VOL. 18, NO. 19, OCTOBER 2023 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

STUDY OF THE SURFACE PROPERTIES OF ALKYL-DEA FROM PALMITIC ACID FOR CLEANING AND COSMETIC APPLICATIONS

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ABSTRACT

A surface active agent is a substance added to a liquid that is useful for increasing the spreading properties by weakening the surface tension of the liquid. The need for biosurfactants continues to increase along with industrial developments and increasing human awareness of good health and the environment. In this study, the surfactant alkyl diethanolamide (Alkyl-DEA) was synthesized using one type of amine alcohol, namely diethanolamine, through an amidation reaction between palmitic acid and using hexane-isopropanol solvent and calcium oxide catalyst. Surface properties in the form of acid number, saponification number, and HLB value were studied by observing the effect of the reaction variables on the three surface properties. This study showed that the best conversion of palmitic acid was obtained at 70^{o}C and 80^{o}C for a reaction time of 5 hours and a stirring speed of 150, 200, and 250 rpm. The relationship between reaction rate and time is directly proportional; the longer the reaction time, the reaction rate will increase. However, increasing the reaction time did not give significant results to the surfactant product. The relationship between reaction temperature and conversion gain decreased with increasing reaction temperature. The acid number obtained under the best conditions was 39.27, the saponification number was 30.85, and the HLB value was 4.29.

Keywords: alkanolamide, diethanolamine, amidation reaction, tert-amyl alcohol.

Manuscript Received 12 August 2023; Revised 20 November 2023; Published 11 December 2023

INTRODUCTION

Surfactants are wetting agents that lower the surface tension of liquids, allowing easier spreading, and can also lower the interfacial tension between two liquids. Petroleum-based surfactants are not biodegradable. In contrast, surfactants from vegetable oils such as alkanolamide are mostly biodegradable and environmentally friendly. Alkanolamide is a non-ionic surfactant from the reaction between primary and secondary alkanol amines with triglycerides or fatty acids [1, 2, 3].

The possible chronic effects caused by surfactants on living things and the potential impact on the environment should be minimized. This depends on its biodegradability and surfactant toxicity [4, 5]. Biosurfactants containing amide bonds are potential compounds that are substitutes for emulsifiers derived from petroleum. The advantage of this surfactant is that the toxicological effect of this amide is lower than that of petroleum emulsifiers [6, 7, 8].

Alkanolamides are condensation products of the reaction of primary or secondary alkanol amines with fatty acids, methyl esters, or triglycerides. Their chemical properties vary depending on the length of their hydrocarbon chains and the nature of the substituents on the nitrogen atom. Fatty alkanol amides are compounds that exhibit high reactivity and thermal stability. Because amide bonds are chemically stable and not easily degraded in alkaline media, they are very attractive for applications that require a relatively stable emulsifier. Alkanolamide has various uses, such as cosmetic preparations, medicines, shampoos, and detergents [2, 9].

Diethanolamine is widely used to synthesize important heterocyclic compounds such as morphine, piperazine, oxazolidine, dioxazine, crown ether, and ionic liquids. Diethanolamine and its derivatives have wide applications in the pharmaceutical, surfactant, polisher, and cosmetic industries. Diethanolamine is an intermediary in the rubber chemical industry and an emulsifier and dispersing agent in various agricultural products. Diethanolamine is also used in adhesives, cement, coatings, electroplating, printing inks, lubricants, paints, paper, petroleum, coal, polymer production, and textile finishing. Diethanolamine derivatives exhibit a broad spectrum of biological activities, including antibacterial, anti-fungal, anti-tuberculosis, anti-cancer, local anesthetic, antiplatelet aggregation, and antioxidant. Therefore, diethanolamine can synthesize surfactants [10, 11].

Economical methods with environmentally friendly reaction conditions, and attention to health aspects for amide synthesis, have become research advantages in this industry in recent years. Heterogeneous catalysts can be a suitable and attractive alternative because of their low consumption, environmentally friendly use, easy separation from the reaction mixture, and recyclability [12]. One of the most widely used catalysts is CaO because it has many advantages such as low price, long catalyst life, high activity, and only requires moderate reaction conditions. However, some disadvantages are found in CaO catalysts where the surface area is low and

melts easily [13]. Based on the theory that has been described, it is necessary to conduct research on the synthesis of palmitic acid and diethanolamine surfactants through amidation reactions using CaO catalysts to obtain important information regarding the effect of temperature and stirring speed on the synthesis of the resulting surfactants.

The amidation reaction of fatty acids is important in which fatty alkanolamides are formed as products. The application of this product is related not only to surfactants but also to high-value drugs that exhibit multiple biological effects, such as anti-carcinogenic and activity against Alzheimer's disease. Using heterogeneous catalysts makes this process eco-friendly and less costly, avoiding impractical catalyst separation [14].

MATERIALS AND METHODS

Materials

The materials used are palmitic acid ($C_{16}H_{32}O_2$), diethanolamine (C_2H_7NO), calcium oxide catalyst (CaO), hexane solvent (C_6H_{14}), isopropanol (C_3H_8O) and purification materials in the form of citric acid ($C_6H_8O_7$) and acetone (C_3H_6O). The analytical materials are Potassium Hydroxide (KOH), Phenolphthalein, and Hydrochloric Acid (HCl). All materials were obtained from E Merck.

Amidation Procedure

Hexane and isopropanol solvents were mixed in a 1:2 (v/v) ratio. A three-neck flask equipped with a thermometer and hot plate was prepared. Add 5 grams of palmitic acid and mixed solvent. After being homogeneous, diethanolamine was added with a mole ratio of amine: fatty acid 1:10 (w/w). Next, a catalyst of calcium oxide (CaO) is added with a concentration of 5% for fatty acids. The mixture of ingredients is heated at various temperatures of 70 and 80^{o}C. After the heating temperature was reached, the reaction time was calculated for 5 hours, at variations of stirring speed of 150, 200, and 250 rpm. After 5 hours, 5 ml of 10% stearic acid was added to the product mixture to precipitate the CaO catalyst, then filtered to separate CaO and heated at 90^{o}C to evaporate the solvent. The excess amine was washed with acetone, and the surface properties were observed as the acid number, saponification number, HLB, and identified surfactant produced by FTIR.

RESULTS AND DISCUSSIONS

The reaction of fatty acids or fatty acid methyl esters with alkanol amines produces fatty alkanolamides, such as mono alkanol amides and dialkanolamides. Fatty alkanolamides are prepared by reacting animal or vegetable triacylglycerols with different classes of alkanolamines, such as ethanolamines and diethanolamines. Fatty alkanolamides are multi-purpose oleochemicals commonly used as non-ionic surfactants in cosmetics, personal care, and home products [15].

Palmitic acid is used as a source of fatty acids. Palmitic acid, stearic acid, and oleic acid, when compared to lauric acid, and myristic acid, have a position as a detergent stabilizer, as well as its use as a cosmetic ingredient [16].

Diethanolamine was chosen as the amine source in this study. Diethanolamine is widely used in oil derivatives, cosmetics, pharmaceuticals, soaps, shampoos, cleaners, polishes, and agricultural products. The most likely environmental exposure route for diethanolamine in humans is skin exposure to personal care products (i.e., skin lotions, soaps, shampoos, and cosmetics), detergents, and other DEA surfactants. Cosmetic formulations may have concentrations of DEA ranging from 0.1 to 5% [11].

In the synthesis of palmitic acid with amines to form alkanolamide, the parameters affecting the amide recovery were observed: temperature, reaction time, and stirring speed. For this reason, the results of determining the effect of temperature, reaction time, and stirring speed are given in Table-1.

As with determining the operating parameters that affect the amidation reaction of palmitic acid, the kinetics of the reaction also need to be considered to maximize the amount of palmitic acid converted to amide surfactant.

This study aims to determine the best value of each process variable, where the observed process variables are stirring speed, temperature, and reaction time. This research was carried out by reacting fatty acids and diethanolamine with hexane-isopropanol solvent and calcium oxide catalyst. Determination of the best stirring speed, temperature, and reaction time can be obtained based on the resulting conversion. Conversion values can be carried out by taking samples every hour at hours 1, 2, 3, 4, and 5. Table-1 summarizes the effects of temperature, stirring speed, and reaction time. It can be seen that the highest conversion obtained occurred at 1 hour, at each condition of the reaction temperature of 70 and 80^{o}C, with a stirring speed of 150, 200, and 250 rpm.

Based on the results of these data, at a temperature of 70^{o}C, the conversion of palmitic acid at a reaction time of 1 hour with a stirring speed of 150, 200, and 250 rpm was obtained at 85.938%, 87.500%, and 84.375%, respectively. At 80^{o}C, the conversion of palmitic acid after a reaction time of 1 hour, with a stirring speed of 150, 200, and 250 rpm, was obtained at 88.438%, 90.313%, and 86.875%, respectively.

Relation of Reaction Time (t) to Reaction Rate (-rA)

The results of calculating the relationship between reaction time and reaction rate are given in Table 2, and a graph of the relationship between reaction time and rate (-rA) is shown in Figure-1. From Figure-1, it can be seen that the reaction rate decreased with increasing reaction time. In the first hour, it was obtained that the reaction rate increased until the second hour and decreased with increasing time; this also happened for all observations.

The interaction between surfactant molecules and the substrate can decrease and increase the reaction rate, or it can also change the results of the reaction, where sometimes the surfactant molecules act as the reactants.

The reaction rate of anionic surfactants decreases with increasing chain length of the surfactant [17]. The decrease in reaction rate is affected by the decreasing concentration of reactants caused by increasing reaction time so that more and more reactants react to become products.

The reaction rate is affected by concentration, reaction time, and the constant reaction rate. Where the relationship between reaction rate and reaction time is inversely proportional, the longer the reaction time, the reaction rate will decrease [18]. Based on the research that has been done, it is concluded that the results obtained follow the theory.

Table-1. Summarizes the effects of temperature, stirring speed, and reaction time.

Run	Temp (^oC)	Stirring Speed (rpm)	Time (h)	Acid/ Amine Ratio (v/v)	Substrate/ Solvent Ratio (v/v)	Catalyst (%)	Palmitic Acid Conversion (%)
1			1				85.938
2			2				79.688
3	70	150	3	1/10	1/2	5	81.250
4			4				81.250
5			5				81.250
6			1				87.500
7			2				79.063
8	70	200	3	1/10	1/2	5	82.813
9			4				82.813
10			5				82.813
11			1				84.375
12			2				78.438
13	70	250	3	1/10	1/2	5	82.188
14			4				82.188
15			5				82.188
16			1				88.438
17			2				81.250
18	80	150	3	1/10	1/2	5	85.938
19			4				85.938
20			5				85.938
21			1				90.313
22			2				81.875
23	80	200	3	1/10	1/2	5	89.375
24			4				89.375
25			5				89.375
26			1				86.875
27			2				79.688
28	80	250	3	1/10	1/2	5	85.938
29			4				85.938
30			5				85.938

Table-2. The relationship between reaction time and reaction rate.

Run	Time (h)	KOH (ml)	Conversion (%)	C_A	$(-r_A)$	Log $(-r_A)$ (Y)	Log (-rA) (X)	X^2	X, Y
1	1	4.5	85.938	0.044	0.000	0.000	-1.352	1.828	0.000
2	2	6.5	79.688	0.031	0.014	-1.864	-1.512	2.286	2.818
3	3	6	81.250	0.033	0.006	-2.255	-1.477	2.182	3.331
4	4	6	81.250	0.033	0.004	-2.431	-1.477	2.182	3.591
5	5	6	81.250	0.033	0.003	-2.556	-1.477	2.182	3.776
6	1	4	87.500	0.050	0.000	0.000	-1.301	1.693	0.000
7	2	6.7	79.063	0.030	0.020	-1.696	-1.525	2.326	2.586
8	3	5.5	82.813	0.036	0.007	-2.166	-1.439	2.072	3.118
9	4	5.5	82.813	0.036	0.005	-2.342	-1.439	2.072	3.372
10	5	5.5	82.813	0.036	0.003	-2.467	-1.439	2.072	3.551
11	1	5	84.375	0.040	0.000	0.000	-1.398	1.954	0.000
12	2	6.9	78.438	0.029	0.011	-1.958	-1.538	2.365	3.011
13	3	5.7	82.188	0.035	0.002	-2.610	-1.455	2.117	3.797
14	4	5.7	82.188	0.035	0.002	-2.786	-1.455	2.117	4.053
15	5	5.7	82.188	0.035	0.001	-2.911	-1.455	2.117	4.235
16	1	3.7	88.438	0.054	0.000	0.000	-1.267	1.606	0.000
17	2	6	81.250	0.033	0.021	-1.684	-1.477	2.182	2.487
18	3	4.5	85.938	0.044	0.005	-2.318	-1.352	1.828	3.135
19	4	4.5	85.938	0.044	0.003	-2.494	-1.352	1.828	3.373
20	5	4.5	85.938	0.044	0.002	-2.619	-1.352	1.828	3.542
21	1	3.1	90.313	0.065	0.000	0.000	1.190	1.417	0.000
22	2	5.8	81.875	0.034	0.030	-1.522	-1.460	2.139	2.226
23	3	3.4	89.375	0.059	0.003	-2.546	-1.230	1.514	3.132
24	4	3.4	89.375	0.059	0.002	-2.722	-1.230	1.514	3.349
25	5	3.4	89.375	0.059	0.001	-2.847	-1.230	1.514	3.503
26	1	4.2	86.875	0.048	0.000	0.000	-1.322	1.748	0.000
27	2	6.5	79.688	0.031	0.017	-1.773	-1.512	2.286	2.681
28	3	4.5	85.938	0.044	0.002	-2.799	-1.352	1.828	3.785
29	4	4.5	85.938	0.044	0.001	-2.975	-1.352	1.828	4.023
30	5	4.5	85.938	0.044	0.001	-3.100	-1.352	1.828	4.192

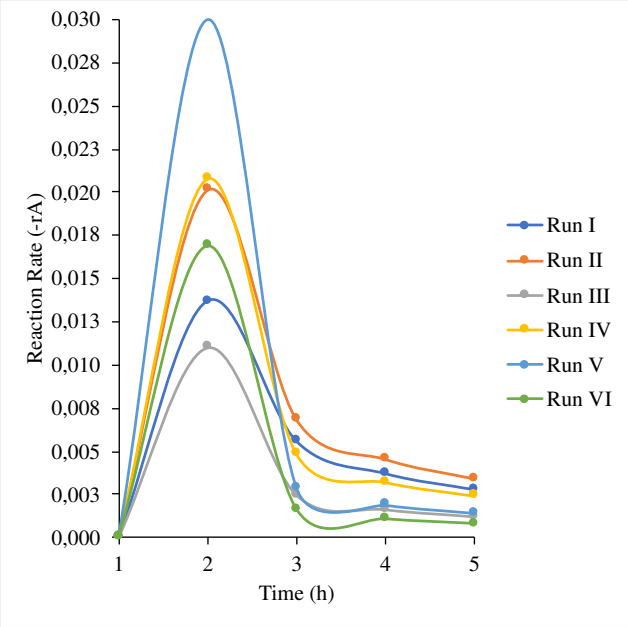

Figure-1. Graph of Interaction between reaction time and reaction rate.

Relation of Reaction Time (t) to % Conversion

The relationship between reaction time and the gain of % conversion at a reaction temperature of 70°C is shown in Figure-2. At a reaction temperature of 70°C, the resulting conversion decreased in the 2nd hour. In the following hours, the percentage of conversion increased. At a stirring speed of 150 rpm, the highest conversion percentage obtained at 70°C was 85.94%. At 200 rpm, the resulting conversion % is 87.50%, and at 250 rpm, the resulting conversion percentage is 84.38%.

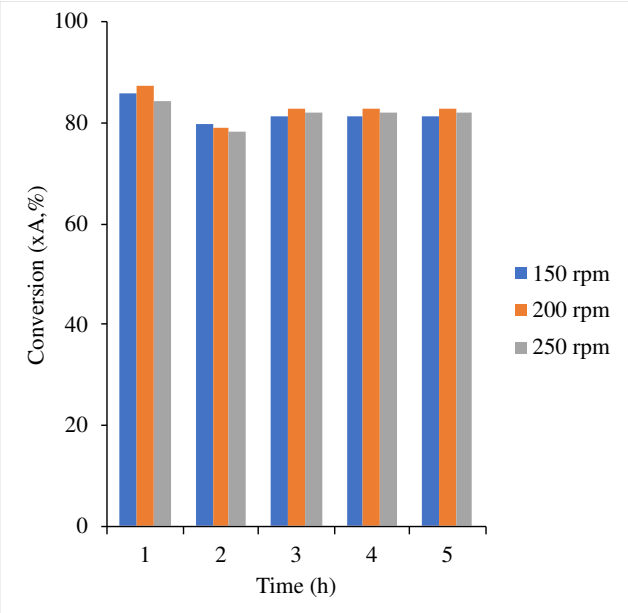

Figure-2. Interaction of reaction time to % conversion at 70oC.

In Figure-3, it can be seen the relationship between reaction time and conversion gain at a reaction temperature of 80°C. It can be seen that the conversions obtained experienced a decrease in conversions in the 2nd hour and an increase in the percentage of conversions in the following hours. At a stirring speed of 150 rpm, the greatest conversion obtained at 80oC was 88.44%. At 200 rpm, the biggest conversion % produced was 90.31%, and at 250 rpm, the biggest % conversion was 86.88%. Product conversion is affected by reaction order, constant rate, reactant concentration, and time. Thus, the relationship between conversion and reaction time is directly proportional, where conversion will increase with increasing reaction time.

However, this does not occur for all fatty acids at a reaction temperature of 70°C or 80°C. Increasing the reaction time will not give significant results to surfactant products [9]. This is possibly due to the emergence of side reactions such as saponification, which contributes to the decrease in conversion gain [5,19]. The optimum reaction time in this study was 3 hours; this optimal time was also caused by using a catalyst that acts as an accelerating reaction [12].

Relation of Reaction Temperature (T) to % Conversion

Figure-4 shows the relationship between the reaction temperature and the conversion gain obtained at a stirring speed of 150, 200, and 250 rpm at a reaction time of 3 hours. It can be seen in the figure that the conversion obtained increases with increasing reaction temperature. This is because the higher the temperature will affect the reaction rate following the Arrhenius equation, where the higher the temperature, the greater the value of the reaction rate [18]. Figure 5 shows the effect of a more significant variable increasing surfactant recovery. In addition to the value of the reaction rate, an increase in temperature also affects the viscosity of a substance. The higher the temperature, the lower the viscosity [16].

FT-IR Spectroscopic Analysis

FT-IR spectroscopy is a tool for detecting the functional groups of a compound using the infrared spectrum of organic compounds, which have unique physical properties [20]. The results of the Alkyl-DEA spectrum obtained are shown in Figure 6. The results of the FT-IR spectrum analysis observed at a reaction temperature of 80°C, and a stirring speed of 200 rpm, showed an absorption peak at wave number 3305.99 cm^{-1}, with transmission of 1.7%, indicating the presence of N-H groups, indicating that there are amine compounds in surfactants where it is also indicated that the amine comes from diethanolamine.

The absorption peak at wave number 2929.87 cm^{-1} at 2.3% transmission indicates the C-H group as a long chain in the reaction and indicates that the product comes from fatty acid raw materials. The absorption peak at wave number 1622.13 cm^{-1} at 8.8% transmission identified a C=O double bond group, indicating an amide compound. The absorption peak at a wavelength of 1053.13 cm^{-1} at

1.8% transmission indicated the presence of C-N compounds, indicating the product contained amine compounds.

Acid Number Analysis

The acid number expresses the amount of fatty acids in the product. A high acid number will affect polarity and foam, reducing the final product's quality. Based on the research results with operating conditions at a substrate ratio of 1:10, a solvent ratio of 1:2, and a catalyst weight of 5%, the resulting acid number under alkyl-DEA conditions is 39.27.

Saponification Number Analysis

The number of milligrams of potassium hydroxide needed to saponify 1 gram of fat is expressed by the saponification number [21]. Based on the research results obtained, the value of the saponification number of alkyl-DEA surfactants is 30.85.

Analysis of HLB Value (Hydrophile-Lipophile Balance)

To determine the usefulness of a surfactant, the HLB (Hydrophile-Lipophile Balance) value is usually determined first [22]. The HLB value of surfactant products was measured using the acid number and saponification number approach and was obtained at 4.29.

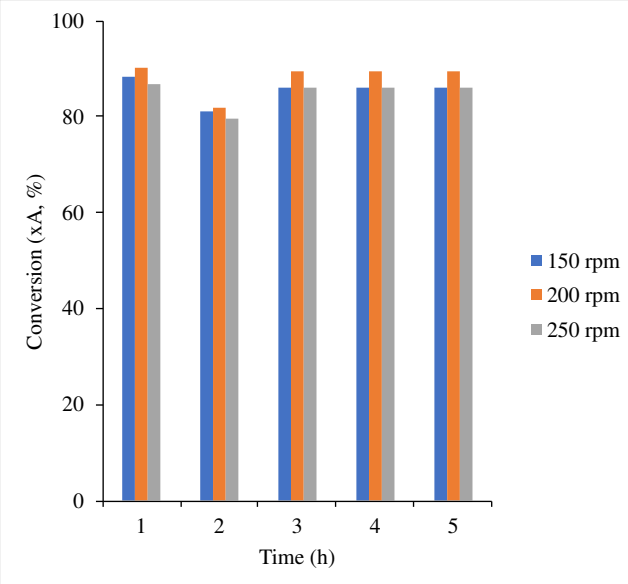

Figure-3. Interaction of reaction time to % conversion at 80°C.

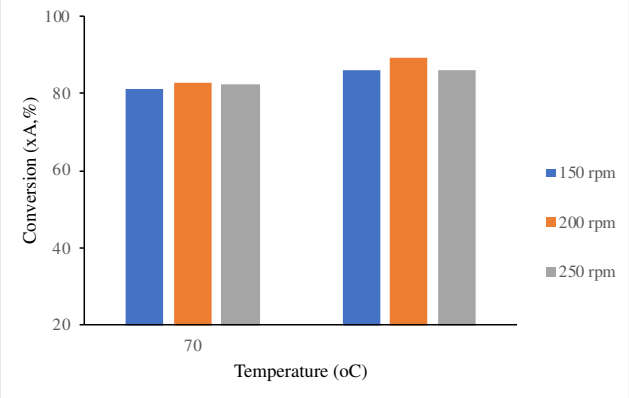

Figure-4. Interaction of reaction temperature to % conversion at a reaction time of 3 hours.

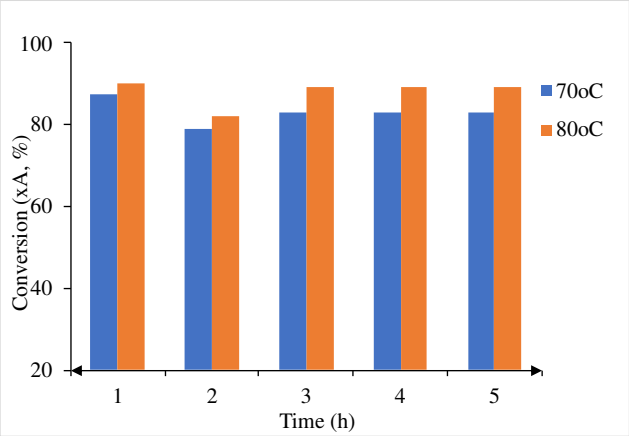

Figure-5. The effect of a more significant variable increasing surfactant alkyl-DEA.

CONCLUSIONS

Surface properties of alkyl-DEA surfactants were studied at a substrate ratio (Palmitic Acid: DEA) of 1:10, catalyst weight of 5%, and solvent ratio of 2:1. At a reaction temperature of 80°C and a stirring speed of 200 rpm, the best time was 3 hours, with a conversion percentage of 89.33%. The reaction rate decreased as the reaction time increased. Where the relationship between reaction rate and reaction time is inversely proportional, the longer the reaction time, the lower the reaction rate. So, based on the research that has been done, the results are appropriate. The acid number for alkyl-DEA is 39.27. At the same time, the initial acid number is 89.70. The saponification number of the alkyl-DEA surfactant at 80°C and 200 rpm is 30.85. The characteristic HLB value is 4.29, where alkyl-DEA surfactant products can be used in the cosmetic and pharmaceutical industries and have a milky white color after being dissolved in water.

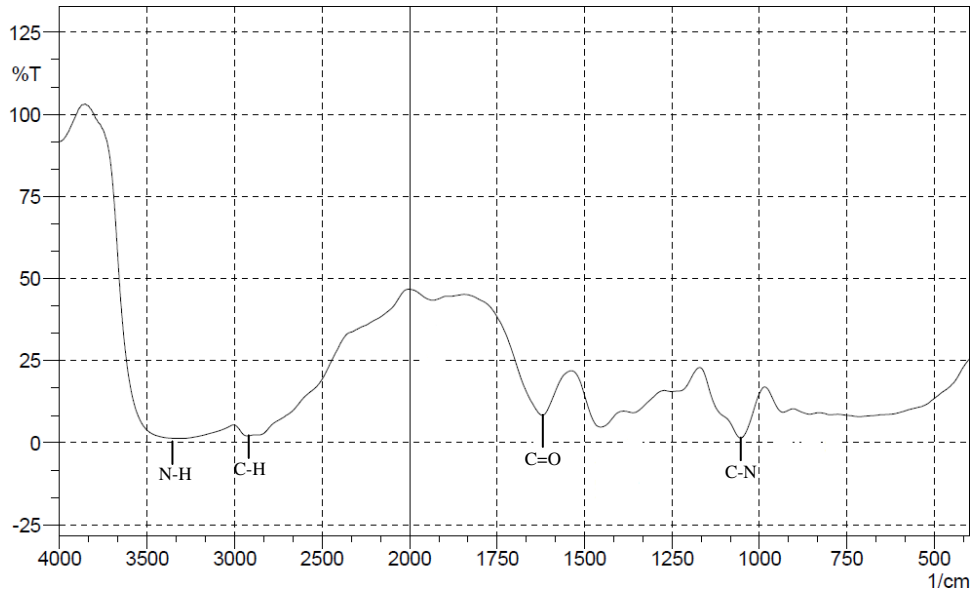

Figure-6. FT-IR Analysis of Alkyl DEA.

ACKNOWLEDGEMENTS

This research is funded by Talenta Universitas Sumatera Utara (USU), through a research grant in the fiscal year 2021.

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