Synthesis and characteristic bioadditive of rubber seed oil as low pour point biodiesel CPO

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Abstract: The bigest point from CPO biodiesel is the high pour point, which is if used at low temperature will cause blockage the filter and fuel lines that make some problem in machine. To solve this problem was using pour point lowering additive, the widely used additive now was chemical commercial additive, which is have highest prices. Methyl ester that made form rubber seed oil have high free fatty acid needed two step reaction, esterification reaction to lowering the free fatty acid to ≤ 2% and transesterification reaction. The reaction variable was temperature, rubber seed oil/methanol ratio mol and concentrations of KOH catalyst. Response Surface Methodology was used at transesterificstion reaction, first to know interaction variables effect in reaction, and seconded to get the optimum point. Optimum yield was obtained at 1/6 oil/methanol ratio mol, 1% concentration KOH catalyst and temperature 60˚C with time reaction was 90 minutes. Reaction at the optimum condition obtains 99.61% conversion methyl ester (bioadditive) rubber seed oil.
Keywords*:*bio-additive, pour point, biodiesel, CPO, rubber seed oil.

Introduction

Pour point lowering additive is a substance added to the high pour point biodiesel to reduce the pour point of biodiesel. Additives are generally synthesized from petroleum derivatives which are relatively has high price and cannot be renewed. In North Sumatra Rubber plants are seeded crop beside to palm oil. The rubber plantation agriculture spread almost throughout the district. The area of rubber plantations in North Sumatra reached 442,516.12 hectares, with details; national estate plantations: 442,516.12 Ha, Foreign Private Estates: 36351.18 Ha and Smallholder: 304 650 hectares, with total production reaching 323 036 680 tons. (Expost Balitbang SUMUT, 2011). Rubber seeds are side product of rubber plantations, only limited use as seed (10% only, so that the remaining 90% are generally thrown away).

Oil content of rubber seed are 45-50% with composition consists of saturated fatty acids; 8.7% stearic acid, 10.2% palmitic acid and unsaturated fatty acids; oleic acid 24.6%, linoleic acid 39.6%, 16.3% linolenic (U.S. Ramadhas, 2005). high content of unsaturated fatty acids that causes rubber seed oil pour point lower, so that it can be synthesized into bio-additive lowering pour point crude palm oil biodiesel. Besides the abundance of raw materials for the manufacture of these additives, rubber seed renewable and environmentally friendly making byproduct of rubber plantation is more valuable economically. Indonesia as the largest producer of palm oil and rubber, especially in northern Sumatra has the potential to develop a palm oil biodiesel with a low pour point. Rubber seed oil is non-edible oil that utilization will not disrupt the stability of edible oil.

Experimental

Materials:

The main materials used in this study are rubber seeds were obtained in smallholder at Langkat North Sumatra. CPO obtained from Oil Palm Research Center Field Medan. Methanol, KOH, n hexane, sulfuric acid p (pa), sodium sulfate anhydrous, n-hexane, benzene obtained from the E'Merck p.a. degree.

Preliminary research

Preliminary study aims to determine the best value of each process variable. Indicator to determine the best value is the amount of conversion of methyl ester (bioadditive) of rubber seed oil produced

$$\text{Esterconcentration } (\%\text{-w/w}) = \frac{100(As - Aa - 18{,}29Ggt)}{As}$$

The raw materials of rubber seed oil has a high content of free fatty acids by 17% the manufacture of biodiesel is done in two stages, the esterification process to lower free fatty acid content to ≤ 2% and to form the biodiesel by transesterification process (Ramadhas et all, 2005). Later in the transesterification process, mole ratio of oil with methanol 1: 6, the catalyst used is KOH 1% oil by weight and temperature 65^{O}C for 90 minutes.

Process Optimization Research

Individual and interactive influences on the synthesis of rubber seed oil bioadditif with other variables are optimized to achieve maximum conversion percentage using Surface Method Remarks (Response Surface Methodology, RSM). Five levels and three studies designed to follow the shape variable Central Composite Design (CCD), which consists of 8 points (points) factorial, central point 6 (Montgomeri, 1997).

Central point in the experimental design of the CCD is the best conversion of each variable obtained through preliminary research. Variables and levels that developed in one of the reactions shown in Table1.while Table2.shows the actual experiments are performed and developed from the model.

Table 1. Variables and Level for Experimental Design 3 Variables

Variable	Level Variables Coded				
	-1,682	-1	0	1	1,682
Temperature oC	55	60	65	70	75
Mole Ratio Oil/Methanol	1/2	1/3	1/6	1/9	1/10
Catalys Concertration KOH % w/w	0,20	0,5	1	1,5	1,8

Table 2. Combination encoded Level to Level Five, and Three Variables

No.	Catalyst	Mole ratio	Temperature
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1,682	0	0

10	1,682	0	0
11	0	-1,682	0
12	0	1,682	0
13	0	0	-1,682
14	0	0	1,682
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Data were analyzed using multiple regressions to fulfill the three following order polynomial equation:

Y = b0 + bixi +bixi2 + biiixiii3 + bbij xixj + bijk xi xj xk

Regression analysis, analysis of variance (ANOVA) and response surface analysis performed using Minitab software R. 16.

Yield Optimization Research

Yield optimization study aimed to determine the effect of the interaction of these three variables in a control composite experimental design (CCD), as well as to determine the optimum yield that can be obtained from the synthesis of rubber seed oil bio-additive.

Result and Discussion

Synthesis of methyl ester (bioaditif) rubber seed oil esterification, followed kemudiaan transesterifiukasi. Selection criteria using this method because of rubber seed oil has a high free fatty acid content of 17% (Ramadhas et.all, 2005) on the esterification process is done to reduce fatty acid content to ≤ 2% and the transesterification process to form methyl ester (bioaditif) oil rubber seeds.

Process Optimization Research

Optimization study aimed to determine the effect of the interaction of these three variables in central composite experimental design (CCD), as well as to determine the optimum conversion which can be obtained from rubber seed oil bio-additive synthesis through esterification and transesterification reactions proceed with.

Analysis of Effect of Variables

Based on a statistical analysis of the research data obtained by the model equation that can show the relationship and interaction of the reaction variables% conversion with an error tolerance value of p> | T | 0.05 obtained as follows:

$$Y = 83,5546 + 2,0842X_1 + 2,4569X_2 + 1,5363X_3 - 3,4926\,X_1X_2 + 0,2372\,X_1X_3$$

$$- 2,5445\,X_2X_3 - 2,8810\,X1^2 - 3,8941\,X2^2 - 4,7685\,X3^2 \text{(Eq. 2)}$$

Obtained a second order models will be plotted as a response surface and contour three-dimensional surface to express the response% conversion of the experiment.

Effect of Catalyst Concentrationagainst Ratio Mol KOH methanol/oil

The surface plot (in fig.1) express that increased conversion of rubber seed oil bio-additive more sharply on increasing the mole ratio oil/methanol compared with the increase of KOH catalyst. Increasing methanol mole ratio will lead to an increase in concentration of the mixture. At a high concentration of the mixture, the chances of a collision between the larger particles, so that the greater occurrence of transesterification reactions.

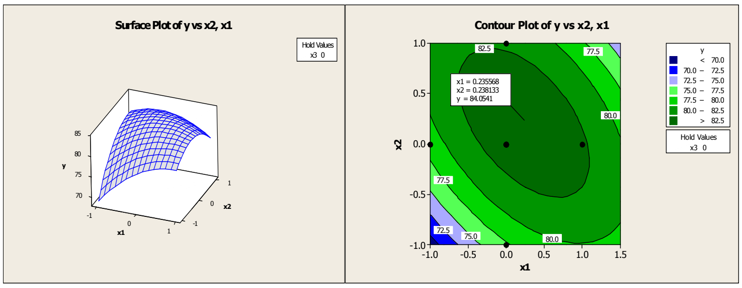

Fig.1 Response Surface and Contour of Plots amount of KOH catalyst VS Mol Ratio Methanol /Oil

This is consistent with the statistical results, that the variable which gives greatest significance and positive is a mole ratio of methanol to oil rubber seed at 2.4569. This shows the transesterification reaction conditions with low catalyst amount (level -2), giving the range of conversions by 76.5% when the mole ratio of methanol / oil increased.

Contour surface shows that the maximum value of the conversion to bio-additive rubber seed oil can be obtained when the mole ratio of methanol / oil rubber seed at the level of 0.25 (mole ratio of methanol / oil rubber seed on 6,75:1), whereas the concentration of catalyst at a level between 0.25 (1.125%). On the reaction conditions, can be obtained bio-additive rubber seed oil conversion reached 84.05% this is followed by a review that to use a mole ratio of methanol / oil rubber seed greater than 0.25 both at the level of the amount of catalyst KOH low or high obtained reduction product conversion.

Temperature Effect against Catalyst Concentration of KOH

Surface expression of the curve shows (in fig.2) that the optimum reaction conditions of temperature lies in the center of the arch curve.

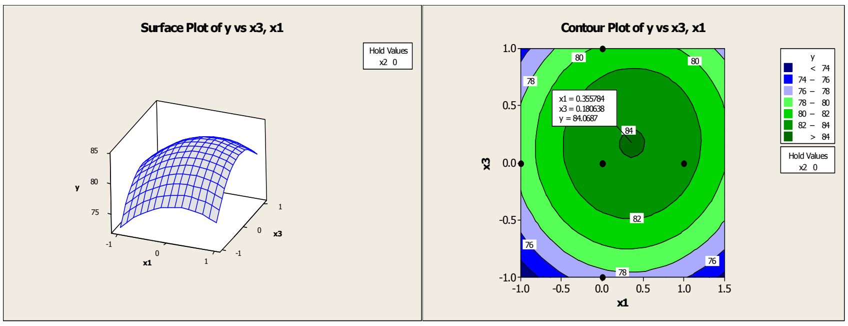

Fig.2Response Surfaceof Plot amount of KOH Catalyst – Temperature

From contour above, it can be seen that the design temperature conditions at the level of 0.18 (66 0C) and the amount of KOH catalyst at the level of 0.36 (1.2% w / w) may result in the acquisition of 84.07% bio-additive maximum conversion. At this temperature level (66 0C) allows an increase in activity towards transesterification catalyst KOH.

Temperature rise in the use of KOH catalyst remains at the level initially will enhance the enjoyment of the product. But in the end, the temperature rise will lower product acquisition. This shows that the temperature level> 0.18 (> 66 0C) catalyst is no longer active. This condition expresses that the temperature can trigger the activity of the catalyst in the transesterification reaction. The use of temperature levels> 0.18 (> 66 0C) may result in decreased catalytic activity, while the length of the reaction (not raised). If the drop occurs, then the catalyst activation energy is reduced and the speed of the reaction will decrease.

Effect of temperature against mole ratio of methanol/Oil
Response surface in Fig.3 Illustrates that at low temperatures (level -2), acquisition bio-additive % conversion of rubber seed oil increase with the use of a mole ratio of methanol / oil rubber seed on transesterefikasi reaction. But significant influence and more sharply given by variable mole ratio of methanol / oil compared with the temperature

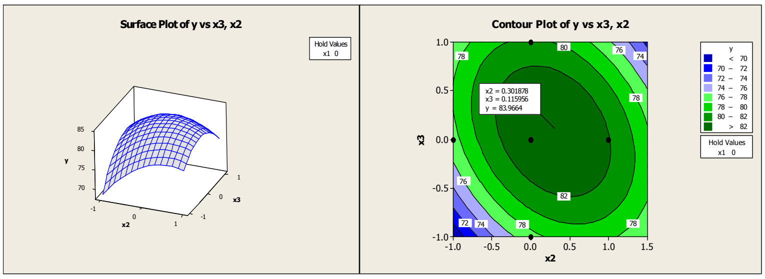

Fig.3 ResponseSurface and Contour of Temperature againstMole RatioMethanol/Oil

The response contours indicate that to obtain the percentage of product acquisition the maximum bio-additive, variable temperature can be designed at the level of 0.1 (65.2 oC°C) and level mole ratio of methanol / oil rubber seed at the level of 0.3 (ratio 7: 1).

In these conditions, the conversion gain can reach 83.97%. Methanol mole ratio gives greater influence of the temperature on the formation of rubber seed oil bio-additive. At moderate temperature conditions (65.2 ° C), mole ratio increased initially to increase sharply acquisition, but in the end will give you the conversion decreased. This condition is seen from the statistical analysis, that the mole ratios of 2.4569 while the effect of temperature only give effect to the product of 1.5363.

Yield Optimization Research
Model equations obtained designate the relationship variable and its interaction reactions percent yield bio-additive rubber seed oil:

$$Y = 99{,}6139 + 2{,}0842\,X1 + 2{,}4541X2 + 1{,}5907\,X3 - 3{,}4857X1X2 + 0{,}2520X1X3 - 2{,}6982X2X3 - 3{,}0056X11 - 4{,}0186X22 - 4{,}8940X33 \quad \text{(Eq. 3)}$$

From equation (3) shows that the maximum percent yield in the reaction of rubber seed oil and methanol is 99.61%.

Characteristics of Biodiesel
Overall results and analysis of the characteristics of palm oil biodiesel are metanolisis rubber seed oil using KOH catalyst according to ASTM method D6751 were conducted in the laboratory of Process Research Organic Chemistry and Industrial Chemistry, State

University of North Sumatra and in one private company National Biodiesel presented in Table 3. (in supplement).

Effect of Addition Ratio AgainstBioaditif MBK Biodiesel Pour Point CPO

The research results are listed in Table 4 (in supplement) seen that the average decline in CPO biodiesel pour point is at 2oC each additional bio-additive rubber seed oil by 5% by volume (95% biodiesel CPO). Pour point ASTM D7651 qualified obtained bio-additive start adding 17% rubber seed oil which is derived pour point of 10 ° C (the minimum required ASTM D6751). Of table 5.seen that the decrease in pour point crude palm oil biodiesel is the liner. This is in line with that obtained by Sarin. R et al in 2007, which reported on his research with the CPO biodiesel blend of jatropha oil biodiesel.

Conclusion

Synthesis bioaditif transesterification of rubber seed oil after a pretreatment has been developed with a reaction time of 90 minutes, a mole ratio of methanol / oil rubber seed 6: 1, 1% KOH catalyst concentration and temperature of 65oC.The results yield optimization bioaditif rubber seed oil synthesis in the process of transesterification of rubber seed oil obtained maximum conversion yield of 83.55% and 99.61% percent.The more the proportion bioaditif rubber seed oil in the mixture, the lower its pour point. Biodiesel low pour dotted mixing biodiesel derived from palm oil with bioaditif rubber seed oil is 10 ° C in the composition of 17: 83, pour point obtained 7oC the optimum composition of 25: 75.
For suggestion, performance testing needs to be done so as to know the influence of the use of biodiesel is lower dotted pour the diesel engine.

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