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Improved yield of solvent free enzymatic methanolysis of palm and jatropha oils blended with castor oil

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HIGHLIGHTS

- Blending castor oil with palm and jatropha oils improved the yield of solvent-free enzymatic methanolysis reaction.
- Blending 20% castor oil with jatropha oil raised the yield of solvent-free enzymatic methanolysis to 78.3%.
- Adding 50% castor oil to palm oil increased the yield of solvent-free enzymatic methanolysis to 76.2%.
- The yield of solvent-free enzymatic methanolysis of blended oils exceeded the maximum theoretical yield of lipozyme TL IM.

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ABSTRACT

In this work, castor oil was blended with palm and jatropha oils to improve the yield of solvent-free enzymatic methanolysis reaction. Transesterification reactions were carried out with stoichiometric ratio of methanol to oil and using lipozyme TL IM as catalyst at 45 °C and 200 rpm for 24 h. By adding only 10% castor oil to the reaction medium a surge in the yield of methanolysis of jatropha oil was observed (i.e. from 21.9% to 65.5%). Increasing the amount of castor oil to 20% raised the yield of methanolysis of jatropha oil to 78.3%. Blending 50% castor oil with palm oil increased the yield of enzymatic methanolysis from 11.9% to 76.2%. Mixing castor oil with jatropha and palm oils improved the yield of solvent free single-step methanolysis reaction to the higher amounts than the maximum theoretical yield of lipozyme TL IM (i.e. 67%).

1. Introduction

Soaring use of fossil fuels has led to depletion of petroleum reservoirs, pollution of the environment and global warming [1]. Developing alternative sources of energy like biodiesel is important for sustainable economic growth and maintain standard of living [2]. Biodiesel that is derived from vegetable oils and animal fats is a promising and eco-friendly alternative to diesel fuel [3]. Biodiesel is a mixture of monoalkyl esters of long chain fatty acids [4]. It is a biodegradable fuel (more than 90% biodiesel can be biodegraded within 21 days) that has higher combustion efficiency, cetane number, and lower sulfur and aromatic contents than petroleum based diesel [5]. Using biodiesel as a blend with petroleum based diesel fuel improves the lubricity of fuel and reduces fuel consumption [6]. Moreover, combustion of neat biodiesel reduces emission of carbon monoxide (by 46.7%), particulate matter (by 66.7%), and unburned hydrocarbons (by 45.2%) [7]. Since this fuel is biodegradable and non-toxic, it is suitable for transportation in highly sensitive environments like marine ecosystems and mining enclosures [8]. Another advantage of biodiesel over conventional diesel fuel is that CO_2 released from its burning is absorbed by plants as a source for photosynthesis [9,10].

Biodiesel is produced by esterification of free fatty acids (FFAs) or transesterification of oils and fats with short chain alcohols such as methanol [11]. The transesterification reaction can be carried out by alkaline-catalysts, acid-catalysts, enzymatic-catalysts, inorganic heterogeneous catalysts or without catalyst in supercritical conditions [12]. Currently, biodiesel is mainly produced using alkali catalyst because it gives high conversion levels in short reaction times. However, it is associated with drawbacks such as; high-energy demand, strict feedstock specifications (FFA and water content), difficulties in recovery of glycerol and catalyst, and treatment of alkaline waste water [13].

Applying biocatalysts (lipases) in transesterification reaction can eliminate some of afore said drawbacks and is environmentally friendly [14]. Enzymatic method proceeds under mild operating conditions [15] and consumes lesser energy [6]. In addition,

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enzymes are able to catalyze both transesterification and esterification reactions and convert triglycerides and free fatty acids to alkyl esters in one step without soap formation. Therefore, in enzymatic method concentration of free fatty acids in feed can be higher than alkali method [16,17]. Since the main products of enzymatic method are biodiesel and glycerol, purity of products is high and removal of lipase is easier [17]. However, high cost of enzyme and its inhibition are major bottlenecks to industrialize enzymatic process [18]. Enzyme inhibition is caused by undissolved methanol (due to low solubility of oil in methanol) and glycerol (by product of transesterification) in the reaction medium. It has been stated that more than 1/2 M equivalent methanol in methanolysis reaction is insoluble in vegetable oil and inactivates immobilized lipases [14,19]. Also, produced glycerol which is insoluble in the oils [20] and low soluble in the methyl esters deposits on the surface of immobilized enzyme and restricts diffusion of enzyme and substrate [21]. Since methanol is more soluble in the methyl esters than in triglycerides, enzyme inactivation caused by methanol is notable at the beginning of the reaction and is diminished by proceeding of the reaction. Negative effect of glycerol becomes larger at higher oil conversions [21]. Stepwise addition of methanol to the reaction system, changing acyl acceptor, and solvent engineering has been proposed to resolve this problem. Stepwise addition of methanol to the reaction system is the most common method to resolve this problem, but complications associated with its operation in large-scale makes it less attractive. Acyl acceptors such as methyl and ethyl acetate have low reaction rates and are expensive in comparison with methanol [11]. Tert-butanol dissolves both methanol and glycerol and eliminates negative effects of both substances on enzyme activity [15,19,21]. However, recovery of solvent (tert-butanol) is associated with complicated downstream separation and purification processes and produces more waste water that deteriorates quality of the environment. In addition, most of chemical solvents are hazardous and their storage and handling imposes strict precautions and additional cost. Therefore, it is essential to find a way to diminish enzyme inactivation problem and improve the yield of enzymatic methanolysis process while avoiding the drawbacks of above mentioned remedies. Trevithick and Lauro [22] stated that castor oil is completely soluble in alcohol, while all other vegetable fats are practically insoluble. They applied this fact (solubility of castor oil in alcohol) to test the purity of samples of castor oil. Also, it has been stated by researchers that castor oil is well soluble in both methanol and methyl esters [23–25]. Considering this characteristic of castor oil and knowing that poor miscibility of vegetable oils and methanol causes enzyme inhibition, it is expected that the presence of castor oil in the reaction medium could improve the yield of enzymatic methanolysis of oils. To test this hypothesis, the effect of mixing castor oil with jatropha and palm oils on the yield of solvent free single-step enzymatic methanolysis reaction was studied. To the best of our knowledge, this is the first time that blends of castor oil with jatropha and palm oils are used as to improve the yield of solvent free lipase-catalyzed methanolysis reaction.

2. Materials and method

2.1. Materials

Lipozyme TL IM a product of Novozymes A/S Company was procured from Eastern Global Summit Sdn.Bhd., Malaysia. Standard fatty acid methyl ester samples, methanol and n-hexane were bought from Sigma Aldrich, Malaysia. Palm oil was purchased from local supermarkets. Jatropha and Castor oils were purchased from Indonesia and Iran, respectively. Table 1 presents the fatty acid composition of castor, jatropha and palm oils according to the gas chromatography analysis.

Table 1
Fatty acid composition of palm oil, jatropha oil and castor oil according to the gas chromatography analysis.

Fatty acid			Palm oil (wt%)	Jatropha oil (wt%)	Castor oil (wt%)
Name	Formula	Structure			
Saturated					
Myristic acid	$C_{14}H_{28}O_2$	C14:0	1.2	0.1	–
Palmitic acid	$C_{16}H_{32}O_2$	C16:0	43.6	15.6	1.2
Stearic acid	$C_{18}H_{36}O_2$	C18:0	4.6	7.7	1.3
Un-saturated					
Palmitoleic acid	$C_{16}H_{30}O_2$	C16:1	–	1.2	–
Oleic acid	$C_{18}H_{34}O_2$	C18:1	40.5	44.2	3.6
Linoleic acid	$C_{18}H_{32}O_2$	C18:2	10.1	31.2	4.7
Linolenic acid	$C_{18}H_{30}O_2$	C18:3	–	0.4	–
Ricinoleic acid	$C_{18}H_{34}O_3$	C18:1(OH)	–	–	89.2

2.2. Enzymatic transesterification procedure

In enzymatic methanolysis of palm and jatropha oils, different portions of castor oil (10%, 20% and 50% based on the total oil weight i.e. 10 gr) were added to the reaction medium. For all reactions ratio of methanol to oil was 3:1 (stoichiometric ratio) and 15% of lipozyme TL IM, an inexpensive immobilized lipase from *Thermomyces lanuginosus* was used as catalyst. Methanolysis reactions were carried out in 50 ml flasks in a temperature-controlled rotary shaker at 45 °C and 200 rpm for 24 h. Reaction product was centrifuged, and an appropriate amount of upper phase was mixed thoroughly with n-hexane in 5 ml volumetric flask. Prepared samples were filtered using 0.45 μm nylon syringe filter for gas chromatography (GC) analysis.

2.3. Analytical procedure

The fatty acid methyl ester (FAME) content of the product was analyzed using automated split injector gas chromatograph HP6890, Agilent Technology. This apparatus was equipped with DB-23 capillary column (60 m × 0.248 mm × 0.15 μm) and flame ionization detector (FID). The column temperature was held at 50 °C for 1 min, heated to 175 °C at 25 °C/min then increased to 230 °C at 4 °C/min and held for 5 min [26]. To analyze ricinoleic acid methyl ester the column temperature was kept at 50 °C for 1 min, heated to 175 °C at 25 °C/min then raised to 240 °C at 4 °C/min and kept for 8 min. The temperature of injector and detector were set at 250 °C and 280 °C, respectively.

Yield of methanolysis reactions that is percentage of fatty acid methyl esters in the product was calculated from peak areas in GC results.

3. Results and discussion

Fig. 1 presents the yield of solvent free single-step enzymatic methanolysis of pure jatropha oil and its blends with castor oil. The yield of methanolysis of jatropha oil in its pure form was low in comparison with systems that contained different portions of castor oil; however, it was higher than the yield of pure palm oil at similar reaction conditions. By adding 10% castor oil (based on total oil weight) to the reaction system the yield of methanolysis