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Optimization of methyl ricinoleate synthesis with ionic liquids as catalysts using the response surface methodology

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HIGHLIGHTS

- A novel Brønsted acid ionic liquid, [Hmim]HSO_4, was used as the catalyst for ricinoleic acid transesterification.
- The methyl ricinoleate content reached 89.82% under conditions optimized using the response surface method.
- The catalytic activity of [Hmim]HSO_4 remained high even after 4 cycles.

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ABSTRACT

Methyl ricinoleate (MR) was synthesized from castor oil and methanol using ionic liquids as catalysts, by a transesterification reaction. The product was characterized using mass spectrometry. The efficiencies of four different catalysts, 1-methyl imidazole hydrogen sulfate salt ([Hmim]HSO_4), 1-butyl-3-methylimidazolium hydroxide salt ([Bmim]OH), NaOH, and H_2SO_4 were compared. The effect of the methanol/castor oil mole ratio, reaction temperature, reaction time, and catalyst dosage on the MR content was investigated by single factor experiments. Based on single factor experiments and the Plackett–Burman design, the transesterification of castor oil and methanol was optimized using the response surface methodology. The results showed that the most effective catalyst was the ionic liquid [Hmim]HSO_4. The optimal conditions were as follows: methanol/castor oil mole ratio 6:1, reaction time 4 h, reaction temperature 77 °C and [Hmim]HSO_4 dosage 12%. Under these conditions, the MR content reached 89.82%. The catalytic activity of [Hmim]HSO_4 still remained high after 4 cycles.

1. Introduction

Castor oil is the non-volatile oil that consists of various fatty acids and glycerin [1]. Ricinoleic acid, one of the most abundant fatty acids in castor oil, making up 80–90% of the composition, can substitute edible oil in biodiesel preparation [2]. Hence, it can mitigate the gap between food and fuel requirements [3]. Methyl ricinoleate (MR) is widely used in perfumes [4], plasticizers [5], lubricating oils [6], and cosmetics and fine-chemical industries [7,8], as well as for biological diesel oil applications [9–11]. Both the requirement and profit margins of MR have increased due to its widespread use in the abovementioned fields, in domestic as well as overseas markets.

MR can be synthesized from castor oil and methanol by transesterification in the presence of a catalyst, wherein hydrogen ions are supplied by the catalyst to promote the forward reaction [12,13]. Fig. 1 shows a schematic of the synthetic route, which involves three steps and includes the catalytic transesterification reaction. First, one mole of triglyceride reacts with one mole of methanol to generate one mole each of diglyceride and MR; second, one mole of diglyceride and one mole of methanol produce one mole each of monoglyceride and MR; third, one mole of monoglyceride and one mole of methanol form one mole each of glycerinum and MR. As a result, in the net reaction, 1 mol glycerinum and 3 mol MR are generated with the consumption of 1 mol triglyceride and 3 mol methanol. The main catalysts used in the ester-exchange reaction are strong acid, alkali, novel ionic liquid, etc. [14,15]. However, although strong acids and alkali impart relatively high catalytic efficiency, their use has some drawbacks such as severe equipment corrosion and environmental pollution. Apart from the above mentioned drawbacks, these catalysts also present problems such as recycling difficulty and high costs. Such drawbacks will result in various environmental problems, which will eventually disrupt human life. Therefore, the growing need for environmental

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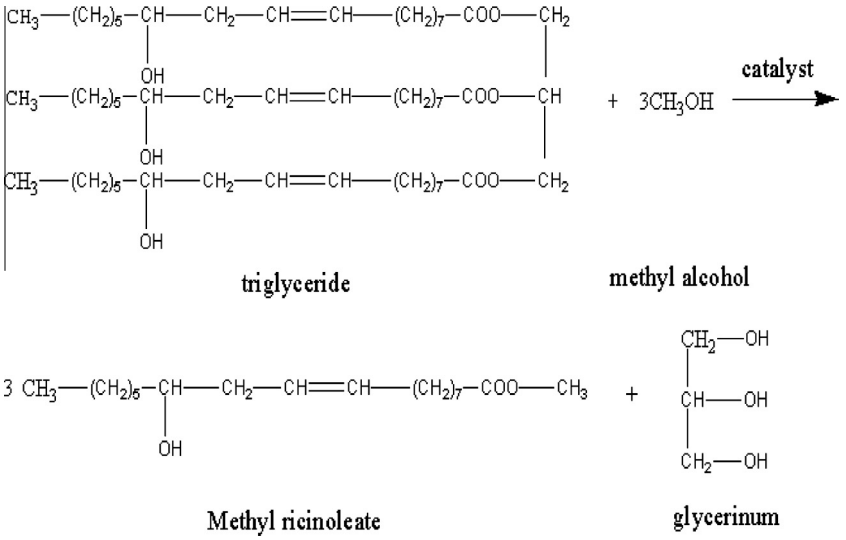

Fig. 1. Schematic of the overall synthetic route.

protection is prompting scholars to try to intensify research efforts in this field, and developing an environment-friendly catalyst with high catalytic activity for the ester exchange reaction has become an important research objective [16].

Ionic liquids (ILs) are liquid salts that are widely applied to the catalytic field [17].

The acidic strength of ILs can be adjusted; hence, a series of catalysts with different acidic strengths can be designed appropriately. In addition, ILs are readily separated from the reaction mixture because of their excellent thermal and chemical stability. Compared to conventional catalysts ILs result in less environmental pollution because of their reusability [18]. As shown in Fig. 2, the acid-catalyzed transesterification reaction involves the initial dissociation of H^+ (proton) from the catalyst, which then combines with the carbonyl group of the triglycerides to form the carbocation intermediate. Subsequently, methanol, which has an affinity for H^+, combines with the carbocation intermediate to form a tetrahedral intermediate. Finally, the intermediate decomposes into the methyl ester and diglycerides, and then generates a proton to catalyze the next cycle. The diglycerides and monoglycerides also react according to the above mentioned mechanism. 1-Methyl imidazole hydrogen sulfate salt ([Hmim]HSO_4) is a Brønsted acid ionic liquid composed of 1-methyl imidazole and concentrated sulfuric acid [19]. Hajipour et al. [20] prepared acylals using [Hmim]HSO_4 as the catalyst and aldehydes, together with acetic anhydride, as the raw materials. Li et al. [21] reported the [Hmim]HSO_4-catalyzed synthesis of N-substituted pyrroles. Rodriguez-Guerrero et al. [22] synthesized biodiesel from castor oil using sodium hydroxide (NaOH) as the catalyst. Barbosa et al. [23] prepared biodiesel from castor and soybean oils using potassium hydroxide (KOH) as catalyst. However, use of NaOH and KOH in the above reactions often leads to recycling difficulty, corrosivity, and environment pollution [24,25]. ILs, those are easy to recycle, non-corrosive to equipment, and environment-friendly, are considered suitable for industrial production [26].

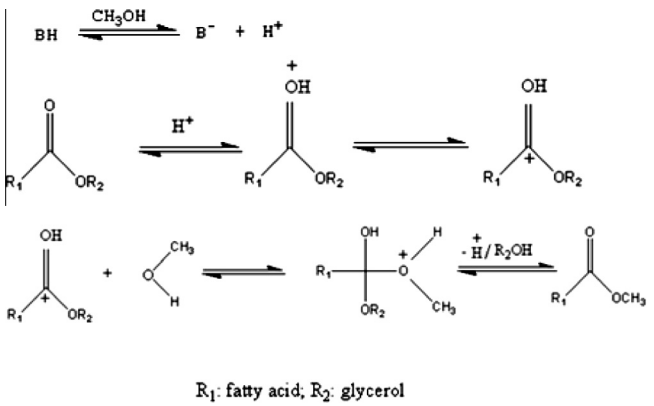

Fig. 2. Mechanism of acid-catalyzed transesterification.

In the current study, the efficiency of [Hmim]HSO_4 was studied by comparison with other catalysts such as 1-butyl-3-methylimidazolium hydroxide salt ([Bmim]OH), NaOH, and concentrated sulfuric acid (H_2SO_4), and the reaction conditions were optimized. Based on single factor experiments, the response surface methodology was applied to optimize the process parameters of the transesterification reaction catalyzed by the ionic liquid [Hmim]HSO_4. The products were characterized by gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Reagents and materials

Analytical reagent-grade castor oil, NaOH, and H_2SO_4 were procured from Nanjing Chemical Reagent Co., Ltd. Guaranteed reagent-grade ionic liquids [Hmim]HSO_4 and [Bmim]OH were purchased from Shanghai Chengjie Chemical Co., Ltd. De-ionized water was prepared in our laboratory.

2.2. Preparation of MR

Castor oil, methanol, and various catalysts were mixed and stirred in a three-necked round-*bottom* flask (Fig. 3). Then, the reaction was carried out for a period of time at a certain temperature. Excess methanol was recycled using reduced-pressure distillation. The faint yellow solution containing the catalyst was collected for recycle use after stratification in the flask, and the supernatant was washed with deionized water. MR was concentrated after removing excess moisture by reduced-pressure distillation. The MR content in each experiment was measured in triplicate, and the average value was considered.