The Use of Ethanol as an Alternative Solvent to Replace 2-Propanol in the Determination of Total Acid Number in Lubricant by Potentiometric Titration

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Abstract. In determining the quality of lubricant, acid content affects the quality of the lubricant. The acid content in the lubricant can be determined by using ASTM D664 Standard Method to determine Total Acid Number. The purposes of this research are to obtain the optimum ratio of a solvent mixture of Toluene and Ethanol to determine the Total Acid Number using the Potentiometric titration method and set the value of its accuracy and precision. This research aims to compare the value of the total acid number of the modified method to the standard method (ASTM D664). The modified method in this research uses toluene and ethanol, with ratios 70 percent: 30 percent. Kolmogorov Smirnov normality test shows that both methods produce normal data, and based on the t-test result, it is showed that both methods produce the results that are not significantly different. Based on the measurement of accuracy and precision, the method generates accurate and precise data. From the overall result, it can be concluded that the solvent mixture of Toluene and Ethanol with ratios 70 percent: 30 percent, can be used as an alternative solvent mixture to replace the solvent mixture in ASTM D664 Standard Method.

Keywords: potentiometric, toluene, ethanol, 2-propanol, ASTM D664

1. Introduction
The high acid content affects the quality of lubricant, and its determination is a necessary parameter to assess the quality of lubricant. Oxidation from lubricants occurs due to heating at high temperatures. Measuring the acid number of a lubricant is a way to find out whether a lubricant has oxidized or not. In general, the results of this analysis are used to prevent the lubricant from oxidizing, so additives are added. This test also serves as a control tool to determine the oxidation of the lubrication system on the turbine engine. This test is also used to determine when the lubricant should be replaced [1].

Determination of Total Acid Number According to ASTM D664 Method Determination of Total Acid Number with this method is a Potentiometric Titration method. The principle of potentiometric titration is based on the change of electrode potential by the addition of a certain volume of titrant to the solution to be analyzed. The endpoint of a titration is calculated when the total volume of titrant needed to reach the equal potential with its buffer solution. Total Acid Number is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that are needed to neutralize the acids in one gram of oil/lubricant [2]. This parameter is an important measurement to determine the quality of oil/lubricant. This method can monitor the change that occurs during the use of lubricant when oxidation occurs without considering other characteristics. The new or old lubricant can contain acid from additives or product degradation during the usage by means of oxidation of the product [3].
This research aims to find an alternative solvent to replace the solvent mixture in the ASTM D664 Standard Method. In this research, 2-propanol is replaced by ethanol as a polar solvent. Ethanol is a cheaper solvent compared to 2-propanol with the same degree of purity and ethanol, also known as ethyl alcohol, grain alcohol or just alcohol. Its chemical formula is C\textsubscript{2}H\textsubscript{5}OH, also written as C\textsubscript{2}H\textsubscript{6}O. It is used as a solvent because it can dissolve many other chemicals and is not very toxic [4].

With those backgrounds, then the research of Use of Ethanol as Solvent Alternatives 2-Propanol On Determination of Total Acid Numbers In Lubricants Sample by Potentiometric Titration Method is conducted.

2. Research Method

In the determination of Total Acid Number by using the ASTM D664 Method, the lubricant sample is weighed and dissolved into 120 mL of solvent mixture 2-propanol and toluene by a ratio of 50%:50%. Then lubricant sample is titrated with KOH 0,1 mol/L. The result then is showed in a monitored device in mgKOH/g unit, or calculated by using the equation below:

\[
\text{Total Acid Number (mgKOH/g)} = \frac{[(A-B) \times M \times MW KOH \times F]}{W}
\]  

Where, A= volume of KOH that is needed for sample titration; B= volume of Blank titration; M = concentration of KOH; MW KOH = molecular weight of KOH; F = correction factor of KOH concentration; and W=weight of a sample [2]. Toluene, as a nonpolar solvent in this mixture, acts as a solvent for oil/lubricant, and 2-propanol as a polar solvent acts as a solvent for acids in oil/lubricant.

The preliminary test uses the solvent mixture of toluene and ethanol in different ratios. The aim of this preliminary test is to determine the crude ratio of the solvent mixture that produces the same result as the standard method. From this preliminary test, it is obtained the results as described below:

- ASTM D664 Standard Method (Toluene 50% : 2-Propanol 50%) gives result of Total Acid Number = 3,320 mgKOH/g
- Ratio Variation I (Toluene 50% : Ethanol 50%) gives result of Total Acid Number = 2,701 mgKOH/g
- Ratio Variation II (Toluene 55% : Ethanol 45%) gives result of Total Acid Number = 2,777 mgKOH/g
- Ratio Variation III (Toluene 60% : Ethanol 40%) gives result of Total Acid Number = 2,973 mgKOH/g
- Ratio Variation IV (Toluene 65% : Ethanol 35%) gives result of Total Acid Number = 3,138 mgKOH/g
- Ratio Variation V (Toluene 70% : Ethanol 30%) gives result of Total Acid Number = 3,324 mgKOH/g
- Ratio Variation VI (Toluene 75% : Ethanol 25%) gives result of Total Acid Number = 3,399 mgKOH/g

The preliminary test concluded that Ratio Variation V, which was solvent mixtures of 70% toluene and 30% ethanol with Total Acid Number of 3,324 mgKOH/g was almost as the same value as Total Acid Number in Standard Method, which is 3.320 mgKOH/g. From that data, that variation was chosen to be researched further. The obtained data was compared to the ASTM D664 Standard Method. Also, the precision and accuracy tests were also performed. The normality test was performed to check the distribution of data from both methods. The independent t-test was performed to check a difference that would probably occurred between those methods and to determine whether the difference is significant or not.

The object of research was a lubricant with a known total acid number as control. Materials used were 2-Propanol, Toluene, Ethanol, KOH 0,1 mol/L, Buffer pH seven, and Buffer pH 10. The equipment used is one unit of Potentiometer Merk Aqua Counter Type COM-1700, beaker glasses 200 mL, magnetic stirrer, Graduated Flask, dan Analytical Weight Balance.
As the first step, the solvent mixture for the ASTM D664 Standard Method was toluene and 2-propanol, with a ratio of 50%:50%. Toluene was measured by graduated flask until the volume is 500mL for 1 Liter of solutions, then the solution is kept in a reagent bottle. 2-Propanol is measured by graduated flask until the volume is 500mL, and is put in the same reagent bottle as toluene. The mixture was homogenized and labeled.

The second step was the making of a solvent mixture of modified method, which was toluene and ethanol with a 70%:30% ratio. Toluene was measured with a graduated flask until the volume is 700 mL and kept in a reagent bottle. Ethanol was measured with graduated flask until the volume was 200 mL and kept in the same reagent bottle with toluene. The mixture then was homogenized, and the bottle was labeled.

The third step was the preparation of equipment. The potentiometric titration device was on. The thermostor temperature is set by comparing it to the calibrated temperature device. We made temperature adjustment to avoid a difference between the temperature reading in the device and in the room. Verification of neutral pH at seven by pushing the calibration mode button in device and electrode is put in beaker glass filled with the solution with a pH value of 7. The electrode was left to rest in the solution for about 2 minutes until the potential value is stable, then the “Enter” button is pushed. Verification of basic state by dipping electrode in beaker glass filled with a solution pH value of 10. An electrode is a rest for 2 minutes until the reading is stable, then the “enter” button is pushed. 0.1 mol/L KOH is poured to the automatic burette, and the device is ready to be used.

The fourth step was the Blank measurement. Before measuring the sample, blank measurement is made, that is: 120 mL of standard solvent mixture (Toluene and 2-Propanol) or modified solvent mixture (Toluene dan Ethanol) is poured to beaker glass. The magnetic stirrer is put in beaker glass, and the blank titration is carried on without putting any sample on S-File. “Titration” button in the device is pushed, and the device will start. After the blank titration was finished, then the titration volume was recorded.

The fifth step was the measurement of the sample by the ASTM D664 Standard Method. The sample was weighed as much as the control’s with analytical weight balance (± 2 gram) and was put to the 200 mL beaker glass. A magnetic stirrer was put on the bottom of the beaker glass, and the solution was stirred in the 120 mL standard solvent mixture. Sample titration was carried out by pushing the S-File button. Data on the weight of the sample, blank titration volume were put into the device. The sample identity was also put to the device, and the “Titration” button was pushed. The result is presented in the monitor in mg KOH/g unit, or can be calculated by this equation:

\[
\text{Total Acid Number (mgKOH/g)} = \left\{\left(\text{A-B}\right) \times M \times \text{MW KOH} \times F\right\} / W
\]

Where A= volume of KOH that is needed for sample titration; B= volume of Blank titration; M = concentration of KOH; MW KOH = molecular weight of KOH; F = correction factor of KOH concentration; and W=weight of the sample. Replication is made eight times.

The sixth step was the measurement of the sample. Modified Method sample was weighed by analytical weighing balance. ± 2 grams of sample was in 200 mL beaker glass was weighed by analytical weighing balance. The magnetic stirrer was put, and 120 ml of a solvent mixture of toluene and ethanol (70%:70%) is poured into the glass, and the solution is stirred. Sample titration is carried on by pushing the S-File button. Data on the weight of the sample, blank titration volume are put into the device. The sample identity is also put to the device, and the “Titration” button is pushed. The result is presented in the monitor in mg KOH/g unit. Replication is made eight times.

The seventh step was the determination of precision and accuracy. This step was carried in 8 times of replication of the sample by two methods. From the measurement, the average and standard deviation were obtained. Precision and accuracy were calculated with equations:

\[
\text{Precision} : (CV) = \frac{SD}{\overline{x}} \times 100 \%
\]

SD = standard deviation
x = average of measurement data
Data is précised if RSD (%) < 2/3 CVH

\[
\text{Accuracy} = \frac{|x - TV|}{TV} \times 100\%
\]  

(4)

\(x\) = average of measurement data  
\(TV\) = true value (control sample concentration)  
Data is accurate if %Error < 5 %

The eighth step was Normality Test and Independent T-Test (T-Test). All the research data was statistically tested to determine the normality and independent-test by using SPSS Software.

3. Result and Discussion

After the research on the comparison of total number acid by ASTM D664 standard method to modification method, is carried on, the obtained data were:

**Table 1. Results of Measurement Control Sample by using the solvent mixture of the ASTM D664 Standard Method.**

| Replication | Resulted data from Standard Method ASTM D664 (mgKOH/g) |
|-------------|--------------------------------------------------------|
| 1           | 3,323                                                   |
| 2           | 3,329                                                   |
| 3           | 3,323                                                   |
| 4           | 3,330                                                   |
| 5           | 3,327                                                   |
| 6           | 3,323                                                   |
| 7           | 3,325                                                   |
| 8           | 3,323                                                   |
| **Average** | **3,325**                                               |
| **SD**      | **0,00292**                                             |
| **RSD (%)** | **0,088**                                               |
| **CV Horwitz** | **2,36**                                      |
| **2/3 CV Horwitz** | **1,57**                                    |

**Table 2. Results of Measurement Control Sample by using Modification Method**

| Replication | Resulted in data from the Modification Method (mgKOH/g) |
|-------------|----------------------------------------------------------|
| 1           | 3,323                                                    |
| 2           | 3,329                                                    |
| 3           | 3,323                                                    |
| 4           | 3,330                                                    |
| 5           | 3,327                                                    |
| 6           | 3,323                                                    |
| 7           | 3,325                                                    |
| 8           | 3,323                                                    |
| **Average** | **3,325**                                               |
| **SD**      | **0,00292**                                             |
| **RSD (%)** | **0,088**                                               |
| **CV Horwitz** | **2,36**                                              |
| **2/3 CV Horwitz** | **1,57**                                           |
In the determination of Precision and Accuracy from the data obtained by measuring sample by ASTM D664 Standard Method in Table 1, precision and accuracy are determined by Horwitz CV. Horwitz CV is a constant or equation to determine that coefficient of variation (CV) of these data is acceptable. Generally speaking, in analytical chemistry, if calculated CV (RSD) is lesser than 2/3 CV Horwitz, then the analytical method is good. CV Horwitz is calculated by equation CV Horwitz = 2/3 x (2(1-0.5log C)). The c value is the average concentration of measurement based on its unit, then for the concentration unit of mg/g, then C is multiplied by 10\(^{-1}\). Then the calculation of RSD (%) and CVH is:

\[
\text{RSD} \% = \frac{\text{SD}}{\text{X}} \times 100 \%
\]

\[
\text{RSD} \% = \frac{0.00093}{3.320} \times 100 \% = 0.028 \%
\]

\[
\text{CVH} = 21 - 0.5 \log C
\]

\[
= 21 - 0.5 \log 0.332
\]

\[
= 21.24
\]

\[
\text{CVH} = 2.36
\]

\[
\frac{2}{3} \text{CVH} = 1.57
\]

Based on the calculation above, then it was concluded that RSD (%) ASTM D664 Method Standard was lesser than 2/3 CV Horwitz. This shows that this method has precisied data [5]. While for the determination of accuracy, it was calculated from this equation:

\[
\% \text{Error} = \frac{|\text{nilai analisis}-\text{TV}|}{\text{TV}} \times 100\%
\]

\[
= \frac{|3.320-3.300|}{3.300} \times 100\%
\]

\[
= 0.02/3.30 \times 100\%
\]

\[
= 0.61\%
\]

A set of data is accurate if %Error < 5% [5]. From the calculation above, it is showed that %Error is lesser than 5 %. This shows that the ASTM D664 Standard Method has accurate data.

The determination of precision and accuracy from Modification Method Data can be seen in Table 2. The results of measurement of Sample Control by using modification method (a solvent mixture of toluene and ethanol70%: 30%), the calculation of RSD value (%) and CVH are:

\[
\text{RSD} \% = \frac{\text{SD}}{\text{X}} \times 100 \%
\]

\[
\text{RSD} \% = \frac{0.00292}{3.325} \times 100 \% = 0.088\%
\]

Based on the calculation above, it can be seen that RSD value (%) of the modification method is lesser than 2/3 CV Horwitz. This shows that this method has a precisied set of data [5]. While to determine accuracy, the calculation is:

\[
\% \text{Error} = \frac{|\text{nilai analisis}-\text{TV}|}{\text{TV}} \times 100\%
\]

\[
= \frac{|3.325-3.300|}{3.300} \times 100\%
\]

\[
= 0.025/3.30 \times 100\%
\]

\[
= 0.76\%
\]

From the data calculation above it is shown that %Error is lesser than 5 %. This shows that this method has an accurate set of data [5].

The next step is the Normality Test that aims to measure whether the data has a normal distribution so statistical parametric can be applied to the data. The determination of the Normality Test in this research uses Kolmogorov-Smirnov, which is to compare the data in the quest and the normally distributed data and to see whether it is normal or not. If the set of data is normally distributed, then statistical analysis can use the parametric approach, while if it is not normally distributed, then the analysis uses a non-parametric approach [6]. From the determination of Kolmogorov-Smirnov Normality Test, the results of both sets of data from two methods are obtained:
Table 3. Result of Kolmogorov-Smirnov Normality Test from data ASTM D664 Standard Method and Modification Method by using SPSS Software

| SPSS Result       | Modification Method | Standard Method |
|-------------------|---------------------|-----------------|
| N                 | 8                   | 8               |
| Mean              | 3.325375            | 3.320000        |
| Standard Deviation| .0029246            | .0009258        |
| Absolute          | .292                | .375            |
| Positive          | .292                | .375            |
| Negative          | -.208               | -.250           |
| Kolmogorov-Smirnov Z | .825              | 1.061           |
| Asymp. Sig. (2-tailed) | .504              | .211            |

a. Test distribution is normal

Sig > 0,05

If the significant value is more than 0.05, then a set of data is normally distributed, and if lesser than 0.05, then a set of data is not normally distributed (Henry C at al, 2002). Based on the table above, it can be seen that Asymp. Sig. (2-tailed) 0.05. Both methods are more than 0.05. Sig value for the standard method is 0.211 Sig value for the modified method is 0.504. From those results, it is concluded that data from both methods are normally distributed.

The independent-samples t-test (or independent t-test, for short) compares the means between two unrelated groups on the same continuous, dependent variable [6]. Conditions to be met before applying this T-Test are:

- It should be a set of quantitative data (interval data or ratio data).
- Data should be normally distributed.
- Data should be homogenous.
- This test is done to a set of data of less than 30 data.

Hypotheses that can be taken are:

- Ho: There is no difference between the average standard and modification method.
- Ha: There is a difference between the average standard and modification method.

Principle of decision making in T-Test is:

- If Significance of value or Sig. (2-tailed) > 0.05, then Ho is accepted, and Ha is rejected.
- If Significance of value or Sig. (2-tailed) < 0.05, then Ho is rejected, and Ha is accepted.

From the determination of T-Test Independent from both data, it is obtained that value of Sig. (2-tailed) both methods show a value of more than 0.05, which is 0.846. Then it is concluded that if the value of Significance or Sig. (2-tailed) > 0.05, then Ho is accepted, and Ha is rejected. That means there is no difference between the average of the standard method and the modified method.

In results, the modified solvent mixture is optimum when toluene and ethanol at a ratio of 70%: 30%. With that ratio, it is obtained the precise and accurate data, and there is no significant difference with a standard solvent mixture that is toluene and isopropanol with a ratio of 50%:50%. From the preliminary test, it is obtained that the decrease of ethanol gives a higher acid concentration. It is known that acid mixture in the lubricant is acids from hydrocarbon that react with air or other compounds to form carboxylic acids. Short-chain carboxylic acids are polar acids, while long-chain carboxylic acids are less polar. The higher the volume of ethanol causes, the more reactions between these carboxylic acids to form an ester. The reaction is:
Carboxylic acids that should be dissolved in toluene and react with KOH to produce salts, it turned out to form a neutral ester, and the content of acids detected is low. While from the ratio of the volume of isopropanol (in a solvent mixture in standard method) with ethanol (in a solvent mixture of modified method) differs for each ratio in the mixture. If isopropanol in mixture with toluene, it needs 50% of isopropanol, while if ethanol in mixture with toluene, it needs 30% of ethanol. It is known from the data of general characteristics that the polarity of ethanol is higher than isopropanol with a dielectric constant for ethanol is 30, while for isopropanol is 18. In the determination of precision accuracy, based on the measurement and calculation of each method, it is obtained RSD (%) < 2/3 CV Horwitz and % Error < 5%. According to JC. Miller and JN. Miller, an assay, is said to be accurate if % Error < 5 % and said to be precise if RSD (%) < 2/3 CV Horwitz.

Because this research compares two methods, then the statistic test must be conducted to find out whether there is a difference between the averages of these methods. The statistic test in this research is Independent T-Test.

The independent-samples t-test (or independent t-test, for short) compares the means between two unrelated groups on the same continuous, dependent variable (Sugiyono, 2007). Conditions to be met before applying this T-Test are:

- It should be a set of quantitative data (interval data or ratio data).
- Data should be normally distributed.
- Data should be homogenous.
- This test is done to a set of data of less than 30 data.

Based on the conditions above, then data in this research must be tested for its normality to find out whether the data is normally distributed or not. If the data is normally distributed, then T-Test with Independent T-Test can be done.

The determination of the Normality Test in this research used Kolmogorov-Smirnov, which was to compare the data in the quest and the normally distributed data and to see whether it is normal or not. A set of data is said good and appropriate to be used in research when it is normally distributed. The normality test is carried out before data is treated based on research models. If data is normally distributed, then statistical analysis uses a parametric approach, while if a set of data is not normally distributed, then statistical analysis uses a non-parametric approach. The solution for not normally distributed data is non-parametric approach Mann Whitney Test data from normality test from standard method shows the significant value of 0.211, and from modification method, significant value is 0.504. it can be said that both data from both methods had normal distribution because significance values are lesser than 0.05. After the Normality Test is conducted, and the result is obtained, then it is shown that both data are normally distributed. Then Independent T-Test can be conducted. There are two steps in Independent T-Test: the first step is to test whether the variance of both methods can be assumed to be the same. The second step was conducted to find out the difference between average of both methods. To have a conclusion on whether two methods show the same variance, then F-Test is conducted. Hypotheses for variance test are:

- Ho: Both variances in two methods are identical (variance of the standard method and modification method are the same)
- Ha: Both variances in two methods are not identical (variance of the standard method and modification method are different)

Decision making (variance test) is:
• If the value of Sig > 0.05, then Ho is accepted

• If the value of Sig < 0.05, then Ho is rejected.

From the table of Independent T-Test: it is shown that the F value is 1.861 with Sig.value is= 0.194. because of Sig. Value is > 0.05, then Ho is accepted, or variance of both data are identical (variance of standard method and modification method are the same). After the F Test Analysis, then T-Test is conducted. Hypotheses that can be made for the T-Test is:

• Ho: There is no difference between the average standard and modification method.

• Ha: There is a difference between the average standard and modification method.

The decision making in T-Test is:

• If significant value or Sig. (2-tailed) > 0.05, then Ho is accepted and Ha is rejected

• If significant value or Sig. (2-tailed) < 0.05, then Ho is rejected and Ha is accepted

From the table of Independent T-Test, it can be seen that Sig. Value (2-tailed) from both method with the assumption that variances are equal (equal variances assumed), it shows the value greater than 0.05 that is 0.846. Because the value of Sig > 0.05, then Ho is accepted, and Ha is rejected. That means there is no difference between the averages of the standard method and the modified method.

From the research, it can be seen that generally, the difference is not too wide. This shows that the use of ethanol in the mixture with toluene can be used as an alternative solvent.

Research in finding new alternative methods in determining Total Acid Number (TAN) is not a new thing. Alternative methods on the previous research consist of solvent type modification, solvent and sample size modification, and also entirely new method. This previous research can be seen in Table 4.

| New Alternative Method                                               | Type                  | Usage                                                                 | Reference |
|---------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------|-----------|
| Aqueous potassium hydroxide (0.1 M KOH) was used as standard titrant instead of 0.1M KOH in alcoholic solution, and acetone was used as titration solvent instead of mixtures of toluene and IPA as specified in the ASTM method. | Solvent type modification | This method is applicable for bio oils lubricant which are soluble in polar solvents and partially soluble in water. | [8]       |
| This method proposed entirely new way in determining Total Acid Number (TAN). This method uses two 4-hydroxystyryl N-octylpyridinium bromides dyes as indicators rather than conduct potentiometric titration technique. | New method            | This method is applicable for different kind of engine fuels, especially biodiesel with special conditions. | [9]       |
| This method proposed usage of modification solvent instead of standard 1:1 toluene : isopropanol mixture. The modification solvent is 1:1 ethanol : water mixture with the addition of phenolphthalein.  | Solvent type modification | This method is tested on biodiesel lubricant. | [10]      |
| This modification method recommends a reduced amount of titration solvent and the use of a small sample size instead of a larger sample size as stated | Solvent and sample size modification | This method is claimed to be applicable for determining acid number | [11]      |
This method is also developing a time-efficient electrode cleaning procedure that eliminates the use of toxic solvents as a conventional electrode cleaners. Solvent and sample size modification of biodiesel and biodiesel blends. This method proposed a modification of ASTM D664 procedures, reducing 50% the amount of sample and using only 50 ml solvent mixture against 125ml for the official method.

4. Conclusion
Based on the research that has been done, then the conclusion that can be drawn:

- The result of research on the use of solvent mixture toluene and ethanol with optimum ratio can be used as an alternative to replacing solvent mixture in a standard method.
- It is obtained that the optimum ratio of a solvent mixture of toluene and ethanol for determination of Total Acid Number by using the Potentiometric Method is 70%: 30%.
- The use of mixture toluene and ethanol with the optimum ratio as a solvent mixture in the modification method gives a set of data that is precise and accurate.

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