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Kinetics of Oxidation Decomposition on *Jatropha Curcas* Biodiesel

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Abstract. High free fatty acid jatropha curcas oil was use as a feedstock of biodiesel through two step esterification, first by reaction of Jatropha curcas oil with methanol catalyzed by sulfuric acid, and second step is transesterification process with methanol catalyzed by sodium hydroxide. After purification step, 120 ppm pyrogallol was introduced into Jatropha curcas biodiesel. Accelerated controlled oxidation process was performed using rancimat test equipment with the dry airflow to the reaction tube is 10 L/min. Assuming that oxygen only reacts with double bond of the compound that compose biodiesel, measurement the quantity changes of double bond on biodiesel by the changes of the value of iodine number will brought to the rate of reaction. While reaction rate constant determine by Arrhenius law was calculated from the data of time to reach induction period in a certain temperature. It was found that total rate of oxidation process was determined by chemical reaction rate rather than mass transfer rate of oxygen to the body of biodiesel, both on biodiesel with or without pyrogallol. While in a presence of 120 ppm pyrogallol on jatropha curcas biodiesel, Arrhenius constant was determined by the value of frequency factor (A) = 28.47 x 106/ sec and activation energy (E) = 97,31 kJ/mol. This mean that on the ambient temperature 30 oC, Jatropha curcas biodiesel in a presence of 120 ppm pyrogallol will decrease their iodine value 3.4% after 2.3 years.

1. Introduction

One of the most promising sources for petrodiesel substitution is biodiesel, which is almost similar on physical and chemical properties to petrodiesel. For this reason, biodiesel could apply as fuel on the conventional internal combustion engine with a minor modification. There are some feedstocks for biodiesel production, as vegetable oil, waste from the slaughter house and fish processing, and also from microalgae [1-7] The final biodiesel product characteristic will depend on the feedstock source. The difference between biodiesel and petrodiesel is on the stability due to oxidation process during storage. In petrodiesel there is no significant influence on the oxidation process to their stability and quality [8] while oxidation process on biodiesel will affect significantly to at least 6 parameters on biodiesel standard (kinematics viscosity, cetane number, total acid number, flash point, cooper strip corrosion, iodine number) [9]. Oxidation on biodiesel will occur on double bond in fatty acid chain and highly correlated to unsaturated fatty acid that composed the feedstock of biodiesel. Feedstock contain high unsaturated fatty acid will produce biodiesel with high unsaturated fatty acid methyl ester. In a presence of oxygen, the unsaturated fatty acid compound on biodiesel will oxidize to free

fatty acid which will perform simultaneous and complex reaction on a secondary oxidation process. The final products of the oxidation process are aldehyde, carboxylic acid, alcohols and hydrocarbon compound [10].

To determine the rate of oxidation process on biodiesel, measurement of changes on the component that compose biodiesel could conduct on the different temperature of the oxidation process. Total double bond on the fatty acid component in biodiesel could be determine by iodine number method [11] in case that double bond was oxidized it will show by decreasing the total iodine number of biodiesel. Determination of oxidation process in fatty acid by iodine number method is simple and accurate compare to determination of increasing acid number or any other substance as a result of oxidation on biodiesel because the product of the oxidation process is unstable and tend to decompose to any other substance [10].
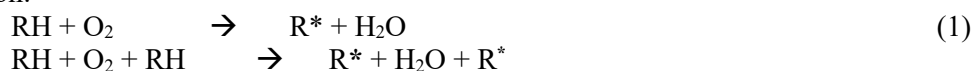
There are some methods to reduce and prevent oxidation process on biodiesel for example removing substance that trigger and boosting oxidation process (water, metal and other contaminant substance), hydrogenation of biodiesel that converted unsaturated compound into saturated compound even this could increase viscosity of biodiesel, and the other method is introducing antioxidant into biodiesel [12-14].

The term Induction period (IP) on rancimat test analysis show the time when the oil starts to oxidize and produce volatile organic compound that dilute in the water and change significantly the conductivity of the water. The time when the conductivity changes namely Induction Period (IP). In this point a small amount of the double bond in biodiesel compound start react with oxygen and shown by decreasing of biodiesel iodine number. Initial oxidation reaction will form free radical that trigger chain reaction as shown in the equation (1) to (5) [15,16].
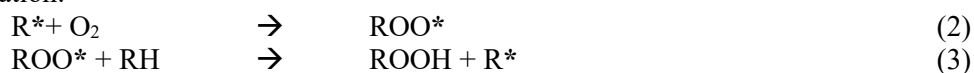
1.1. Biodiesel Oxidation

There are several sources for biodiesel decomposition, biological, physical and chemical source. Microorganism activity is main source for biodiesel decomposition by biological source, while heat, metals and light are physical source. Water, oxygen and free fatty acid are chemical source for biodiesel decomposition [17,18]. These sources could work separately or simultaneously on biodiesel and resulted on decompose of biodiesel. As one of the chemical source on biodiesel decomposition, oxygen could react with double bond on unsaturated fatty acid that composed biodiesel. Decomposition due to oxidation reaction on biodiesel could bring a serious problem on the engine because biodiesel could change viscosity, acid value, water content, cetane number, and also its caloric value.

Initiation:
$$RH + O_2 \quad\rightarrow\quad R* + H_2O \tag{1}$$
$$RH + O_2 + RH \quad\rightarrow\quad R* + H_2O + R^*$$

Propagation:
$$R* + O_2 \quad\rightarrow\quad ROO* \tag{2}$$
$$ROO* + RH \quad\rightarrow\quad ROOH + R* \tag{3}$$

Peroxide decomposition
$$ROOH \quad\rightarrow\quad RO* + {}^*OH$$
$$2\ ROOH \quad\rightarrow\quad RO* + ROO* + H_2O$$

Termination:
$$ROO* + ROO* \quad\rightarrow \text{inactive product} \tag{4}$$
$$ROO* + IH \quad\rightarrow ROOH + I \tag{5}$$

where

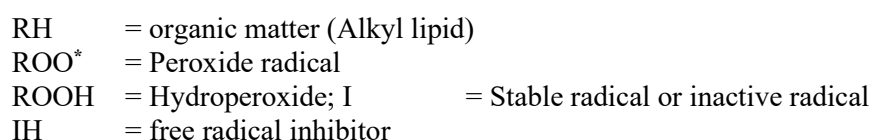|	
RH	= organic matter (Alkyl lipid)
ROO^*	= Peroxide radical
ROOH	= Hydroperoxide; I = Stable radical or inactive radical
IH	= free radical inhibitor
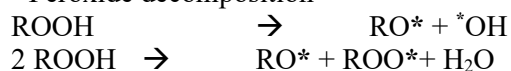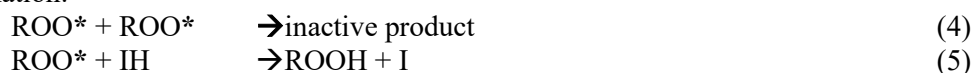
In the oxidation process, oxygen will react with the components that have double bond on the molecular chain, thus mean that the oxidation reaction to biodiesel will reduce the number of double bond in biodiesel compound. While double bond compound on biodiesel was found on the unsaturated chain on biodiesel component. The changes on the percentage of unsaturated chain could be analyzed by evaluation on Iodine number.

Antioxidant

Most of the oil and lipid came with their original antioxidant, it was namely natural antioxidants. Tocopherols, ascorbic acid, ascorbic acid ester, and carotenoids are example of natural antioxidant that exists in lipid [19] Natural antioxidant was decrease significantly in biodiesel due to the process steps, from oil extraction, pretreatment to remove gums and phospolipid, also esterifcation process to reduce high free fatty acid in case that biodiesel production use transesterification route with alkali catalyst, purification of biodiesel to fulfill the standard requirement. For this reason, introducing new antioxidant should be done to improve biodiesel quality in a term of oxidation stability.

Synthetic antioxidants are a manmade and mostly are phenols based [10]. Phenolic derivatives usually contain more than one hydroxyl or methoxyl group. Synthetic phenolic antioxidants are *p* substituted, while natural phenolic antioxidants are *o* substitutes.

There are two classification of antioxidant, primary and secondary antioxidant. Primary antioxidant refers to chain breaking antioxidants, because the chemical nature of these molecules they can act as free radical acceptors and delay or inhibit the initiation step or interrupt the propagation step of auto oxidation. Mechanism of primary antioxidant is shown in the equation (6) to (8) [20]

R•   + AH   → RH   + A•   (6)
RO•   + AH   → ROH + A•   (7)
ROO•   + AH   → ROOH + A•   (8)
Where: R•, RO•, ROO• = free radical

Radical from the antioxidant will react with radical from fatty acid to form stable complex compound as shown in equation (9) to (11).

R•   + A•   → RA   (9)
RO•   + A•   →ROA   (10)
ROO•   + A•   →ROOA   (11)

1.2. Measurement method of biodiesel stability.

There are several methods to measure stability of biodiesel. Some of them base on the assumption that biodiesel stability is depend on oxidation on the biodiesel due to the presence of oxygen. These include the weight gain and headspace oxygen uptake method for oxygen absorption, chromatographic analysis for changes in reactants, iodometric titration, ferric ion complexes, FTIR method for peroxide value, spectroscopy for conjugated dienes and trienes. While for expressing antioxidant activity, there are some methods, ie. Induction Period (IP), Oxygen Stability Instrument (OSI) and also PetroOXY test [10]. European Standard for biodiesel (EN 14214), and Indonesian Standard (SNI-04-7182) were applied Induction Period to measure biodiesel stability. The requirement of Induction Period in EN 14214 standards was increase from 6 hours in EN 14214-2003 to 8 hours in EN 14214-2012.

1.3. Mathematical Model

According to one-layer mechanism of reaction, Oxygen (B) will diffuse to the interface of gas-liquid system, and then chemical reaction step will occur in a liquid body of biodiesel (A) as seen in Fig. 2 [21]
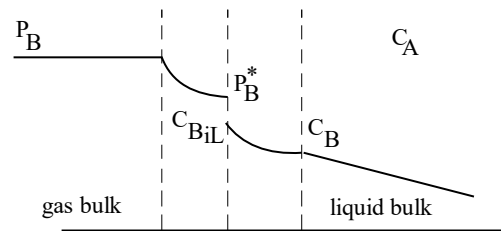
Figure 1. Mechanism of oxidation reaction in biodiesel according to quasy steady state reaction.

Unsaturated fatty acid component on biodiesel were dominated by oleic acid ($C_{18:1}$), linoleic acid ($C_{18:2}$) and linolenic acid ($C_{18:3}$). Oxidation reaction on each component could write as shown in equation (12) to (15).

$$C_{18:1} + O_2 \rightarrow P, \text{ written as } A_1 + B \rightarrow P \qquad (12)$$

$$C_{18:2} + 2\ O_2 \rightarrow P, \text{ written as } A_1 + 2\ B \rightarrow P \qquad (13)$$

$$C_{18:3} + 3\ O_2 \rightarrow P, \text{ written as } A_1 + 3\ B \rightarrow P \qquad (14)$$

Equation (12) to (14) then could be written as

$$A + 6\ B \rightarrow P \qquad (15)$$

In a presence of antioxidant (M) on biodiesel, antioxidant will react as shown in equation (16)

$$M + O_2 \rightarrow \text{ written as } A_4 + B \rightarrow P \qquad (16)$$

Equation (5) and (16) then could written as

$$A + 7\ B \rightarrow P \qquad (17)$$

Solving for both mass transfer and chemical reaction for the equations (15) and (17) under quasy steady state condition will give equation (18) and (19) as follows

$$r_A = \frac{k.\frac{P_B}{H}\alpha C_A}{6k.C_A - \alpha} \qquad (18)$$

$$r_A = \frac{k.\frac{P_B}{H}\alpha C_A}{7k.C_A - \alpha} \qquad (19)$$

Where

$$k^* = k.\frac{P_B}{H}\alpha \qquad (20)$$

$$\alpha = \frac{1}{k_g a H} + \frac{1}{k_L a} \qquad (21)$$

2. Methods

2.1. Materials

A source of the biodiesel feedstock is high free fatty acid (FFA) jatropha curcas oil which come with 18% of FFA was purchase from PT Pura Green Energy, Kudus Indonesia. Methanol was use as alcohol source for esterification and transesterification. Sodium hydroxide was use as transesterification catalyst, while sulfuric acid was use as catalyst in esterification process. All chemicals use in biodiesel production and analysis are reagent grade.

2.2. Methods

Biodiesel source for the experiment was prepare refer to Supriyono et al. [22] High free fatty acid jatropha curcas oil was treated by esterifcation process to decrease free fatty acid. The process was performed under operation condition 65 oC, 120 minute, methanol to oil volume ratio is 40% and sulfuric acid to oil volume ratio is 2%. Oil phase which contain jatropha curcas oil and fatty acid methyl ester was further process on transesterification step which conduct on 60 oC, 60 minute, methanol to oil volume ratio is 40% and sodium hydroxide is 2% of oil weight. Biodiesel phase was purifying on the following step. The rest of methanol on biodiesel product was remove by vacuum distillation on 65 oC, 200 mmHg, sodium hydroxide on biodiesel phase was neutralizing by HCl 0,5%, rinse by distilled water until pH of the waste water close to pH of distilled water. The rest of the water on biodiesel adsorb by Na2SO4. The final product then analyzed according to EN 14214-2012 standard method.

Controlled oxidation process was performed using rancimat test equipment as shown in Fig. 1, which is operated in 10 L/min air flow on the various temperature and time. About 3 grams of biodiesel sample was use in each test. Previous experiments work by Supriyono et al. [22] show that pyrogallol was the best antioxidant for jatropha curcas biodiesel compare to TBHQ, propyl gallate and baynox plus on the standard induction period by rancimat test. For the purpose to anticipate longer induction period requirement, the work also present equation that correlate between concentrations of pyrogallol on Jatropha curcas biodiesel to the time of induction period of Jatropha curcas biodiesel. Base on the result on previous work, pyrogallol utilized as antioxidant in jatropha curcas biodiesel and further analysis the rate of oxidation stability was performed. After certain time of controlled oxidation process, biodiesel sample from reaction tube of rancimat equipment was analyzed the iodine number. Base on the changes of iodine number of biodiesel, the rate of oxidation reaction on 110 oC could be calculated. To determine Arrhenius constant of the oxidation reaction, similar experiment was performed in a difference temperature of rancimat equipment on the range of 90 ºC to 140 ºC.
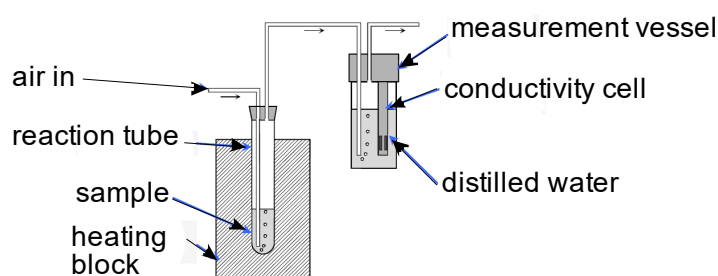

Figure 2. Schematic arrangement of rancimat test equipment.

3. Results and Discussion

3.1. Jatropha curcas biodiesel

The analysis of biodiesel was performed on the parameter of FAME content, kinematic viscosity at 40 oC, acid value, iodine number, water content, flash point, density at,15 oC and oxidation stability, 110 oC. The parameter that analyzed was fulfills the requirement on EN 14214 -2006 standard except for oxidation stability which has value 1.37 hours and far from the standard of 6 hours. Thus, jatropha curcas biodiesel is vulnerable to oxidation process. The high value on Iodine number in Jatropha curcas biodiesel is one of the suspect that responsible to oxidation process in biodiesel, because compound with double bond on biodiesel easy to react with oxygen. Jatropha curcas biodiesel start to oxidized and decompose after 1.37 hours of reaction. The result of oxidation reaction is a compound that catalyzed increasing of the acid value on biodiesel. While increasing in acid value on biodiesel the other parameter such viscosity, cetane number, caloric value and kinematic viscosity will change, the water content on biodiesel also increase for the reason that oxidation reaction also produce water.

3.2. Rate of oxidation reaction

One of the methods to determine stability of biodiesel due to oxidation process is biodiesel rancimat test method also known as accelerated reaction test because the reaction was performed in a temperature higher than ambient temperature. Latest European Standard for biodiesel (EN 14214-2012) protocol shown that temperature requirement for oxidation stability test by rancimat equipment is 110 ºC and dry air flow rate 10 L/h, thus oxygen was available on the excess amount compare to the amount of unsaturated fatty acid methyl ester and assuring that oxidation process depend only on unsaturated compound on biodiesel. The idea of accelerated test is to find the shorter time to determine parameter of oxidation kinetics from which the data could be extrapolated to the ambient temperature condition. However, in the case of antioxidant activity test, high temperature experiment could decrease activity of antioxidant itself. Tert Butyl Hydroquinone (TBHQ) in soybean biodiesel could maintain oxidative stability in 544 hours on the 45 ºC, but when the temperature was raises to 98 ºC, the oxidative stability will decrease to 28 hours [10]. This could make sense if previous experiments could have different

result, even with the same materials and also the same antioxidant. Reaction between gas phase and liquid phase always involve mass transfer and chemical reaction. The overall reaction will determine by the slower step. To analyze which step is the slower, quasy steady state reaction model could be applied. In this experiment, biodiesel with and without antioxidant were heated in biodiesel rancimat test equipment at 110 ℃. In a certain time, iodine number of the sample was analyzed. The value of iodine number was shown the amount of double bond on biodiesel, which has correlation to the amount of biodiesel that decompose by oxidation reaction. Fig. 3 and fig. 4 show the result of the analysis of iodine number for biodiesel with and without antioxidant.
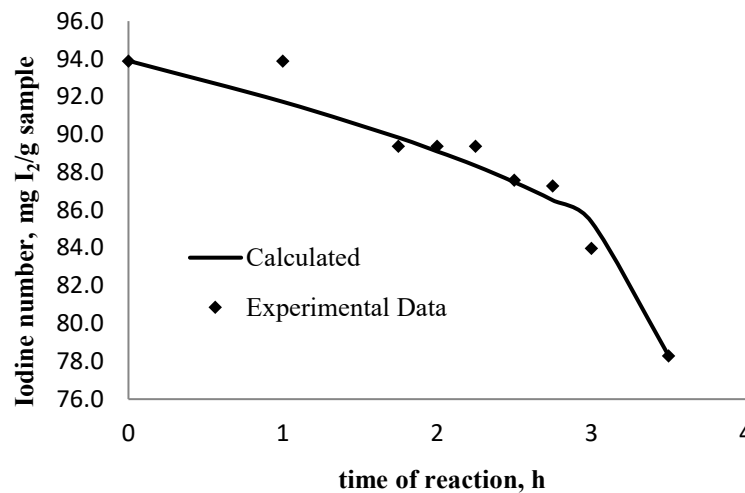

Figure 3. Correlations between Iodine number of biodiesel without antioxidant and reaction time on accelerated reaction test, 110 ℃

As shown in Fig.3, iodine number of biodiesel without antioxidant will start to decrease in periods of 1 hour to 2 hour after reaction was started. This mean that oxidation reaction to the double bond of the compound in biodiesel started in a period 1 to 2 hour after reaction was initialized. The results of iodine number analysis also agree with analysis of stability on biodiesel by rancimat test method which has result 1.37 hour on induction period. Fitting of the experiment data with the developed equation (18), (20) and (21) give the result as follows

α = 10,29466; k^* = 0,03644; k = 0,02130; Average of deviation is = 3.04%
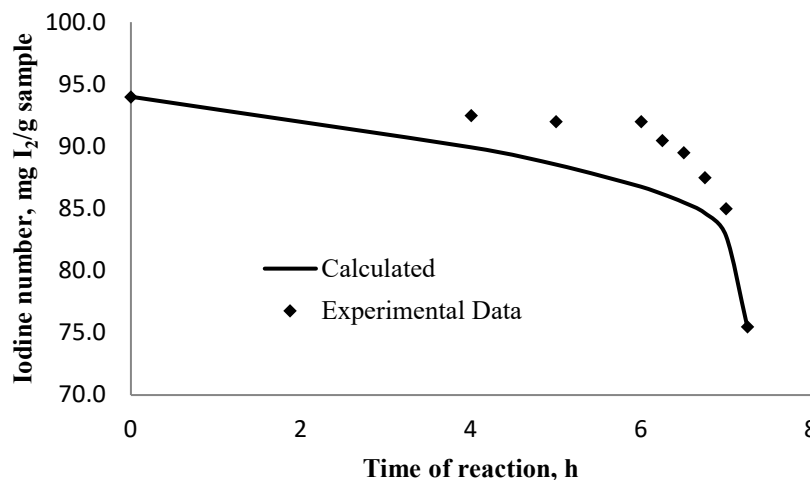
$\frac{P_B}{H}$ = 0,021107

Figure 4. Correlations between Iodine number of biodiesel with pyrogallol 120 ppm and reaction time on accelerated reaction test, 110 ℃

From Fig. 4, Iodine number slowly decrease until 6 hours of accelerated test then sharply decrease the value of iodine number after 6 hours. This result agree with the experiment that Jatropha curcas biodiesel contain 120 ppm pyrogallol has induction period time 6.02 hours, which is fulfill the requirement of biodiesel standard according to EN 14214-2003 and SNI 04-7182-2006. For the newer European Standard (EN 14214-2012) the amount of pyrogallol that should introduced will be higher because EN 14214 requirement is 8 hours for the induction period time.

Fitting of the data give the result for equations (20) and (21) as follows

α = 10.29466; k* = 0.04357; k = 0.05977; Average of deviation is = 0.77%,

$$\frac{P_B}{H} = 0.166183$$

By comparing the value of chemical reaction constant (k) and mass transfer constant (H) it was concluded that overall reaction was determine by chemical reaction step.

3.3. Jatropha curcas biodiesel

The The value of activation energy and frequency factor for the oxidation process on jatropha curcas biodiesel with 120 ppm pyrogallol was determine by re arrange equation

$$C_A = C_{A0}.e^{-kt}$$

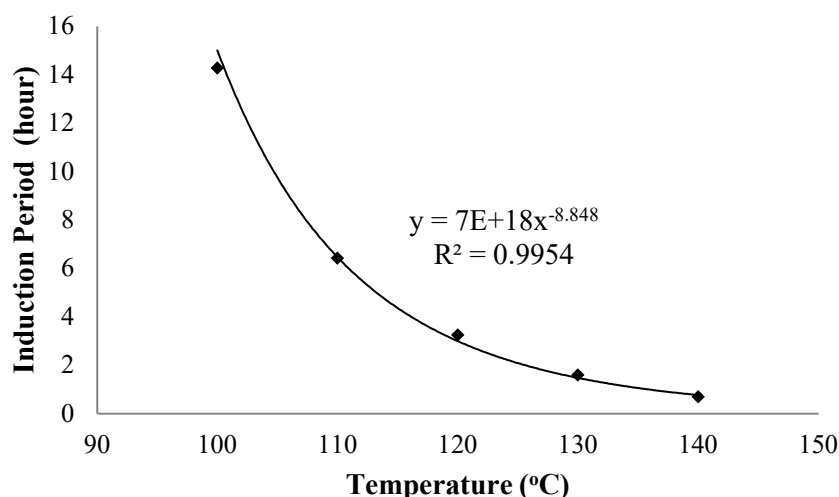$$\frac{\ln\left(\frac{C_{Ao}}{C_A}\right)}{t} = k$$

(22)

Figure 5. Induction Period value on biodiesel with pyrogallol 120 ppm

On the Induction Period (IP) point, the double bond on biodiesel was start oxidized to acidic volatile compound that absorbed on the measured vessel and increasing conductivity of the distilled water in a vessel. In this experiment, the measurement of iodine number in the IP point is 90.8 mg I_2/100 gram of sample, while initial iodine number is 94 mg I_2/100 gram of sample. For the same sample, the ratio of iodine number on the IP point (C_A) to initial iodine number value (C_{AO}) is constant, thus a set of data could have derived as shown in Table 1.

Table 1. Calculation of reaction constant (k) base on time of reaction

Time of reaction, t (hour)	Temperature of reaction T (K)	C_A	C_{AO}	$\ln(C_{AO}/C_A)$	1/t	k	$\ln(k)$	1/T
0.72	413	90.8	94	0.03464	1.38889	0.04810	3.03437	0.00242
1.38	403	90.8	94	0.03464	0.72464	0.02510	3.68496	0.00248
2.81	393	90.8	94	0.03464	0.35587	0.01233	4.39606	0.00254
6.07	383	90.8	94	0.03464	0.16474	0.00571	5.16623	0.00261
14.1	373	90.8	94	0.03464	0.07092	0.00246	6.00905	0.00268
35.81	363	90.8	94	0.03464	0.02793	0.00097	6.94110	0.00275

$$\ln k = \ln A - (E/RT) \tag{23}$$

Correlation between lk k and 1/T was shown in Fig. 6.

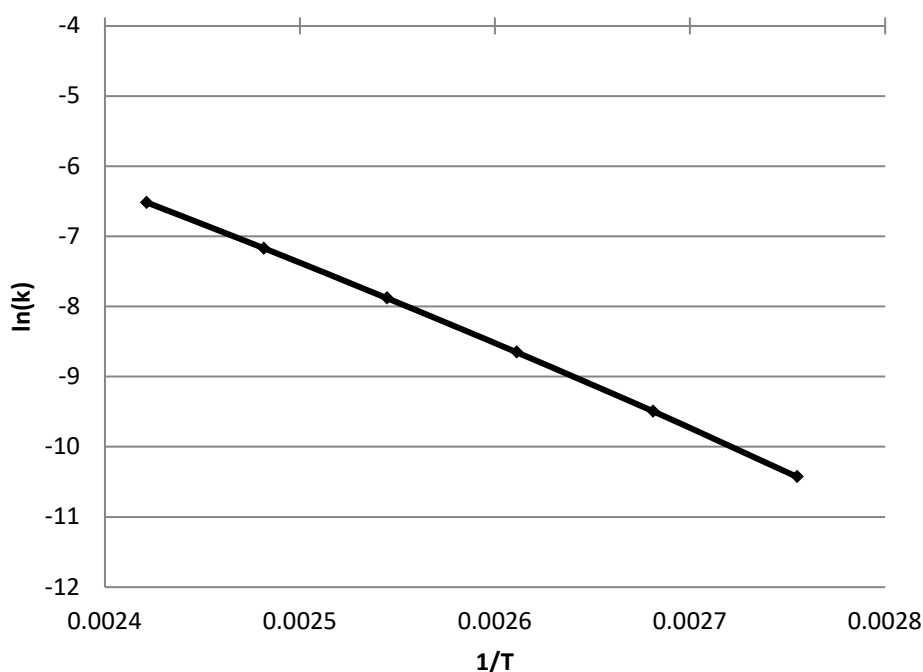**Figure 6.** Correlation between 1/T and ln k in the oxidation process on jatropha curcas biodiesel with pyrogallol 120 ppm

The value of
A = exp (25.353) = 1.025 x 10^{11}/ hour
E = 11705 x 8.314 = 97315.37 J/mol

Base on the value of activation energy and pre exponential Arrhenius equation, it could be estimated that introducing 120 ppm pyrogallol on the jatropha curcas biodiesel and stored in 30°C Iodine number will decrease 3.4% during 2.3 years' storage. However, this calculation base on the oxidation reaction only without any other source that could interfere the result, such as moisture, light and metal that in some research is significantly to changes the rate of reaction [23]. A study on the thermal behavior of Jatropha curcas biodiesel [24] shown that weight loss in a range of 280-400 ^{o}C is about 96% on both nitrogen and air medium. Thermogravimetric (TGA) analyzer for this study was operating under heating rate 10 ^{o}C/min and constant flow of nitrogen and air at a rate (20±0.5) ml/min. Furthermore, the study also shown that activation energy on biodiesel weight loss in nitrogen medium is smaller (17.81 – 20.70 kJ/mol) than in air medium (22.69 – 24.71 kJ.mol). Base on the definition of activation energy in which minimum energy required to cross the barriers for initiating a chemical reaction, the rate of thermal decomposition on jatropha biodiesel is faster in nitrogen medium than in air medium. Comparing the result of thermal decomposition to the oxidation decomposition, it was shown that activation energy on oxidation decomposition is much higher with the value is about 97.35 kJ/mol. Thus rate of thermal decomposition is higher than oxidation decomposition on a temperature above flash point of Jatropha curcas biodiesel (175 ^{o}C).

The frequency factor of a reaction expressed by 'A', is show the degree of collisions of a reaction per hour. The value of frequency factor on jatropha curcas biodiesel oxidation reaction is 1.025 x 10^{11}/ hour = 28.47 x 10^6/ sec. Comparing to thermal decomposition of Jatropha curcas biodiesel in which has frequency factor 10.44 – 12.20 /sec [24], it shown that oxidation reaction has higher collision, however this collision does not propagate to the chemical reaction between oxygen with biodiesel. It seems that higher collision frequency is more between oxygen to antioxidant in which in this case is

pyrogallol. As shown in a study by Fattah et al [25] which is concluded that Pyrogallol is found to be the most effective antioxidant to improve the oxidation stability in case of almost all biodiesels reviewed.

4. Conclusion

Oxidation reaction on biodiesel could determine by measuring iodine number changes, because oxygen will react with double bond on unsaturated fatty acid compound in biodiesel. Rate of oxidation reaction on jatropha curcas biodiesel determined by chemical reaction step compared to mass transfer step with or without antioxidant. In a presence of 120 ppm pyrogallol, the value of activation energy and frequency factor on Arrhenius constant is A = 1.025 E+11/ hour (28.47 x 10^6/ sec) and E = 97315.37 J/mol. Extrapolation of the data for the ambient temperature condition 30 ℃ shown that during 2.3 years the number of iodine number for jatropha curcas biodiesel will decrease 3.4%. However, this result should be considered that the calculation does not count on the effect of metal, light and microbiology process to the decomposition by oxidation process and total decomposition that might be also take a place on the Jatropha curcas biodiesel.

Acknowledgement

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