

Analysis Of Methanol And H₂so₄ Usage On Biodiesel Esterification Reaction And B20 Effect On Exhaust Gas Emission

Idzani Muttaqin*, M. Suprpto, Budi Setiadi*****

Faculty of Technique, Industrial Technique Programme*, Mechanical Technique Programme** Informatics
Technique Programme***

Universitas Islam Kalimantan Muhammad Arsyad Albanjari Banjarmasin

ABSTRACT

Biodiesel is one of alternative energy sources that are environmentally friendly and updatable. In this study, the materials used to make biodiesel were CJO (Crude Jatropha Oil) or castor oil whose contents were Free Fatty Acid (7,72%), Acid Value (15,44 mg KOH/g), and Gum (39,98 ppm).

In the process of biodiesel production, especially in esterification, the use of chemical such as (50%) methanol (CH₃OH) and (3%) Sulfuric Acid (H₂SO₄) tend to be excessive and the reacting time also tend to be longer (3 hours) to avoid failure in the process of esterification reaction.

This research could save the use of chemicals such as methanol (19%) and sulfuric acid (0,5%) in one year, the cost could be saved about Rp 122.885.684 where the reduction percentage of the cost for catalyst esterification was about 63% of the previous one and the time of esterification reaction could be shortened to (1 hour) at a ratio of better quality, while comparing the quality of emissions produced in the form of CO values (Carbone Monoxide) and NO₂ (Nitrogen Dioxide) with diesel and B20 (80% fuel 20% biodiesel) as a material for testing on the engine generator by using Komatsu 160-7 EGS (140 Kva).

Keywords : Reaction, Esterification, Emission and Biodiesel

PRELIMINARY

The fuels commonly used for all this time still depend on fossil fuels which are gradually diminished and finally exhausted. Biodiesel is one of the alternatives for fuel. Biodiesel fuel is one kind of fuel which consists of mono-alkyl ester mixture from the long chain of fatty acid, so biodiesel fuel is made of renewable fuel such as animal fat or plants.

Biodiesel fuel may be called as one of the right solutions for alternative energy to substitute fossil fuels, in which fossil fuel is the main energy source for worldwide transportation.

Biodiesel is biodegradable; there is only a tiny or even almost no sulfur inside, even though the production process is not environmentally friendly. The alternative of this fuel consists of ethyl ester or so-called methyl; it results on trans esterification both from triglyceride (TG) or esterification of free fatty acid (FFA). The biodiesel fuel is more attractive because of its benefit to the environment. Nowadays, most of biodiesels are made of safe and consumable resource trans esterification, such as animal fat, vegetable oil, and even cooking oil waste, with reaction process. Albeit, biodiesel is currently more expensive than fuels derived from fossil or crude oil because of high consumption of catalyst and suds formation, and also the low harvest production as biodiesel basic ingredients.

Biodiesel

Biodiesel is made of mono alkyl ester which is fatty acid ester comes from vegetable oil. Fuel from vegetable oil (biodiesel) is known as

environmentally friendly, non-harmful for air, easily biodegradable and renewable ingredients derived product. Biodiesel can also be derived from trans esterification reaction of triglyceride or free fatty acid esterification reaction which depends on the quality of vegetable oil as the ingredient. Trans esterification is a process that reacts the triglyceride inside the vegetable oil or animal fat with short chain alcohol such as methanol or ethanol (methanol is mostly used in biodiesel production for now) so that it produces fatty acids methyl esters (FAME) and glycerol (glycerin) as additional product. Catalyst used in trans esterification process is base/alkali, usually potassium hydroxide (KOH) or sodium hydroxide (NaOH).

According to content materials of FFA for vegetable oil, biodiesel processing commercially can be distinguished into 2 processes:

1. Esterification by using acid catalyst for vegetable oil with high FFA contents.
2. Trans esterification by using base catalyst for refined oil or vegetable oil ingredients with low FFA contents.(Kurniasih, E, 2013)

Jatropha Curcas

Jatropha curcas or commonly called Jatropha, is a plant which has been existed since a long time ago. This woody shrub plant is known for its endurance towards dryness and the breeding is easy with cuttings, this plant can be easily found in tropical area. Since old time, this plant has been known that it could be used for medical ingredients

and poison antidote; these days, Jatropha plant is drawing attention for its usefulness as biofuel source whose oil contents in its seed can be used as diesel.

Jatropha Seeds Oil

Jatropha seeds oil is one of non-food oil material sources which are generated from plants. Because of its high oil contents and different characteristics, it is interesting to use it in biodiesel production. Jatropha oil extraction is usually done with mechanical compression which is more worthy economically.

Jatropha seeds contain vegetable oil rendemen as much as 35 to 45 percent. The oil can be processed into biodiesel oil (substitute for diesel) and fuel (substitute for kerosene). Jatropha chemical composition is: Oil 54%, carbohydrate 13%, fiber 12.5%, ash 2.5%, protein 18%; while fatty acid contents in Jatropha oil are ricinoleic acid 86%, oleic acid 8.5%, linoleic acid 3.5%, stearic acid 0.5 – 2.0%, and dihydroxy stearate acid 1 – 2%. Shown in Table 1.

In case of using Jatropha seeds oil as biodiesel, it should be processed firstly through methylation process, just like any other vegetable oil. Then, Jatropha seeds oil can be used as it is or it can be mixed with diesel oil in specific composition.

Biodiesel made of plant oil such as Jatropha, palm, etc., can be easily found in Indonesia because abundant of materials are there. However, the obstacle is about how we build this energy production chain. Starts from farmers as the main cast in providing materials for the distributors in which availability and sustainability would not impair the farmer's farm production.

Countries, such as West European countries and Japan, that have high awareness for the environment are now ruling the obligation to sell biodiesel in gas station (Setyadi and Susiantini, 2005)

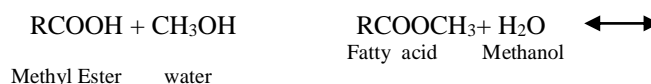
Table 1 Jatropha oil characteristics (Biodiesel Laboratory PT Alam Tri Abadi)

Characteristics	Value
FFA	7,72 %
Acid Value	15,44 mg KOH/g
Gum Content	< 40 ppm

Esterification

Esterification is a reaction process between acids, in this case, free fatty acids (FFA) with alcohol; the alcohol used is the short chain alcohol (methanol or ethanol), so that it forms fatty acids methyl esters (FAME) and water. Catalyst used in esterification reaction is acid, mostly uses sulfuric acid (H₂SO₄) or phosphoric acid (H₂PO₄).

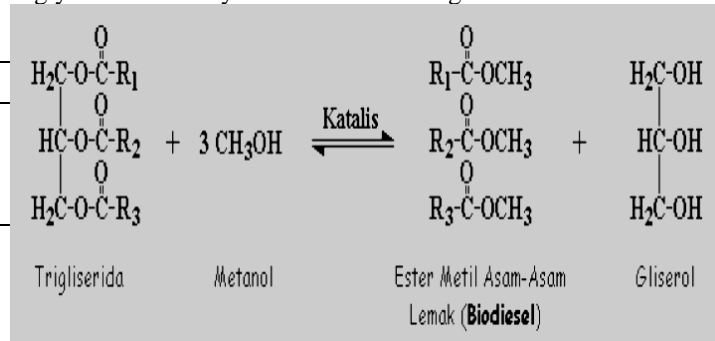
In order to boost the reaction to run perfectly on low temperature (e.g. the highest is 120°C), then methanol reactant should be added in larger amount than usual (usually larger than 10 times stoichiometric ratio) and water contents from follow-up product of reaction should be eliminated from the phase, which is oil phase. Through the combination of reaction which is done correctly from the reaction condition to water elimination method, then the perfect conversion from fatty acids to methyl ester can be done in around 1 hour to only several hours. The esterification reaction from fatty acid to methyl ester is as following:



This esterification is usually done to make biodiesel from oil whose free fatty acids contents are high (P acid-value 5 mg-KOH/g). On this step, free fatty acids will be converted into methyl ester. The esterification step is usually followed by trans esterification step. However, before the esterification product is processed by trans esterification step, water and the biggest part of acid catalyst inside should be eliminated first. (Ketta, 1978)

Trans esterification

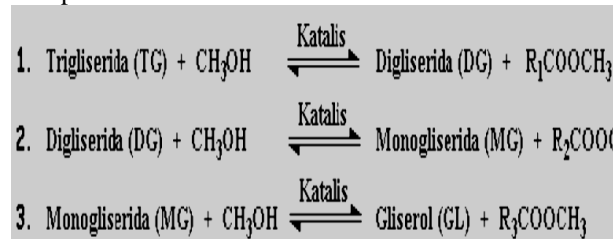
Trans esterification is a reaction of organic exchange from triglyceride (vegetable oil) into alcohol (alkyl ester). Then, this reaction will result on side product which is glycerol. Among the monohydric alcohols that are included in alkyl ester group, methanol is the most commonly used because the price is affordable and the reactivity is the highest (so this reaction can be called as methanolysis). Therefore, in most parts of the world, the practical biodiesel is identical to fatty acids methyl ester. The trans esterification reaction of triglyceride to methyl ester is as following:



The purpose of trans esterification reaction in biodiesel processing is to wholly eliminate the triglyceride contents, decrease the flash point, decrease the boiling and freezing point, and decrease the reacted oil viscosity. Meanwhile, catalyst which is usually used in trans esterification reaction is the

base catalyst because this catalyst can fasten the reaction.

Trans esterification reaction can be done in 3 steps:



The expected products from trans esterification are fatty acids (methyl ester). There are some ways of processing to make the equilibrium more towards the products, which are:

- a. Separate the glycerol.
- b. Add more methanols into the reaction process.
- c. Lower the temperature when the reaction process is running. (Freedman, et al., 1984)

Research Framework

This research was done based on several experiments by using fixed variables and the change corresponded to the specified parameter, with the measuring parameter used were according to EN 14214 standards which have been adjusted to biodiesel factories' needs.

For the best quality of biodiesel, we used B20 composition, whose contents were 20% biodiesel + 80% diesel, as the comparison for measuring exhaust gas emission on KOMATSU EGS 160-7 generator set. The measured exhaust gas emissions were diesel, B20 before the analysis, and B20 after the analysis of its chemical materials usage.

EN 14214 Standards (Europe Number)

Biodiesel's energy contents are far less than conventional diesel. There are several biodiesel specification standards, such as: European biodiesel standards EN 14214:2002(E), ASTM D6751-02a, and also SNI/Kep Dirjen EBTKE No.723K/10/DJE/2013. Basically, biodiesel specification standards in the world were developed by referring to European and American standards. European biodiesel standard EN 14214:2002(E), copes almost all parameters set in American and Indonesian biodiesel standards.

The technical definition of biodiesel is a kind of fuel which is suitable for diesel engine seen from the fatty acid mono alkyl esters processing gained from oil or fat production biologically, such as vegetable oil, animal fat, and micro algal oil. Biodiesel fuel can also be produced by using any other kind of alcohol, such as ethanol to produce fatty acid ethyl esters but this type of biodiesel does not meet the standards of EN 14214 compared to methyl esters to produce biodiesel by using methanol.

One of the biodiesel percentages, e.g. B100 consists of pure biodiesel contents, B99 means that the biodiesel contents are 99%, 1 % petro diesel; while B20 consists of 20% biodiesel and 80% diesel/fuel (wikipedia).

Emission

Exhaust gas emission is a pollutant that harms the air produced by vehicle exhaust gas. Vehicle exhaust gas means the residual gas from the combustion process discharged into the air through the vehicle exhaust. Exhaust gas emission contains many chemical compounds. For the composition of contents on its chemical compounds depends on: driving condition, engine type, fuel emission controller tool, operation temperature, and other factors which make the emission pattern complicated. There are five elements in vehicle exhaust gas, which are: HC (Hydrocarbon), CO (Carbon Monoxide), CO₂ (Carbon Dioxide), O₂ (Oxygen) and NO_x (Nitrogen Oxide) compounds. While other countries whose emissions are not too strict only measure 4 element compounds of exhaust gas, which are HC, CO, CO₂, and O₂. The type of fuel which is considered as pollutant is discharged by engine, whether it is fuel or diesel which is the same, the only thing to differentiate is the proportion because the engine operation is different. Visually, we can see the smoke out of the exhaust of the vehicle with diesel fuel, while it cannot be seen in vehicle with fuel. The exhaust gas of vehicle contains element compounds which are not too dangerous, such as nitrogen, carbon dioxide, and water vapor, albeit, there are also other compounds with quite large amount which could harm our health and environment. The pollutant materials in vehicle exhaust gas are carbon monoxide (CO), hydrocarbon compounds, and nitrogen oxide (NO₂) compounds, and also some other materials such as hydrocarbon and organic lead compounds, will be discharged into the air because of vaporization of fuel system. Then, the compounds of exhaust gas which are discharged into the air will change because of the reaction between them and sunlight, water vapor, or other similar compounds. Some reaction process between the compounds happen fast and some are slow; from this reaction, some other compounds will be produced, such as: there is a reaction that changes nitrogen monoxide (NO) into the more reactive nitrogen dioxide (NO₂), and the reaction between hydrocarbon compounds with nitrogen oxide will produce ozone and other oxides; these compounds cause photochemical smog (wikipedia).

RESEARCH RESULT AND DATA ANALYSIS Esterification Process

The research data is in form of converted data on each variable provided in the following table 2 and figure 1.

Table 2 Esterification Reaction Time Optimization

reaction time (min)	% FFA (<1 % w/w)
0	7,72
30	1,1
60	0,589
120	0,25
180	0,25

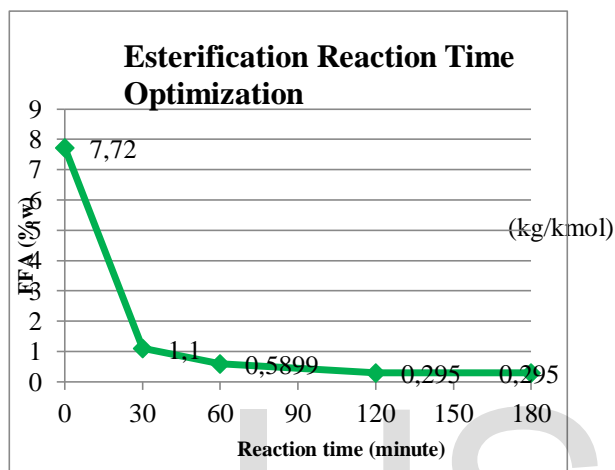


Figure 1. Esterification Reaction Time Optimization

The FFA standards allowed in esterification is <1% and from the figure 1 it can be concluded that it did not need a long time to react the esterification, in 1 hour FFA could be reduced to 0.5899% so that there was not much time wasted in the esterification process.

From the table 2 and figure 1 above, it is shown that the longer the reaction time is, the more conversion decreased and it was relatively constant on minute 120. This was because the longer the reaction time is, the possibility of hydrolysis ester to be happened is larger.

Esterification reaction is a reversible reaction which produces side product in form of water.



This reaction was done in batch; the existence of water would cause the reaction to move to the left so that methyl ester would be hydrolyzed. Moreover, if the reaction equilibrium was already reached, then the addition of reaction time would not be beneficial because it would not enlarge the result. From the gained data, the optimum condition for esterification was on the standard catalyst amount of MeOH 50% v/v and reaction time of 1 hour. (Ketta, 1978)

Esterification Reaction and the Effect towards FFA

The calculation based on stoichiometric to determine the variable value with the formulation.

$$V_{MeOH} = \frac{AV}{MR.KOH} \times \frac{\rho_{oil} \times V_{oil}}{1000 \times (\text{coefficient} \times MR.MeOH)} \times \rho_{methanol}$$

Note:

- V_{MeOH} = Volume of Methanol (ml)
- AV = Acid Value (mgKOH/g sample)
- $MR.KOH$ = Relative Mass of KOH (kg/kmol)
- ρ_{oil} = Oil Density (kg/l)
- V_{oil} = Oil Volume (ml)
- $coefficient$ = Assumption
- $MR.MeOH$ = Relative Mass of Methanol
- $\rho_{methanol}$ = Methanol Density (kg/l)

a. Coefficient 10

$$V_{MeOH} = \frac{15,44}{56,1} \times \frac{0,87 \times 200}{1000} \times \frac{(10 \times 32)}{0,792}$$

$$V_{MeOH} = 19,349 \text{ ml}$$

$$\%_{MeOH} = \frac{19,349}{200} \times 100\%$$

$$\%_{MeOH} = 9,7\% \approx 10\%$$

b. Coefficient 15

$$V_{MeOH} = \frac{15,44}{56,1} \times \frac{0,87 \times 200}{1000} \times \frac{(15 \times 32)}{0,792}$$

$$V_{MeOH} = 26,31664 \text{ ml}$$

$$\%_{MeOH} = \frac{26,31664}{200} \times 100\%$$

$$\%_{MeOH} = 14,5\% \approx 15\%$$

c. Coefficient 20

$$V_{MeOH} = \frac{14}{56,1} \times \frac{0,87 \times 200}{1000} \times \frac{(20 \times 32)}{0,792}$$

$$V_{MeOH} = 38,698 \text{ ml}$$

$$\%_{MeOH} = \frac{38,698}{200} \times 100\%$$

$$\%_{MeOH} = 19,349\% \approx 19\%$$

d. Coefficient 25

$$V_{MeOH} = \frac{14}{56,1} \times \frac{0,87 \times 200}{1000} \times \frac{(25 \times 32)}{0,792}$$

$$V_{MeOH} = 48,3725 \text{ ml}$$

$$\%_{MeOH} = \frac{48,3725}{200} \times 100\%$$

$$\%_{MeOH} = 24,2\% \approx 24\%$$

Table 3 . Comparison of Biodiesel Quality

Parameter	Units	EN 14214 Standard	Test Method
Phosphorus Content	Ppm	Max 4	FBI A03-03
Monoglyceride	%/wt	Max 0,8	EN 14105
Diglyceride	%/wt	Max 0,2	EN 14105
Triglyceride	%/wt	Max 0,02	EN 14105
Free Glycerol	%/wt	Max 0,25	EN 14105
Total Glycerol	%/wt	Min 96,5	EN 14103
Ester content	Hours	Min 6	EN 14112
Oxidation Stability	Ppm	Max 500	EN ISO 12937
Water Content	mg/KOH	Max 0,5	AOCS Cd 3d-63
Acid Value	/g		

Parameter	Units	EN 14214 Standard	Test Method
Phosphorus Content	Ppm	Max 4	FBI A03-03
Monoglyceride	%/wt	Max 0,8	EN 14105
Diglyceride	%/wt	Max 0,2	EN 14105
Triglyceride	%/wt	Max 0,02	EN 14105
Free Glycerol	%/wt	Max 0,25	EN 14105
Total Glycerol	%/wt	Min 96,5	EN 14103
Ester content	Hours	Min 6	EN 14112
Oxidation Stability	Ppm	Max 500	EN ISO 12937
Water Content	mg/KOH	Max 0,5	AOCS Cd 3d-63
Acid Value	/g		

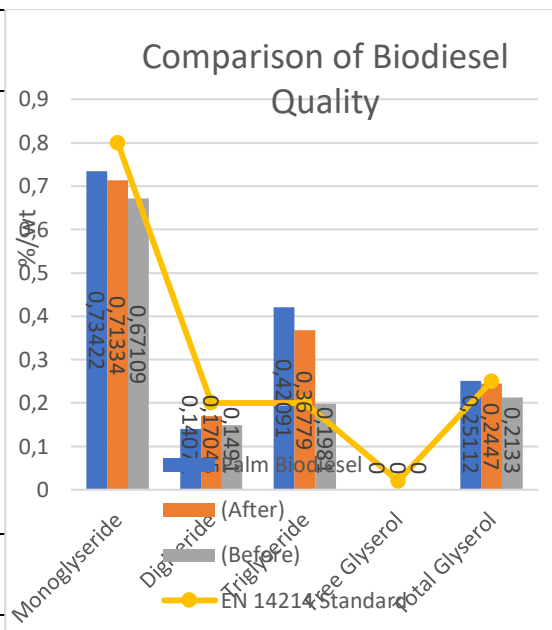


Figure 2. Comparison of Biodiesel Quality

From the table 3 and figure 2 of comparison above, it can be concluded that the quality of biodiesel produced in this research could increase the quality of Triglyceride value. It could be seen from the old method, both from CPO or CJO materials, the triglyceride value was high; it was even out of the standard. Moreover, some measuring parameters which were shown on the standards of EN 14214 and the previous large number could be decreased; the number on Mono-di-tri highly affected the change of glycerol total value, therefore the safe number for each quality was expected to be included in standards to meet the standards value of total glycerol.

In esterification step, there was a conversion of FFA into ester, so that the initial CJO FFA contents (free fatty acids) were decreased. If the high CJO free fatty acids were not decreased through the esterification step, then on the trans esterification step it would form more suds as the reaction side product. This condition would obstruct the purification process and affect the quality of biodiesel product.

Comparison of Biodiesel Quality

From the analysis of Chromatography gas (attached) that we have done, esterification process as the effort to use Jatropha oil as biodiesel processing materials could produce methyl ester. The Table 3 above is a methyl ester components table from our biodiesel based on GC MS analysis.

Exhaust Gas Emission Test

The test was done on a generator set branded Komatsu EGS 160-7 with capacity of 140 kva and 1 sample point by using three sample tests.

Sample testing steps:

1. The first emission test was done by using diesel fuel or by directly testing the generator set standards emission.
2. The second sample was B20 (80% diesel + 20% biodiesel) which was produced before, prepared in a container and then used for the next generator set fuel, after 1 hour the emission was re-measured.
3. On the third sample, we used B20 (80% diesel + 20% biodiesel) which was freshly made based on the new analysis and the same testing step as the second step.

From the emission testing result by using the measuring tool branded Testo 350-XL, the three samples applied on generator set of Komatsu EGS 160-7 provided as following:

Table 4. Emission Testing Result Using Generator Set Komatsu EGS160-7

Measuring Parameter	Unit	Komatsu EGS 160-7 (140 Kva-2010 B)		
		Standards of PERMEN LH No.13 TH 2009	Diesel (5)	Old B20 (6)
Carbon Monoxide (CO)	mg/Nm ³	600	230	133
Nitrogen Dioxide (Nox as NO ₂)	mg/Nm ³	1000	749	742
Low velocity	m/s	-	8,3	8,2

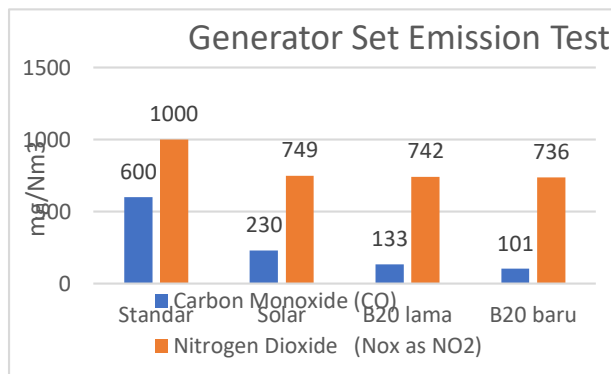


Figure 3. Generator Set Emission Testing Result on Komatsu EGS 160-7

From the emission testing result, it could be seen on the table 4 and figure 3 that the produced emission of biodiesel was less than that of diesel, especially the produced CO; meanwhile, the emission of old B20 and new B20 had value of CO and NO₂ in quite similar amount but there was still a difference in which the new B20 had slightly smaller value.

There were several factors causing the difference of CO and NO₂ value on above fuel emission:

1. CO on diesel was higher than other B20 because biodiesel characteristics were easier to catch oxygen so that the combustion was more perfect, diesel was in the contrary.
2. CO and NO₂ value on new B20 was better than the old one because the new B20 was still fresh and not oxydated.

In order to get the maximum production, industries would usually do everything for that target but there are times that they press the cost as minimum as possible and get the same production value.

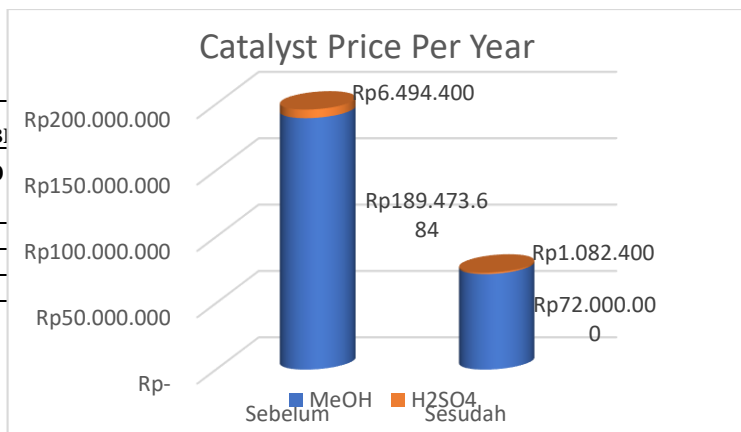


Figure 4. Comparison of Esterification Catalyst Price in 1 Year

From the figure 4 above, it can be seen that the catalyst 1 price was higher than catalyst 2 with the Rp 465.476 /Batch in one working day, in one month (22 working days) was Rp 10.240.474, and for 1 year was Rp 122.885.684 in which the reduction of esterification catalyst price was around 63% compared to before.

Conclusion

1. The reaction time of esterification was only 60 minutes to reduce the FFA value by <1%.
2. The addition of methanol 19% and H₂SO₄ 0.9% were enough to produce biodiesel with EN 14214 standards with CJO materials and FFA value of 7.72%.
3. The produced emission of new B20 was better than that of diesel and old B20 seen from NO₂ (Nitrogen Dioxide) and CO (Carbon Monoxide) value in which the contents of new B20 were lower, even though those were not too significant.

BIBLIOGRAPHY

Kurniasih, E, “PRODUKSI BIODIESEL DARI CRUDE PALM OIL MELALUI REAKSI DUA TAHAP” Jurusan Teknik Kimia Politeknik Negeri Lhokseumawe.

Freedman, B., Pryde.E.H., Mounts. T.L., 1984, *Variables Affecting the Yields of Fatty Esters from Transesterfied Vegetable Oils.*

Julianti Elisa, “PENGEMBANGAN MINYAK JARAK PAGAR SEBAGAI BIODIESEL” Departemen Teknologi Pertanian Fakultas Pertanian USU.

Ketta, Mc.,J.J., 1978, *Encyclopedia of Chemical Processing and Design*, Vol.1, Marcel Dekker, New York.

Kuncahyo Priyohadi, Aguk Zuhdi M. Fathallah, "ANALISA PREDIKSI POTENSI BAHAN BAKU BIODIESEL SEBAGAI SUPLEMEN BAHAN BAKAR MOTOR DIESEL DI INDONESIA" Jurusan Teknik Sistem Perkapalan, Fakultas Teknologi Kelautan, Institut Teknologi Sepuluh Nopember (ITS).

Perry, R.H. and Green, D.W., 1984, *Perry's Chemical Engineering Handbook*, 8th ed, Mc Graw Hill Book Company, Inc, New York.

Setyadji Moch dan Endang Susiantini, "PEMBUATAN METIL ESTER (BIO-DIESEL) DARI MINYAK JARAK PAGAR DAN METANOL DENGAN KATALISATOR NATRIUM HIDROKSIDA" P3TM – BATAN

Suhartanta dan Zainal Arifin Staf Pengajar FT UNY "PEMANFAATAN MINYAK JARAK PAGAR SEBAGAI BAHAN BAKAR ALTERNATIF MESIN DIESEL"

Soerawidjaja, Tatang H., 2005, *Minyak-lemak dan produk-produk kimia lain dari kelapa*, Handout kuliah Proses Industri Kimia, Program Studi Teknik Kimia, Institut Teknologi Bandung.

<http://rumuspelajar.blogspot.com/2010/02/laju-reaksi-dan-kesetimbangan-kimia-sma.html>

<http://id.wikipedia.org/wiki/Emisi>

http://id.wikipedia.org/wiki/Minyak_jarak

<http://www.biofuelsystems.com/specification.htm>

http://www.en.wikipedia.org/wiki/EN_14214