Optimization Study in Rubber Seed Biodiesel Production Using Nano-Magnetic Catalyst and Subcritical Methanol

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Abstract

Thailand is number the one natural rubber tree producer in the world. Rubber seed, and the agricultural residues that consider as waste in the natural rubber industry, has recently been found to be a potential non-edible source for biodiesel production. This rubber seed biodiesel can be produced and used as a major renewable energy in Thailand. In this study, the optimized condition of rubber seed biodiesel production was determined using Box-Behnken experimental design to improve FAME yield. Box-Behnken was selected in this work due to it is a suitable experimental designs for response surface methodology to understand the effect of each independent variable. Subcritical methanol or subcritical fluid, the novel clean technique, was selected as the environmental friendly method to enhance yield percentage in biodiesel production together with the presence of $KF/CaO\text{-}Fe_3O_4$ nano-magnetic catalyst. In conventional biodiesel production, the high free fatty acids (FFA) content of rubber seed oil was reduced by the esterification process from 16.72% to 1.6%. The properties of synthesized nano-magnetic catalyst was characterized by Scanning Electron Microscope (SEM), Brunauer–Emmett–Teller (BET) and the yield of fatty acid methyl ester (FAME) content was determined using Gas Chromatography (GC). The optimum condition which produced 91.92% FAME yield for rubber seed biodiesel production in this work is 20:1 molar ratio of methanol:oil, 2.47%wt of catalyst loading and 42.34 min of reaction time at 220ºC.

Keywords: *rubber seed oil, biodiesel production, nano-magnetic catalyst, subcritical methanol, two-step process and box-behnken design*

1. Introduction

Nowadays, the role of energy is strongly effecting human activities and all processes, also is the key input to sustainable development. It is well known that Thailand is the country of agriculture, thus the alternative energy such as biodiesel could be produced from many types of crop to fulfill energy security needs. Rubber is one of the most beneficial non edible plants which Thailand can produce up to 35 percent of the total world's rubber production (Reshad, Tiwari, & Goud, 2015). In 2014, estimated para rubber trees in Thailand were about 35,482.7 square kilometers (3,548,274 ha) and is increasing each year (Roschat, Siritanon, Yoosuk, Sudyoadsuk, & Promarak, 2017). Rubber seed, the waste from rubber industry (Samart et al., 2015), has attracted attention to be the potential crops for biodiesel production due to its 40 percent oil content and 20-25 percent humidity (Gimbuna et al., 2013). This potential biodiesel source has a high free fatty acids (FFA) content and must be reduced through an esterification process (Ramadhas, Jayaraj, & Muraleedharan, 2005).

Biodiesel was commonly produced through transesterification. For the conventional technique, transesterification was carried out with homogeneous catalyst such as potassium methoxide or potassium hydroxide (Daud, Abdullah, Hasan, & Yaakob, 2015; Refaat, 2011). The homogeneous catalysts were known as high activity and conversion, but they produce a large amount of chemical waste water, long-time consuming production, expensive and the catalyst are hardly possible to reuse or recoverable (Dwivedi, Jain, & Sharma, 2013). Therefore, the heterogeneous catalyst was studied to replace the homogeneous catalyst in the future. Unlike the homogeneous catalyst, the heterogeneous catalyst is environmental friendly and easy to be removed. One of the separating methods of heterogeneous is to involve a magnetic separation technique. Nano-catalyst exhibits good catalyst properties which have high activity and a large surface area. After combining the magnetic and nano-catalyst together, then nano-magnetic catalysts were formed (Tang et al., 2012; Hu, Guan, Wang, & Han, 2011).

Subcritical fluid technique was developed as one of the methods for biodiesel production and this technique also has been applied in various biodiesel productions such as biodiesel production from palm oil, castor oil, canola oil, sun flower oil and soybean oil. The main advantage of transesterification in subcritical condition for biodiesel production was high conversion and reaction rate due to the properties of subcritical fluids (Micic, Tomić, Kiss, Nikolić-Djorić, & Simikić, 2015; Sitthithanaboon et al., 2015). Subcritical technique has been applied in various biodiesel productions and also mostly considered as an environmental friendly and cost saving due to the decreased production time. Compared to the conventional technique, the biodiesel production cost could be reduced by applying subcritical fluid technique.

In this research, nano-magnetic catalyst was synthesized and applied to increase biodiesel yield. These heterogeneous catalysts with magnetic properties can be easily removed by a permanent magnetic. Subcritical methanol was selected as the method to produce the biodiesel production from rubber seed oil with the presence of a nano-magnetic catalyst. For biodiesel production, the optimum condition of supercritical fluids being investigated starts from design and sets up the laboratory-scale reactor. Box-Behnken experiment design was used to determine the optimum condition of rubber seed biodiesel production.

2. Objectives

The objectives of this study were to improve the FAME yield of rubber seed biodiesel production by combining subcritical fluid technique, subcritical methanol, with the presence of synthesized nano-magnetic catalyst which is easy to be removed and investigate the optimum condition for rubber seed biodiesel production using Box-Behnken experiment design.

3. Materials and Methods

3.1. Raw Materials

Rubber seeds from Phatthalung, Thailand. The rubber seed oil was extracted from rubber seeds by a mechanical pressing method. First of all, the rubber seeds were inserted to the deshelled machine and were dried after deshelled. Next, the rubber seeds were crushed and pressed to produce rubber seed oil using mechanical hydraulic pressing machine.

3.2. Nano-magnetic Catalyst Preparation

Magnetic core was prepared by a convenient co-precipitation method based on literature (Hu et al., 2011; Meher, Kulkarni, Dalai, & Naik, 2006; Tang et al., 2012) with some modifications. Firstly, $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3$ were mixed then dissolved in deionized water, $NH_3.H_2O$ was then added dropwise to the solution in a water bath of 60°C and with vigorous stirring for 60 min. The final pH value of the aqueous solution was maintained at 12.0. The black solid was separated by a permanent magnet and washed with distilled water until the pH value of filtrate decreased to 7.0. After that the black solid was dried at 60°C for 24 h, the precipitate was pulverized. Nano-magnetic solid base catalyst was prepared by an impregnation method. The resultant Fe_3O_4 magnetic core was fully mixed with CaO. Then, the mixture was completely dipped in aqueous solution of KF with different mass in range of 5.0–45.0 g and subsequently dried at 105°C for 24 h. Finally, the dried material was calcined in temperatures range of 300–800°C for 3 hours in a muffle furnace. The final catalyst $KF/CaO\text{-}Fe_3O_4$ was stored in a desiccator. Compared to the CaO catalyst these heterogeneous catalysts with magnetic properties can be easily removed by a permanent magnetic.

3.3. Esterification Process of Rubber Seed Oil

An esterification process was used to reduce the free fatty acid content in the rubber seed oil before biodiesel production. Rubber seed oil has high free fatty acids (FFA) content and must be reduced through the esterification process. The initial FFA content was measured to be 16.72%. In this process, rubber seed oil was heated to 60°C, methanol was added with molar ratio between methanol:oil at 6:1 and sulfuric acid was added in the amount of 2.5%wt. The solution was mixed for 30 minutes and then was aged for 3 days.

3.4. Transesterification Process of Pretreated Rubber Seed Oil

Transesterification reaction is a major path to produce biodiesel. For conventional process, the pretreated rubber seed oil was heated to 55°C according to the work of Gimbun et al., 2013, then methanol was added in molar ratio of 6:1 and KOH was used as a homogeneous catalyst for 1%wt. The mixed solution was stirred continuously for 67.5 min. Then the two phases of liquid which were methyl ester and glycerol were from each other by using a separation funnel. For a novel clean technique or a subcritical fluid technique, the process was run at a fixed temperature at 220°C under subcritical methanol conditions. The molar ratio between methanol:oil was varied to be 8:1, 14:1 and 20:1.The amount of catalyst was varied to be 1.5, 3, 4.5%wt oil and the reaction time was also varied to be 30, 45 and 60 minutes. After the reaction was completed, the nano-magnetic catalyst was separated using a permanent magnet. Then, the two phases of liquid, methyl ester and glycerol, were separated by using a separation funnel.

3.5. Nano-magnetic Catalyst Properties Analyzation

The morphology of KF/CaO-Fe_3O_4 nano-magnetic catalyst was analyzed by a Scanning Electron Microscope (SEM). The surface area (m^2/g) and pore size (nm) were analyzed using Brunauer-Emmett-Teller (BET).

3.6. FAME Yield of the Resultant Rubber Seed Biodiesel Analyzation

The FAME yield percentages were analyzed by a Gas Chromatography (GC) in the PE-5 column (0.25 mm x 60 mm x 0.25 µm).

3.7. Rubber Seed Biodiesel Production Optimum Condition

The optimum condition of rubber seed biodiesel production was calculated by a Response Surface Methodology (RSM) from Box-Behnken experiment design.

4. Results and Discussion

4.1. Rubber Seed Oil Properties

The properties of rubber seed oil before the pretreatment were shown in Table 1. The result shows that the viscosity of the experimental rubber seed oil is similar to one from the literature, but both didn't fulfill the standard value. Rubber seed oil density of both experimental and literature has achieved the standard value. Rubber seed has a high FFA content, the initial FFA content before the esterification pretreatment was 16.72%. In general, free fatty acid value of rubber seed oil was measured and reported that it is always higher than other plant biodiesel sources, but in this research, the free fatty acid was reduced from rubber seed oil before being used in biodiesel production to be 1.6% which is <2% (fulfill the standard value). Hence, the experimental free fatty acid was adjusted to the standard value.

Table 1 Physical and chemical properties of rubber seed oil from experimental compared to literature

Properties	Experimental	Literature[2]	Standard[3]
Viscosity (mm^2/s)	31.81	30.30	3.5-5
Density (kg/m^3)	881	920	860-900
Free Fatty Acid (%)	16.72	7.50	<2

[2]Pactcharapon et al., 2007.
[3]Widayat, Wibowo, & Hadiyanto, 2013.

4.2. Nano-magnetic Catalyst Properties

The properties of KF/CaO-Fe_3O_4 nano-magnetic catalyst was first analyzed by Brunauer-Emmett-Teller (BET). The BET results reported that the surface area of KF/CaO-Fe_3O_4 was 61.22 m^2/g and the pore size of the catalyst was measured to be 10.58 nm.

The morphology of KF/CaO-Fe_3O_4 nano-magnetic catalyst was shown in Figure 1. The Scanning Electron Microscope (SEM) image shows that the catalyst particles were mostly agglomerated and formed into the larger crystal structure. Even though the particles were agglomerated, the surface area of the synthesized catalyst was still high due to the special properties of a nano catalyst. In addition, the most outstanding properties of this heterogeneous catalyst is it was easily removed by a permanent magnet after the biodiesel production is completed.

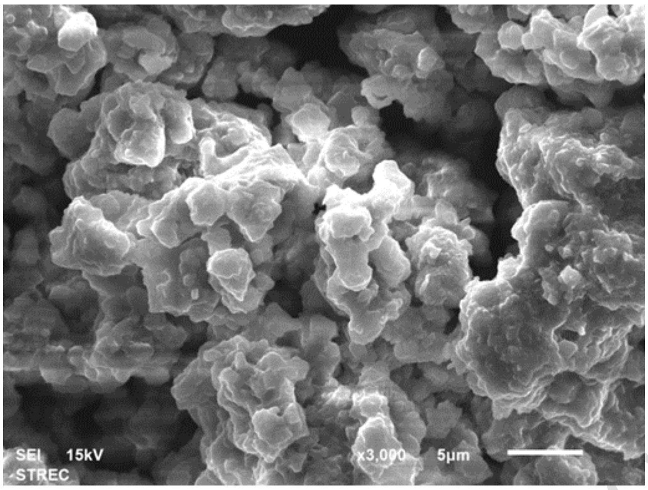

Figure 1 The morphology of KF/CaO-Fe_3O_4 nano-magnetic catalyst at 3000x magnification

4.3. Rubber Seed Biodiesel Production

The rubber seed biodiesel production in this work was divided into two techniques: conventional biodiesel production using KOH homogeneous catalyst and a novel clean technique using subcritical methanol with nano-magnetic heterogeneous catalyst. For the conventional biodiesel production, transesterification reaction with KOH as a homogeneous catalyst produced rubber seed biodiesel with 92.06% FAME for 4 days and used a huge amount of waste water.

For a novel clean technique, the rubber seed biodiesel production using subcritical methanol and nano-magnetic catalyst was studied using Box-Behnken statistical tools. Calculating results from the 15 Box-Behnken experiment designs with Response Surface Methodology (RSM) to investigate the optimum condition for rubber seed biodiesel production using subcritical methanol with the presence of KF/CaO-Fe_3O_4 nano-magnetic catalyst. The linear regression for this experiment is:

$$Y=69.97+13.82X_1-5.76X_2-2.66X_3+7.36X_1^2-8.41X_2^2-5.38X_3^2+1.03X_1X_2+0.39X_2X_3+1.21X_1X_3$$

where Y is the predicted %FAME value, X_1 is the first effecting parameter which referred to molar ratio between methanol:oil (coded with -1, 0, 1), X_2 is the second effecting parameter which referred to the amount of catalyst load (coded with -1, 0, 1) and X_3 is the third effecting parameter which referred to the reaction time (coded with -1, 0, 1). The R squared value for this equation is 0.98 and P-value equals 66.04, which means that the results were reliable and compatible with this analytical method.

The effects of each parameter are shown in Figure 2, 3 and 4. Figure 2 shows the effect of the amount of catalyst load and reaction time for subcritical methanol biodiesel production at constant molar ratio between methanol:oil. At constant molar ratio 14:1, it shows that the %FAME of biodiesel increased with the increasing of the amount of catalyst load, but after it reached 3%wt, the %FAME will be slightly decreased. The highest %FAME was at 71.20% with 2.27%wt of catalyst load and 38 min of reaction time at a constant molar ratio 14:1.

Figure 3 shows the effect of molar ratio between methanol:oil and reaction time for subcritical methanol biodiesel production at a constant amount of catalyst load. At constant 3%wt amount of catalyst load, %FAME rose up to 91.23% at 20:1 molar ratio and a 41.50 reaction time. The prediction graph shows that %FAME will be increased with the increase of molar ratio and reaction time.

The effect of molar ratio between methanol:oil and the amount of catalyst load for subcritical methanol biodiesel production at a constant reaction time is shown in Figure 4. At 45 minutes of constant reaction time, it was found that the molar ratio affected FAME percentage the most. The highest FAME percentage of this effect was observed to be 91.78% with 20:1 molar ratio between methanol:oil and 2.27%wt of catalyst load. The rubber seed biodiesel production FAME yield in this work is higher than the resultant FAME yield in the work of Samart et al. (2015) at 84.0%, and Widayat et al. (2013) at 91.05% was also much faster.

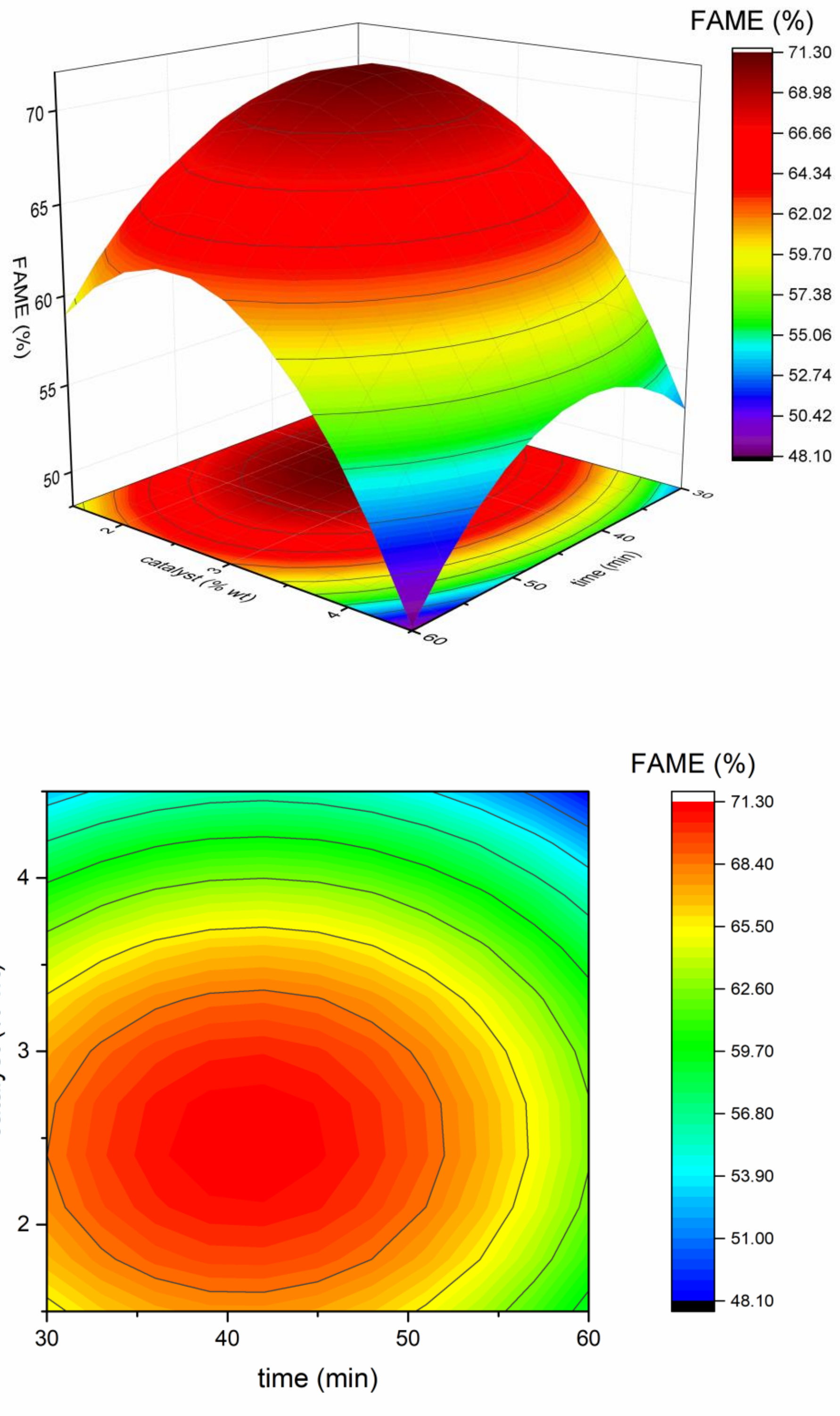

Figure 2 Effect of the amount of catalyst load and reaction time for subcritical methanol biodiesel production at a constant molar ratio between methanol:oil

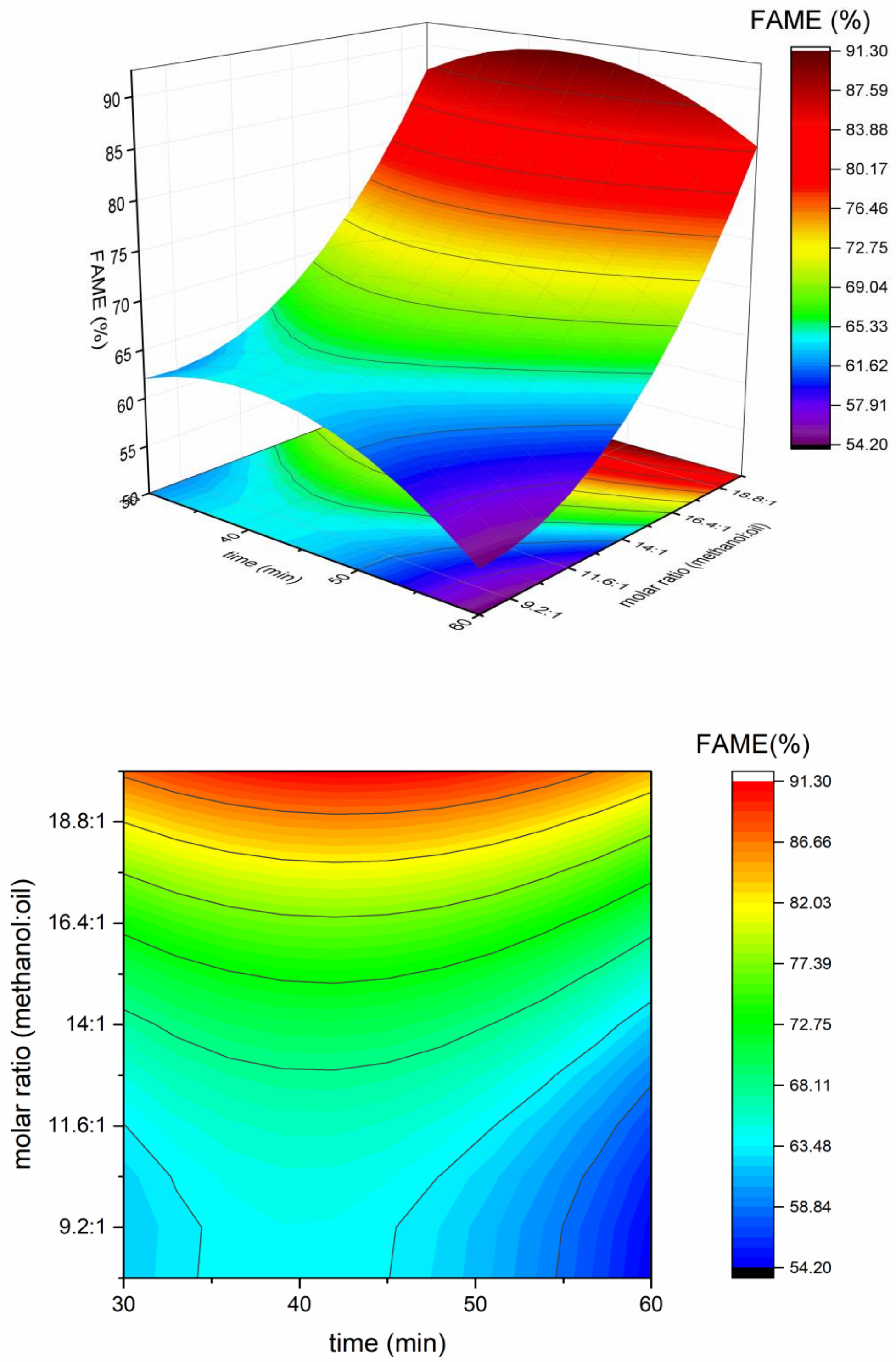

Figure 3 Effect of molar ratio between methanol:oil and reaction time for subcritical methanol biodiesel production at a constant amount of catalyst load

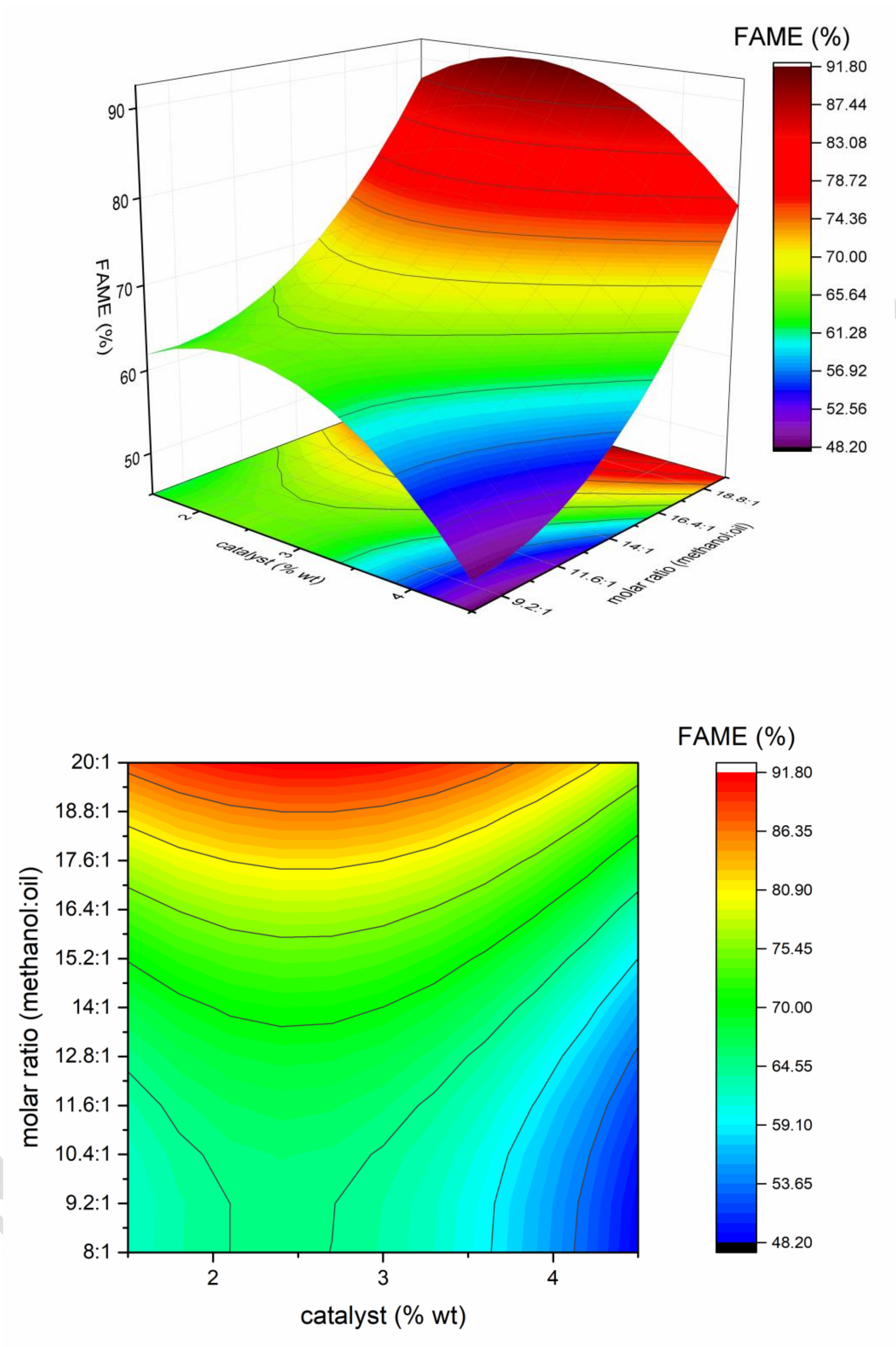

Figure 4 Effect of molar ratio between methanol:oil and the amount of catalyst load for subcritical methanol biodiesel production at a constant reaction time

From Figure 2, 3 and 4, Box-Behnken experimental designs resulted in three response surfaces which explained the effect of the three individual variables, molar ratio between methanol and rubber seed oil, catalyst amount and reaction time. The contours illustrated that the FAME yield increase due to the increase of molar ratio between methanol and rubber seed oil. On the other hand, the FAME yield decreased due to the decreasing of catalyst amount and the reaction time. By reducing catalysts amount and reaction time, the biodiesel production is considered to be more efficient.

The study of the previous effects from the three parameters led to the investigation of optimum conditions, which was then calculated by the Quadratic Regression Mode. The calculated results shows that the optimum condition for rubber seed biodiesel production is at 20:1 molar ratio between methanol:oil, 2.47%wt of catalyst load and 42.34 minutes of reaction time, at this condition the FAME percentage reached 91.92%.

5. Conclusion

Rubber seed oil was extracted from rubber seeds by the mechanical pressing method. The resultant rubber seed oil then was characterized by its properties, the density, viscosity and free fatty acid content were 881 kg/m^3, 31.81 mm^2/s and initially 16.72% (reduced to 1.6% after esterification process), respectively. The KF/CaO-Fe_3O_4 nano-magnetic catalyst were synthesized and used as high efficiency biodiesel production catalyst in this work. The novel clean technique using subcritical methanol with KF/CaO-Fe_3O_4 nano-magnetic catalyst significantly reduced the reaction time to 30 minutes instead of 4 days of the KOH conventional transesterification.

The optimum condition for rubber seed biodiesel production analyzed using the Box-Behnken experiment design and Response Surface Methodology (RSM) was 20:1 molar ratio of methanol:oil, 2.47%wt of catalyst loading and 42.34 min of reaction time. The optimum condition effectively produced rubber seed biodiesel with 91.92% FAME yield. Therefore in this research, the biodiesel was successfully produced from rubber seed oil using an environmental friendly subcritical technique and efficient nano-magnetic catalyst that significantly reduced reaction time.

6. Acknowledgements

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