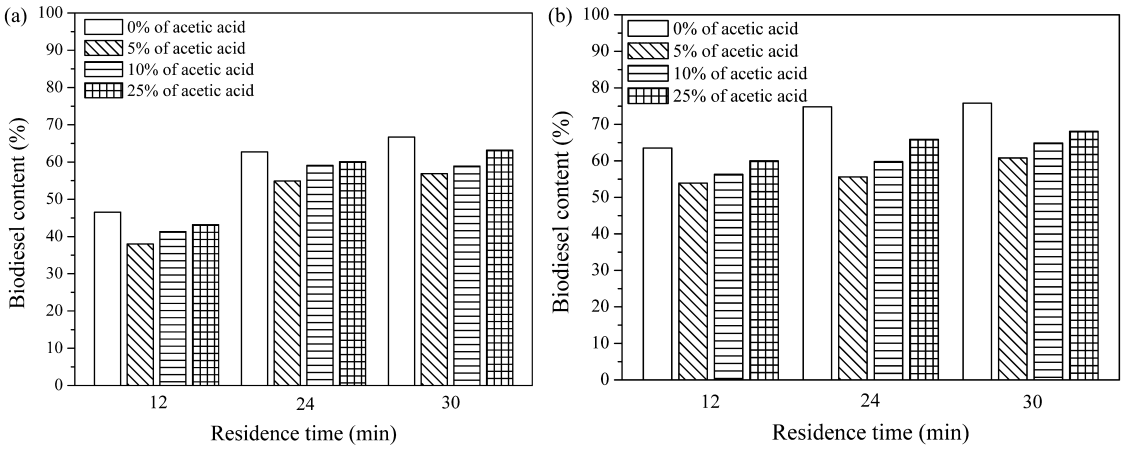

Fig. 3. Influence of acetic acid addition at various reaction temperatures; (a) 250 °C and (b) 300 °C.

These outcomes suggest that the addition of either iso-propanol or acetic acid was not suitable for biodiesel synthesis from RBOFAD. Other methods should be explored to overcome the drawback such as the addition of small amount catalysts.

4. Conclusion

This work examined the influence of operating factors affecting biodiesel content for biodiesel synthesis from RBOFAD. Four main factors including residence time, reaction temperature, and ethanol-to-oil molar ratio were considered. The %Ester of 75% was achieved at the residence time of 24 min, ethanol-to-oil molar ratio of 5:1, and

reaction temperature of 300 °C. The addition of either iso-propanol or acetic acid in the system could not improve the %Ester when compared to the additive-free system (RBOFAD and ethanol).

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