

The potential utilization of coconut oil and palm oil as raw material of alkanolamide under alkaline conditions

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Abstract. Indonesia has a high production of vegetable oils. Coconut oil and palm oil are vegetable oils that can be source of raw material in Industry. The purpose of this research is potential use of coconut oil and palm oil as raw materials of alkanolamide in alkaline condition. Alkanolamide is produced from the reaction between triglycerides and diethanolamine. Phosphoric acid is used as a solvent for the purification of alkanolamide from its mixture with glycerin. So it is expected that alkanolamide produced has a high purity and the resulted alkanolamides have dispersant and detergency properties that are widely used in various industries. The amidation reaction between triglyceride and diethanolamine was mixing in a glass batch reactor for 2 hours using potassium hydroxide catalyst (KOH) 1% (w/w). The temperature reaction was 125 °C. The second step is purification of alkanolamide. The operation condition is preferably performed at 82 °C. The synthesis of palm oil in this study is constrained because it is easily oxidized and the viscosity was higher than coconut oil. So this research is focused on using coconut oil as raw material. From the purification analysis, resulted 85% of alkanolamide (top layer) and 15% glycerine (bottom layer). From FTIR analysis, The amide group (C=O) is formed at a wavenumber of 1618,34 cm⁻¹ for alkanolamide from coconut oil and 1617,45 cm⁻¹ for alkanolamide from palm oil. GC-MS analysis resulted the compound of diethanolamide laurate with the greatest quality percentage of 93% and the largest percentage of 31, 20%.

1. Introduction

Coconut oil and palm oil are potential raw material to be developed in the industry. Coconut oil and palm oil are easily available and the process is easy and fast. Coconut oil and palm oil can be used to replace oil because they are environmentally friendly and biodegradable. Coconut oil and palm oil can be used as raw materials for alkanolamide. Alkanolamides can be made using a variety of reactants. Alkanolamide is produced from the reaction between the reactants is that one reactant is a fatty acid, methyl ester or triglyceride and the other is an alkanolamine, most commonly diethanolamine [1]. The commonly used raw material is methyl ester. Methyl ester will become a serious consideration if it is used because methyl ester produces abundant foam [2]. In the previous research, acid catalyst was used. Acid catalyst has shortcoming because the rate of reaction is low and it needs high temperature reaction and it is corrosive. In this research, the catalyst used is alkaline catalyst potassium hydroxide

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(KOH). It was because the alkaline catalyst has the advantage of being cheap and not corrosive. However, the weakness of this catalyst is that it needs relatively difficult separation process from the product. In the purification process, phosphoric acid is used as a solvent to separate alkanolamide from glycerin so the production of alkanolamide will have high purity. The resulted alkanol amides have dispersant and detergency properties that are widely used in various industries. In its use as a fuel additive, it attracts impurities derived from deposits that form on the intake system or combustion chamber to reduce friction on the engine and can save fuel consumption [3]. Dispersant and detergents in fuel additives are classified as deposit control agent (DCA). Alkanolamide is produced from the amidation reaction. Based on the reaction alkanolamide is produced from the reaction of alkanolamine and the source of fat/oil [1]. The alkanolamide reaction is as follows:

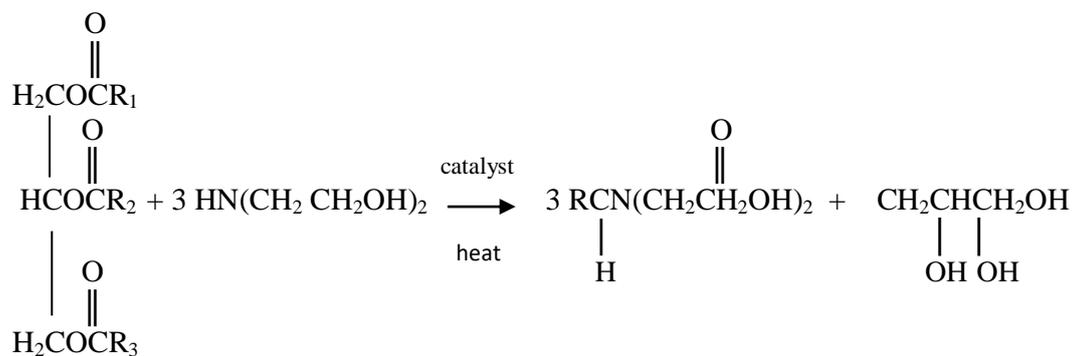


Figure 1. Reaction of alkanolamide.

2. Methodology/experimental

2.1. Material and equipments

The following chemicals were commercially available and used as received Coconut oil, palm oil as source of triglyceride, Diethanolamine as source of amine, KOH (potassium hydroxide) as agent catalyst, Phosphoric acid as purification of alkanolamide. While the equipment are a glass batch reactor, a stirring hot plate, and thermometer. All chemicals used are pro analysis grade.

2.2. Procedure

The method of making alkanolamide has two steps, the first is the reaction of diethanolamine and triglyceride and second is the purification of the alkanolamide from its mixture of with glycerin.

2.2.1 Synthesis of alkanolamide. The amidation, the reaction between triglyceride and diethanolamine, was held in a beaker glass reactor on the top of a stirring hot plate for 2 hours with mole ratio of 1: 1.5 using alkaline catalyst (KOH) 1 % (w/w). The temperature reaction at 125 °C. Under these conditions, the mixture becomes transparent (homogeneous) as a liquid phase. Temperature during mixing is maintained. The reaction is continued until the total reaction time corresponds to the desired variation until the solution is dark yellow. After the reaction time is completed, one-phase solution will be formed, and temperature decreased until 82 °C (should be below 100 °C to prevent condensation).

2.2.2 Purification of alkanolamide. One of the disadvantage of using an alkaline catalyst is the difficulty of separating the product from the reaction. A method for alkanolamide purification is required. H₃PO₄ is used as a solvent for the purification of alkanolamide from its mixture of with glycerin. Phosphoric acid is used to remove the free amine from glycerin. Phosphoric acid used 6-9

parts by weight of phosphoric acid to 100 parts by weight of crude amide. The operation is preferably performed at 82 °C. The layers to be formed consist of the top layer (organic) which is the amide compound and the bottom layer (inorganic) which is glycerin compound. There should be no fatty compound in this lower (inorganic) layer. Analysis of top layer results (amide compounds) is showed below.

2.2.3 Analysis of samples. The analysis include Fourier Transfer Infra-Red (FTIR) (Thermo scientific Nicolet iS5 with iD5 ATR) to know the structure of alkanolamide, Gas Chromatography-Mass Spectrometry (GCMS) (GC 6890 MS 5973 Agilent) that use helium carrier gas to determine the molecular weight of alkanolamide.

3. Results and discussion

3.1. Analysis of purification

In alkanolamide synthesis, the reaction between triglyceride and diethanolamine by using an alkaline catalyst will form one phase, it is necessary to purify to separate the alkanolamide from the byproducts of glycerin. In this case the amide purification is carried out by a simple method by adding a solvent to the amide solution formed. Then used compounds containing phosphoric acid to bind alkanolamides formed. Then the compound used is phosphoric acid, its group contains a proton that can dissociate, leaving a residual molecule with a negative charge. In this case the transfer of grup occurs is phosphorylation. Alkanolamides formed in one phase when added phosphoric acid compounds will form two layers of phosphorylated glycerin and alkanolamine phosphate. Phosphoric acid used 6-9 parts by weight of phosphoric acid to 100 parts by weight of crude amide. The operation condition is preferably performed at 82 °C [2]. The layers to be formed consist of the top layer (organic) which is the amide compound and the bottom layer (inorganic) which is glycerin compound. The phosphate will bind *mono, di*, triglycerides and will be bonded to the bottom layer, or precipitation forming phosphoglycerides. The resulting end product consists of substantially 85% of alkanolamide (top layer) and 15% glycerine (bottom layer) . The results of this top layer will be analyzed using FTIR and GC-MS.

3.2. FTIR Analysis

The characteristic of alkanolamide synthesis with FTIR was used to identify the groups contained from the result of alkanolamide synthesis. Alkanolamide formed can be proven by comparing the results of analysis with raw materials. The FTIR results can be seen in figure 2.

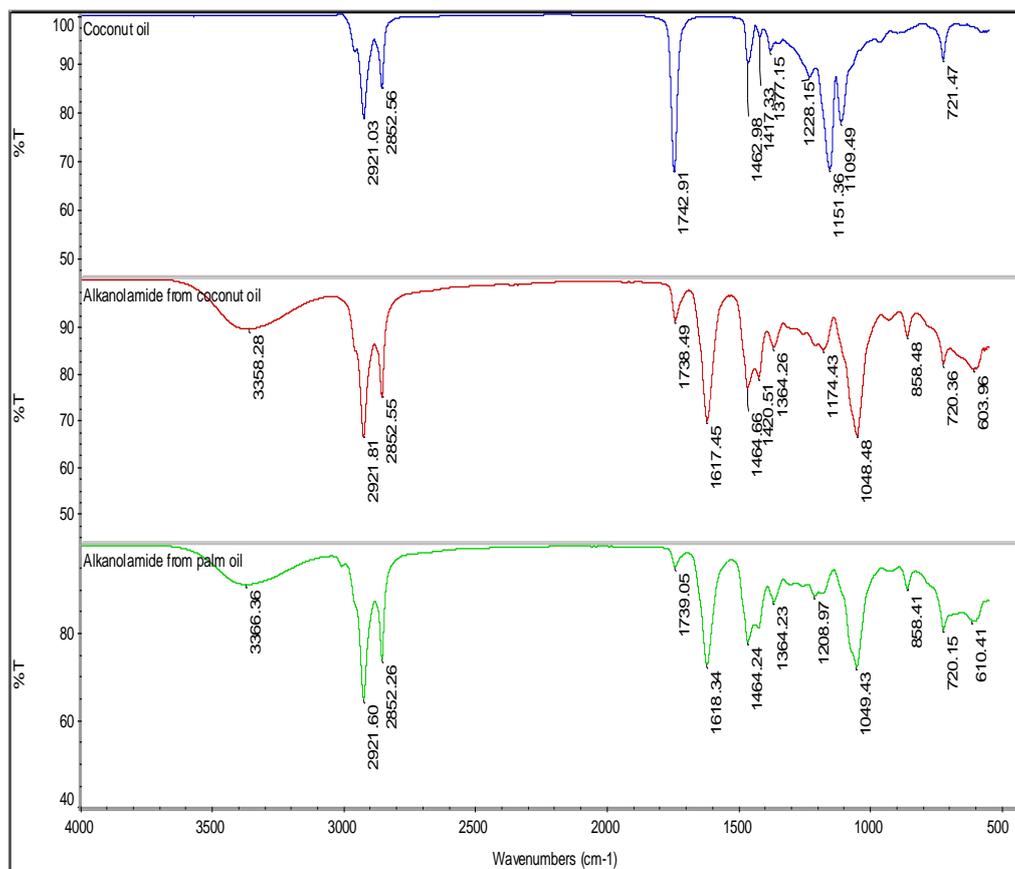


Figure 2. Comparison of IR spectra of alkanolamide and coconut oil.

In this case the results of FTIR alkanolamide analysis will be compared with coconut oil. Figure 2 shows that the alkanolamide has been formed. It can be seen that there is a difference in spectrum results among coconut oil, coconut oil alkanolamide and palm oil. From literatures, alkanolamides were formed by the existence of strong absorption at $C=O$ at $1630\text{--}1660\text{ cm}^{-1}$. If there is hydrogen bonded with nitrogen, there will be formed $N-H$ absorptions at around 3300 cm^{-1} [4]. The difference in spectrum results among coconut oil, alkanolamide from coconut oil and alkanolamide from palm oil spectrum. The differences in the results of the spectrum between coconut oil and alkanolamide with coconut oil and palm oil are characterized by the formation of wave numbers of 3358.28 cm^{-1} for alkanolamide from coconut oil and 3366.36 cm^{-1} for alkanolamide from palm oil for which the absorption of $O-H$ groups are widened and strong, and the $N-H$ group also appears in this area and near with the $O-H$ group so that it is not apparent on the spectrum. The $C-H$ aliphatic group may form at wavenumbers of 2921.81 cm^{-1} for alkanolamide from coconut oil and 2921.60 cm^{-1} for alkanolamide from palm oil. The $C-H$ aliphatic group supports that fatty acids in palm oil and coconut oil are long-chain carboxylic acids. The amide group $C=O$ is formed at a wavenumber of 1618.34 cm^{-1} for alkanolamide from coconut oil and 1617.45 for alkanolamide from palm oil. While, from the FT-IR spectrum of coconut oil triglycerides, it can be seen that the wavenumber of 2921.03 cm^{-1} shows the stretched $C-H$ bond. The typical absorption from triglycerides also appears at wavenumber of 1742.91 cm^{-1} which is an absorption of $C=O$ ester. From two samples of alkanolamide can be seen results that not much different, the difference of intensity only. This is because the constituent groups of each of the same alkanolamides are the OH groups, the NH groups, the $C-H$ aliphatic groups and the $C=O$ amide groups. In this case it can be seen in table 1.

Table 1. Wavenumber of IR spectra of alkanolamide and coconut oil

Sample	Wavenumber (cm ⁻¹)		
	N-H	C-H	C=O
Coconut oil	-	2921.03	1742.91
Alkanolamide from coconut oil	3358.28	2921.81	1618.34
Alkanolamide from palm oil	3366.36	2921.60	1617.45

3.3. GC-MS Analysis

The GC-MS analysis was performed to determine the alkanolamide composition resulting from the amidation reaction between oil and diethanolamine. The result of alkanolamide synthesis from palm oil was not analyzed using GC-MS because the viscosity of alkanolamide from palm oil was high, which performed from the fatty acid structure of the palm oil composite that having a fairly high carbon chain of palmitic acid with the C₁₆ group. The results of GC-MS alkanolamide analysis from coconut oil can be seen in figure 3 and table 2.

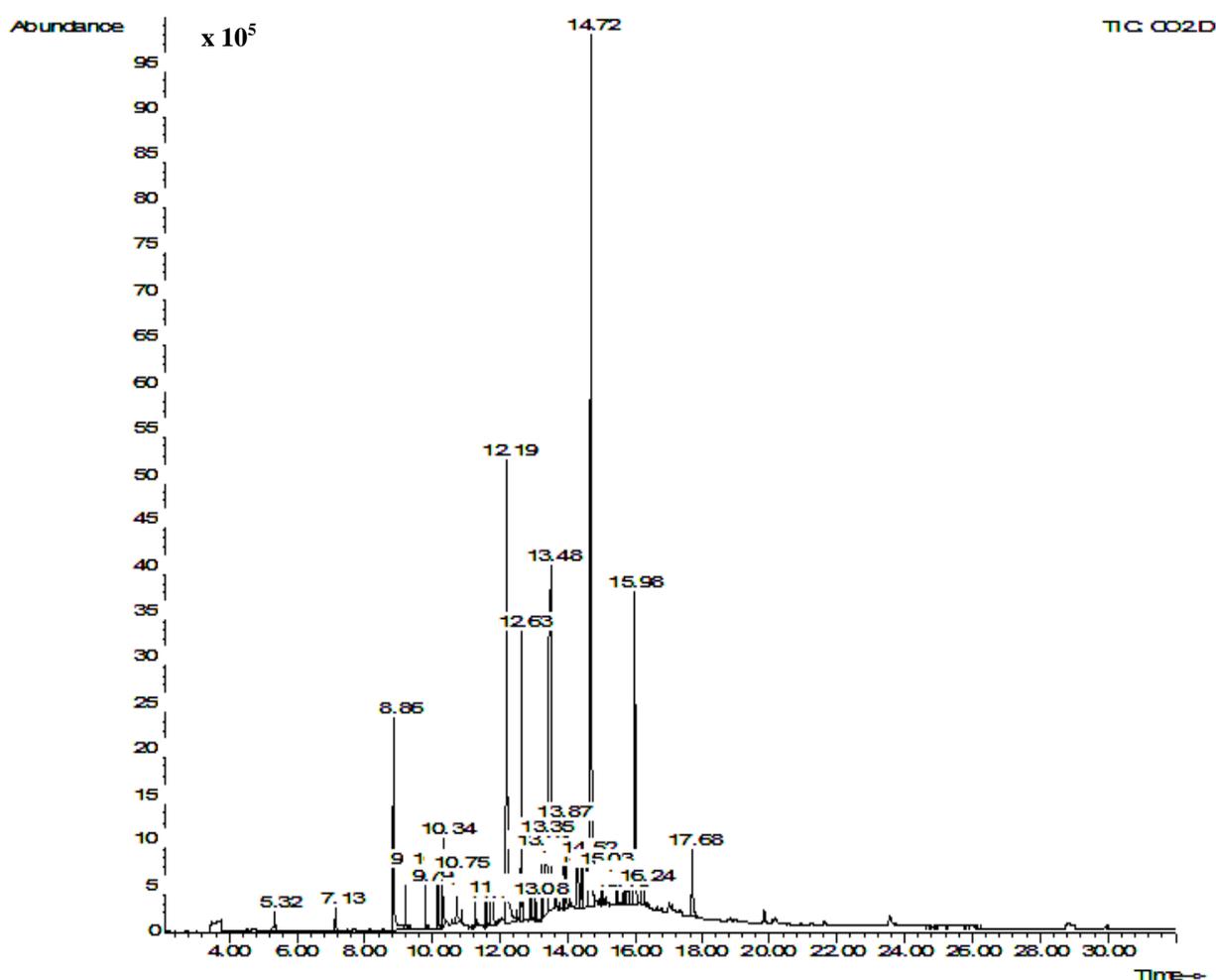
**Figure 3.** GC-MS spectra analysis of alkanolamide synthesis from coconut oil.

Table 2. GC-MS analysis alkanolamide from coconut oil.

Time (min)	Area (%)	Library	Qual/Similarity(%)
8.86	6.80	Dedocanoic acid	99
10.34	1.56	Tetradecanoic acid	99
14.72	31.20	Dedocanamide	93

The most commonly peak analysis result was the dedocanamide or diethanolamide laurate compound with the greatest quality percentage of 93% and the largest percentage of 31.20% which having molecular weight of 287.44 gr/mol with molecular formula $C_{16}H_{33}NO_3$. Diethanolamide laurate formed from derived fatty acid of coconut oil, lauric acid (C_{12}). Diethanolamide laurate is a detergent in bioadditive gasoline because the amine content contained in alkanolamide will attract impurities derived from the deposit formed in the intake system or combustion chamber. Dispersant and detergent in fuel additives are classified into a deposit control agent (DCA). The amide group is used as deposit control agent (DCA), based on the polar head formed from the alkanolamide compound. Where the hydrocarbons formed are hydrophobic and the amide compounds are polar and hydrophilic. The action of the DCA is that the polar part (amine) attracts to the solid particles (such as soot in combustion, wear and dust products) and forms a protective layer on the surface of the deposit precursor thus preventing the deposit from being difficult to agglomerate and difficult to accumulate on the intake valve, injector and combustion chamber. It also acts as a nonionic surfactant as a foam stabilizer, emulsifying, coagulant material [5]. The lauric acid content of the diethanolamide has a function as a lubricant, in which the amount of carbon 8 to 24 is antiwear, this lubricant composition provides strong adhesion and oil wetting on the metal part, thereby reducing wear and tear, improving lubrication and fast pit drilling [6].

4. Conclusion

As mention before about the characteristic of coconut oil and palm oil, this research is focused on using coconut oil as raw material. From the analysis purification, resulted 85% of alkanolamide (top layer) and 15% glycerine (bottom layer). The amide group $C=O$ is formed at a wavenumber of 1618.34 cm^{-1} for alkanolamide from coconut oil and 1617.45 cm^{-1} for alkanolamide from palm oil, GC-MS analysis is the compound diethanolamide laurate with percent area of 32.10%. Diethanolamide laurate fuction as detergent in bioadditive gasoline, non-ionic surfactant surfactant as a foam stabilizer, emulsifying, coagulant material. The lauric acid content of the diethanolamide has a function as a lubricant.

5. Acknowledgments

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6. References

- [1] Anthony J. O'Lenick, Jr 2014 *Surfactants: Strategic Personal Care Ingredients* (USA: Allured Publishing Corporation)
- [2] Lohr, J W, Cincinnati, Ohio 1968 *US Patent 3,040,075* 1-4
- [3] Colucci, William J, Kadkhodayan, Abbas 2013 *US Patent 8,444,720 B2* 1-2
- [4] Wade L G Jr 2010 *Organic Chemistry Seventh Edition* (Boston : Prentice hall)
- [5] Manurung, Renita, Sinaga, Rahmat Akbar, SimaTupang and Rahmat Taufik. 2013 *Int. J. of Innovative Research in Sci. Eng. and Technol* **2** 4205-10
- [6] Gatlin and Larry W 2001 *US Patent 6,194,361 B1* 1-3