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HIGH TEMPERATURE SOLID-CATALYZED IN-SITU TRANSESTERIFICATION FOR BIODIESEL PRODUCTION

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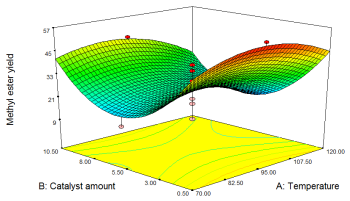
Graphical Abstract



Abstract

In-situ transesterification method is a simplified method for biodiesel production where the oil was simultaneously extracted and transesterified into alkyl ester *in-situ* in one single process. This process combines the steps of lipid (oil) extraction and transesterification. The alcohol used was methanol as it is widely available and economically feasible. In this study, *in* situ transesterification was conducted using solid coconut waste and a novel heterogeneous catalyst synthesized from eggshells and solid coconut waste by calcination. Reaction temperature, catalyst loading, and methanol to solid ratio were varied from 70 to 120˚C, 0.5 to 10.5 wt %, and 8:1 to 12:1 respectively. Meanwhile, reaction time was fixed to 3 hrs. Heterogeneous catalyst can help to reduce the steps in separation and purification of the product. Moreover, utilizing waste in the production can lower the production cost as well as help to save and clean the environment. The highest biodiesel yield was observed at the condition of 95˚C, 0.5 wt % catalyst, and 10:1 methanol to solid ratio.

Keywords: Biodiesel, *in-situ* transesterification, heterogeneous catalyst, eggshells, solid coconut waste

1.0 INTRODUCTION

Biodiesel is a non-petroleum based diesel fuel which made up of the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. It is an environmental friendly fuel that can be used in any diesel engine without modification [1]. It can also be used in neat form or blended with petroleum diesel for use in compression ignition engines [2]. Its physical and chemical properties as it relates to operation of diesel engines are similar to petroleum based diesel fuel. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol in the presence of a catalyst to yield glycerin and methyl ester. Even though the cost of biodiesel is much higher than petroleum based diesel, many governments sustain this production. The cost associated with the production is mainly affected by the cost of the feedstock and the technology applied in order to maximize the yield of biodiesel. Therefore, it is crucial to employ less expensive feedstock as well as catalyst to overcome resource exigency.

There are several methods for biodiesel production and application such as direct use of vegetable oils, microemulsions, thermal cracking (pyrolysis) and transesterification [3]. However, transesterification is widely used for its advantages such as renewability, higher cetane number, lower emissions and higher combustion efficiency [4]. Transesterification consist of three reversible steps of reaction. The first step is the conversion of triglycerides to diglycerides, followed by diglycerides be converted to monoglycerides and then from monoglycerides to glycerols, yielding one methyl ester molecule from each glyceride at each step [5], [6]. Alternative method for biodiesel production is by *in-situ* transesterification. *In-situ* transesterification simplify the steps of oil extraction and consecutively transesterified to alkyl ester in one single process. These integrated stages have promised to reduce the production cost of biodiesel for reduction

of reagents and solvents used. Moreover, concern on waste disposal can be avoided [7].

In this study, solid-catalyzed *in-situ* transesterification was carried out in high temperature to produce biodiesel. Transesterification favours higher reaction temperature to synthesize biodiesel since it is an endothermic reaction in nature [8]. Besides, solid heterogeneous catalyst was used in the process for its advantages such as reusable, environmentally benign, less amount of wastewater produced, and easy to separate from product [9], [10]. The utilization of natural calcium sources from waste materials has become a new trend for the production of biodiesel nowadays [11]. Waste eggshells were used as the catalyst in this work has add value to the green biodiesel process due to their eco-friendly characteristic and cheap cost [12]. This work was conducted to study the effect of reaction parameters such as temperature, catalyst loading, and methanol to solid ratio on biodiesel production.

2.0 METHODOLOGY

2.1 Materials

Solid coconut waste (SCW) was collected from coconut milk shop at Pasar Besar Gombak, Malaysia and eggshells were collected from International Islamic University Malaysia cafeteria. Prior to use, eggshells were washed thoroughly to remove impurities and both wastes were dried overnight in 90˚C oven. After drying, SCW and eggshells were kept in dry container for further usage. Methanol brand Hmbg and n-hexane brand Merck (GC grade) were used in this experiment.

2.2 Catalyst Preparation

SCW and eggshells were mixed with ratio of 5:1 and then undergo calcination process at 900˚C for 4 hours.

2.3 *In-situ* Transesterification

SCW dried in 90˚C oven overnight were used in the reaction. It is the optimum temperature to produce high quality oil, while higher temperature for drying will decrease the quality [13].

In-situ transesterification was conducted in 250 mL shake flask. Reaction temperature was varied from 70 to 120˚C. The temperature was controlled by hot plate and for the agitation by magnetic stirrer was fixed to 600 rpm for 3 hours. The other two parameters, catalyst loading and methanol to solid ratio were varied from 0.5 to 10.5 wt% and 8:1 to 12:1 respectively.

10 g of SCW were mixed with catalyst, methanol, and n-hexane as solvent in the shake flask. Table 1 illustrates the design of experiment. Experiment was designed by Design-Expert 7.0.0 using Central Composite Design package.

Table 1 Design of experiment

Std	Run	Temp. (˚C)	Catalyst (wt%)	Methanol: solid ratio	Biodiesel yield (%)
13	1	95	5.5	8	25.25
19	2	95	5.5	10	20.15
18	3	95	5.5	10	38.05
4	4	120	10.5	8	12.76
5	5	70	0.5	12	31.95
9	6	70	5.5	10	14.63
17	7	95	5.5	10	17.50
11	8	95	0.5	10	56.29
7	9	70	10.5	12	35.41
3	10	70	10.5	8	37.53
2	11	120	0.5	8	51.68
14	12	95	5.5	12	16.67
20	13	95	5.5	10	9.19
6	14	120	0.5	12	22.38
16	15	95	5.5	10	29.61
15	16	95	5.5	10	34.96
1	17	70	0.5	8	49.96
10	18	120	5.5	10	21.70
12	19	95	10.5	10	45.89
8	20	120	10.5	12	33.60

2.4 Analysis

Biodiesel composition was analyzed using GCMS 7683 B (Agilent). 0.1 mL sample was diluted with 3.9 mL n-hexane and 1mL of the sample was injected to column.Biodiesel yield was calculated using Equation (1) [13], [14]:

$$\text{Yield (\%)} = \frac{\text{biodiesel produced (g)}}{\text{Oil used (g)}} \times 100 \qquad (1)$$

3.0 RESULTS AND DISCUSSION

Oil was extracted using n-hexane as solvent. Result showed the average yield of oil is between 6 to 7 wt%. This means that even after the extraction of coconut milk and the drying of SCW, there is 6 to 7 wt% of oil in the residue. GCMS results for biodiesel produced are listed in Table 2.

3.1 Effect of Reaction Temperature

The effect of reaction temperature on the biodiesel yield was investigated to find out the optimum temperature for the maximum yield of biodiesel produced from SCW. The result in Figure 1 shows, biodiesel yield is increasing with the increasing of reaction temperature. This finding is consistent with Farooq *et al.* (2012) findings. Increase in temperature allows reactant to be more miscible which resulted in higher reaction rate [15]. Moreover, transesterification is an endothermic reaction which favours higher reaction temperature for production of biodiesel [16]. Nonetheless, the biodiesel yield decreases as the temperature rise above 95˚C. This indicates that 95˚C is the optimum temperature for transesterification of SCW

to produce biodiesel. The decrease in yield was due to high vaporization of methanol. Methanol remained in vapour phase and resulted in decrease amount of methanol available for the reaction [8]. In addition, methanol loses its polarity in high temperature which decrease the concentration of reactive methoxide species in the reaction mixture [17].

Table 2 GCMS analysis on biodiesel produced

No.	RT	Library/ID
1	7.461	• Lauric acid, methyl ester • Methyl isododecanoate
2	8.181	• Mandelic acid, 3,4-dihydroxy, tetrakis-TMS • Glyceric acid, tris(trimethylsilyl) derive.
3	8.213	• Mandelic acid, 3,4-dihydroxy, tetrakis-TMS
4	8.652	• Methyl isomyristate
5	9.304	• β-Resorcylic acid (TMS)
6	10.257	• Palmitic acid, methyl ester • Methyl 10-methyldodecanoate • Tetradecanoic acid, 10,13-dimethyl-, methyl ester
7	10.834	• Gentisic acid (tms)
8	12.057	• Diethylmalonic acid, monochloride hexadecyl ester • β-Alanine, N-isobutyryl-, ethyl ester • D-Alanine, N-ethoxycarbonyl-, pentadecyl ester
9	12.931	• Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester
10	15.541	• Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester
11	18.623	• Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester

3.2 Effect of Catalyst Loading

Catalyst loading is one of the most important factors that affect the yield of biodiesel. Maximum yield of biodiesel was obtained by using 0.5 wt% catalyst amount (Table 1). Based on Figure 1 and Figure 2, FAME yield was decreasing with the increasing of catalyst amount and slightly increase back at above 6 wt% catalyst loading. However, higher concentration of catalyst load into the reaction will cause soap formation. At higher catalyst concentration the mixture become too viscous and causes mixing problem [8], [18]. In addition, higher catalyst loading in the mixture resulted in catalyst accumulation on the wall of shake flask which has the tendency to diffusional problems and therefore lowering the activity [11], [19].

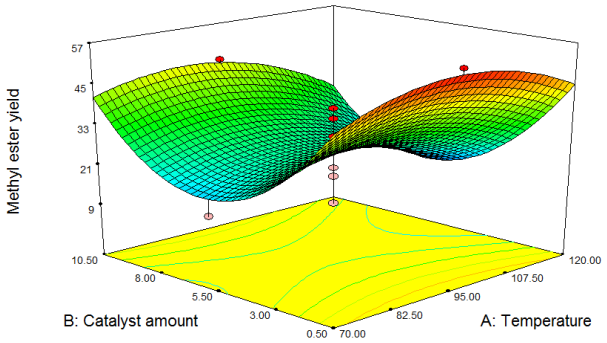


Figure 1 Interaction of reaction temperature and catalyst amount

3.3 Effect of Methanol to Solid Ratio

Stoichiometrically, 3 mol of alcohol are required to transesterify 1 mol of triglyceride to produce 3 mol of alkyl esters and 1 mol of glycerol. Since transesterification is a reversible reaction, an excess of alcohol is required to shift the equilibrium towards the formation of alkyl esters and increase the rate of methanolysis [8], [20]. Figure 3 shows biodiesel yield increase with the increase of methanol to seed ratio and started to decrease when further increase above 10:1 ratio. It is believed that the glycerol was largely dissolved in excessive methanol and thus inhibits the reaction of methanol to the reactant and catalyst subsequently interfering with the separation of glycerin [11]. This resulted in lowering the conversion by shifting the equilibrium in the reverse direction [21]. Based on Figure 3, the optimum methanol to seed ratio for high biodiesel yield is between 9:1 and 10:1. Table 1 stated that highest yield was achieved when methanol to seed ratio of 10:1 was used in the reaction.

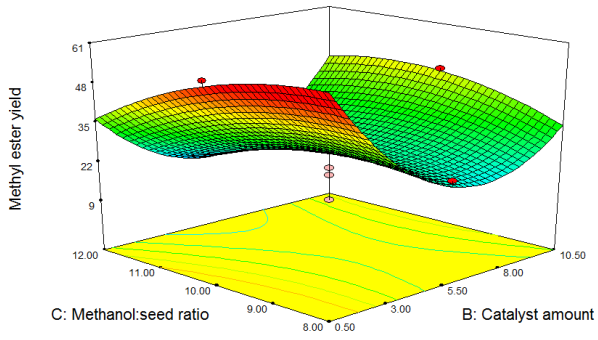


Figure 2 Interaction of catalyst amount and methanol to solid ratio

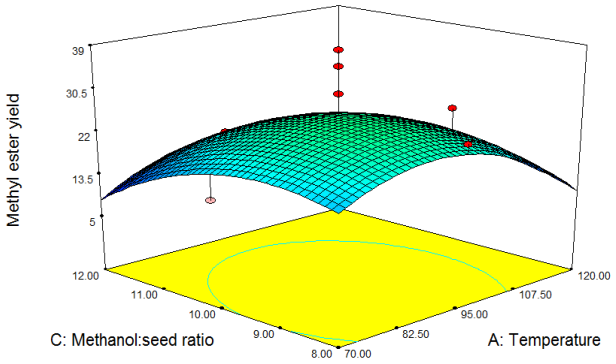


Figure 3 Interaction of reaction temperature and methanol to solid ratio

4.0 CONCLUSION

Solid heterogeneous catalyst synthesized from wastes is a cost effective and environmentally friendly catalyst. In addition, the use of solid coconut wastes as feedstock is a promising technology to have a better waste management and lower the cost of biodiesel production. The findings show, *in-situ* transesterification can eliminates the need of oil extraction and helps in simplification of the downstream processes. Further studies need to be done to find out the best condition for mass production of FAME. Energy and cost effective are the most important issues that need to take care of.

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