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OPTIMIZATION OF ALKYL-DIETHANOLAMIDE SYNTHESIS FROM FATTY ACID METHYL ESTER OF COCONUT OIL USING BOX-BEHNKEN DESIGN

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ABSTRACT

Alkyl-diethanolamide from renewable materials has become much of current interest for the surfactants. Response surface methodology (RSM) and Box-Behnken design were employed to evaluate the effects on stirring speed, catalyst concentration and temperature on percentage acid conversion to alkyl-diethanolamide. Predictive models for amidation of fatty acid methyl esters (FAME) from coconut oil shows that the model prepared is adequate and reproducible to represent the data obtained (R^2 = 95.74%). The fatty acid conversion significantly increased with stirring speed and reaction temperature, and increasing catalyst concentration did not significantly increase the yield of alkyl-diethanolamide. The optimal reaction conditions were predicted at the stirring speed of 350 rpm, catalyst concentration of 4% (w/wFAME) and temperature of 70-75°C. Under optimized condition, the conversion of FAME was up to 97.57% in 3 hr.

Keywords: Coconut Oil, Fatty Acid Methyl Ester, Diethanolamine, Response Surface Methodology, Alkyl Diethanolamide

INTRODUCTION

Surfactants are surface active agents, which can reduce the surface tension by forming films between the two media, such that the interaction is stable, and results in reduced surface tension.[1] Surface tension is an important characteristic of fluids. Simply put, this is a force acting on the surface of a liquid, which tends to minimize the surface area that affects physical properties, such as the ability to wet fluids. Surface tension tends to attract molecules on the interphase inward, thereby reducing the interaction between the two phases.[2]In the dairy industry, for example, milk surface tension is an important characteristic because it has an impact on the formation of emulsions.[3-4]

Alkanolamide surfactant is a product of condensation reaction between alkanolamine with fatty acids, methyl esters or triglycerides.[5-6]Alkanolamide is a compound that shows low reactivity, high thermal stability, very chemically stable and not easily degraded in alkaline media.[7-8] For this reason, alkanolamide is widely applied as an emulsifier and has a broad spectrum of uses such as shampoo, detergent, cosmetics, lubricants, and other home products.[9-10] For this reason, economic materials and methods, and using environmentally friendly reaction conditions have been the hallmarks of studies of these products in recent years.[11]

One of the raw materials for making alkanolamides is economical and abundantly comes from coconut plants. Coconut (*Cocosnucifera Linn.*) Belongs to the *Arecaceae* family, cultivated mainly in the tropics with high humidity, regular rainfall, and sandy soil. Approximately 90% of the total composition of coconut oil consists of Saturated Fatty Acid (SFA).[12-13] The main fatty acids (Fatty Acid, FA) found in

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coconut oil are lauric acid (12:0), myristic (14:0) and palmitic (16:0), each representing 46%, 17% and 9%.[14]

Making alkanolamide from coconut oil can be done by simultaneous transesterification reactions followed by amidation.[15]Transesterification reactions can be carried out using a homogeneous catalyst (alkaline-NaOH, KOH acid-H_2SO_4 and alkali-alcoholic MeOH) or heterogeneous (CaO, MgO, BaO and ZnO/Al_2O_3, oxides of alkali metal-based zeolite, ion exchange resins).[16] In the use of homogeneous catalysts, transesterification reactions can take place at a relatively low temperature and pressure, although high levels of FFA use of homogeneous catalysts is not recommended because it will cause a saponification reaction.[17]

Amidation reaction of fatty acid methyl ester from coconut oil with diethanolamine will produce alkyl-diethanolamide. The use of heterogeneous catalysts in amidation reactions can be an attractive alternative to make this process inexpensive and more environmentally friendly, easy catalyst separation and catalysts can be recycled.[18-19]

One of the most widely used catalysts is CaO. Heterogeneous CaO catalysts have many advantages such as low prices, long catalyst life, high activity and only require moderate reaction conditions, although some weaknesses are found in CaO catalysts where surface area is low and easily melts.[15,20]

On the basis of the theory that has been described, it is necessary to do research on the synthesis of non-ionic surfactants alkyl-diethanolamide from coconut oil and diethanolamine through an amidation reaction using CaO catalyst. The aim of the first experiment was to obtain important information about the effect of temperature and catalyst concentration on the surfactant produced. The objective of this second experiment is to develop empirical models of the factors that influence the amidification of FAME to become alkyl-diethanolamide.

EXPERIMENTAL

Materials

The coconut oil used as the commercial oil that is Braco®. Methanol (CH_3OH¬), sodium hydroxide (NaOH), diethanolamine ($C_4H_{11}NO_2$), calcium oxide (CaO), isopropanol, potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), phenolphthalein ($C_{20}H_{14}O_4$), ethanol (CH_3CH_2OH) and chloride acid (HCl) are obtained from E Merck, Darmstadt Germany.

Transesterification of Coconut Oil

At 60ºC and atmospheric pressure, coconut oil and methanol with a ratio of molar 6/1 were well mixed in 1% of NaOH in the sealed 250 ml vials and placed in a hot plate with oil at 1 (one) h reaction time. After 1 h where the coconut oil was completely converted into FAME and glycerol, the mixture was placed in separating the funnel and left to separate into two layers. The top layer is washed with hot water, and then the obtained FAME can be analyzed.

Design of Experiment

The 3-levels-3 factors Box Behnken design was employed in this study, required 15 experiments. The variables and levels selected for the alkyl synthesis were stirring speed (200-400 rpm), catalyst concentration (3-5% w/wFAME) and temperature (60-80ºC). The design of experiments shown in Table-1. Response Surface Methodology (RSM) was applied to model the CaO catalyzed of alkyl-diethanolamide. RSM is useful for modeling and analyzing problems, where the observed response is influenced by several variables and also aims to optimize the response.[21-22]A software package of Minitab version 17 was used in this study.

Amidification of FAME

The reaction was initiated by addition of diethanolamine and FAME at the substrate molar ratio of 6/1 to isopropanol. The CaO catalyst is added to the solution with a concentration of 3-5% by weight of the total solution. The reaction mixture was shaken at 200-400 rpm and 60-80ºC. After 3 h, a complete of the FAME into the alkyl-diethanolamide was observed. All of the experiments were performed in isopropanol at the isopropanol ratio to FAME 2/1. The reaction was terminated by evaporating methanol and CaO was removed by filtration.

Table-1: The Design of Experiments Employed and the Conversion of FAME.

Test Run	Coded Variables			
	Stirring Speed, X_1	Catalyst Concentration, X_2	Temperature, X_3	Conversion, Y (%)
1	-1	-1	0	90.6010
2	1	-1	0	96.9605
3	-1	1	0	95.4859
4	1	1	0	96.4588
5	-1	0	-1	94.8328
6	1	0	-1	96.3526
7	-1	0	1	95.4407
8	1	0	1	96.4588
9	0	-1	-1	95.1368
10	0	1	-1	96.0486
11	0	-1	1	96.8826
12	0	1	1	96.4029
13	0	0	0	97.5684
14	0	0	0	97.5684
15	0	0	0	97.5684

RESULTS AND DISCUSSION

Transesterification of Coconut Oil

Before the preliminary research, the transesterification reaction of coconut oil was carried out to produce methyl esters. Coconut oil is reacted with methanol at a mole ratio of methanol to coconut oil which is 6/1 and uses a 1% NaOH catalyst, at a temperature of 60ºC and 60 minutes. Stoichiometry, transesterification of 1 mole of triglycerides and 3 moles of alcohol produces 3 moles of fatty acid esters and 1 mole of glycerol.[16]

From the results of the GC analysis, it was found that the purity of the methyl ester produced was 84.08%. When compared to the biodiesel quality requirements, the resulting methyl ester does not meet the requirements as biodiesel. Low levels of methyl esters are caused by improper reaction conditions or come from various small components in the original oil source. So high concentrations of partial glycerides and inseparable glycerol can cause levels of methyl ester below the limit. The most abundant fatty acids contained in coconut oil are lauric acid (C12) which is equal to 46.89 - 48.03% so that the composition of the largest methyl ester from the results of this transesterification is methyl laurate.[13-14]

Preliminary Study

In the preliminary study, a synthesis of alkyl-diethanolamide surfactant from methyl ester and diethanolamine (DEA) was carried out. This preliminary study aims to determine the best value of each process variable. Process variables observed were stirring speed, temperature and catalyst concentration.

Figure-1 shows a graph of the effect of the reaction temperature on the conversion of methyl ester to alkyl-diethanolamide. The observations show that the conversion of methyl ester to alkyl-diethanolamide will increase with increasing reaction temperature. The effect of the reaction temperature for the synthesis of alkyl-diethanolamine surfactants was observed at reaction temperatures ranging from 60ºC to 80ºC. The selection of the reaction temperature is based on the boiling point of the isopropanol solvent at 82.4ºC. From Figure 1 it is also known that the highest percent conversion of methyl ester to alkyl-diethanolamide is obtained when the reaction temperature is 70ºC, with a conversion value of 88.89%.

Figure 2 shows a graph of the effect of the catalyst concentration on the conversion of methyl ester to alkyl-diethanolamide. The results of the observation show that the conversion of methyl ester to alkyl-diethanolamide will increase with increasing catalyst concentration. In this study, the effect of the catalyst concentration for the synthesis of alkyl-diethanolamine surfactant was observed at catalyst concentrations ranging from 1% to 5%. From Fig.-2 it can be seen that the higher the catalyst concentration, the conversion of methyl ester to alkyl-diethanolamide will increase. The highest percent conversion results were obtained when the catalyst concentration was 5% with a conversion value of 88.89%.

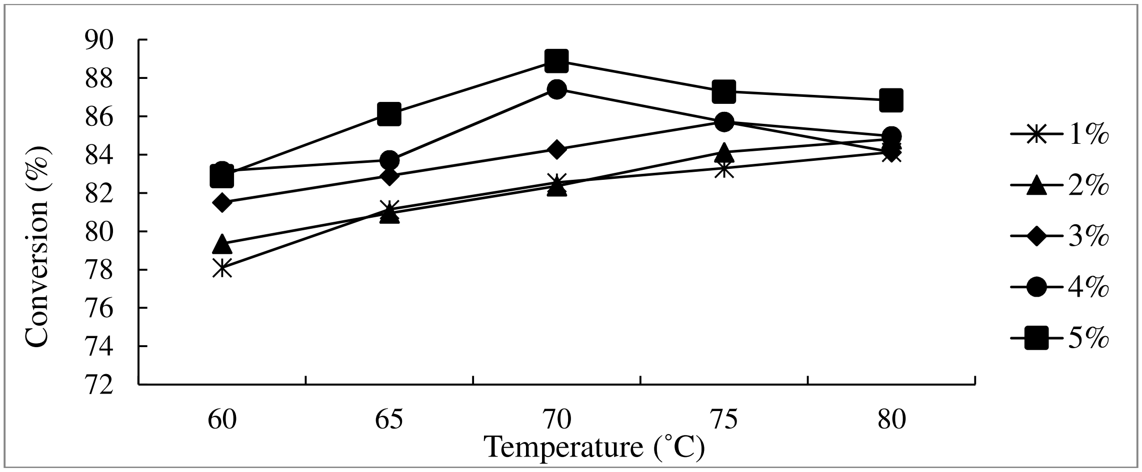

Fig.-1: The Relation Between the Reaction Temperature and the Conversion

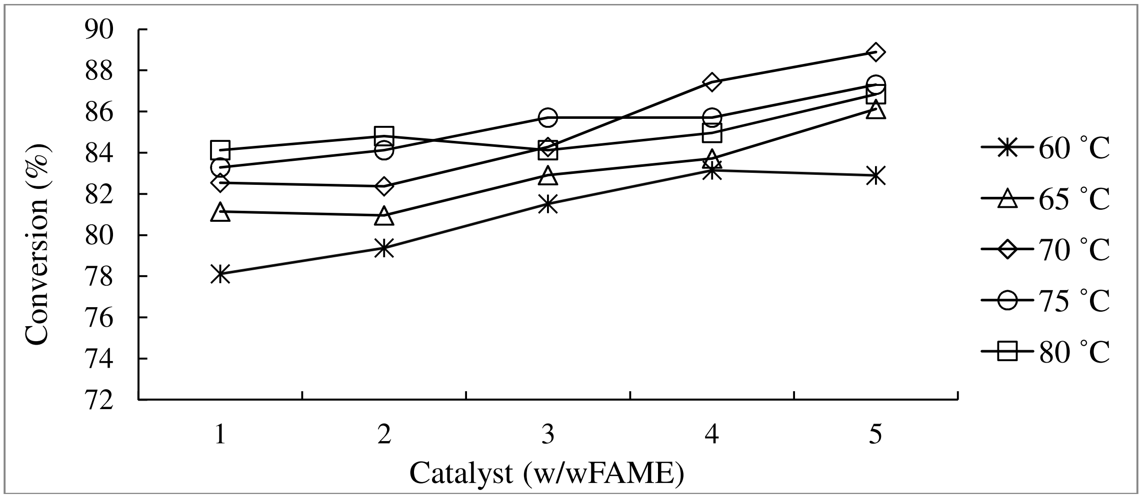

Fig.-2: The Relation Between the Catalyst and the Conversion of Methyl Ester to Alkyl-diethanolamide.

The graph of the effect of stirring speed on the conversion of methyl ester to alkyl-diethanolamide is shown in Fig.-3. Observation of stirring speed was carried out at the mole ratio of amine to methyl ester 6/1 (DEA/FAME), a catalyst concentration of 5% (w/w FAME), solvent ratio 2/1 (v/w FAME). The reaction was carried out at 4 different levels of stirring speed, where the reaction lasted for 3 hours. It can be seen that the highest conversion of methyl ester to alkyl-diethanolamide was obtained at a stirring speed of 300 rpm, which was 87.30%. It is also seen that the conversion decreases at a stirring speed of 400 rpm. Based on the initial study above, the stirring speed of 300 rpm was chosen and the reaction time was 3 hours for further research because it seemed to provide optimum results.

Mutual Effect of Parameters

The next stage of the study was to observe the influence of interaction between three of variables, with the aim of optimizing the response, namely the maximum percent conversion of FAME.

The selection of variables range needs to be extremely precise in studies of RSM.[22-23] Results of the experimental design performed to achieve higher conversion are shown in Table-2. Based on Table-2, the equation model shows the relationship between parameters and their interactions with the percent conversion of FAME are as follows:

$$Y_{FAME} = 97.5684 + 0.8588\,X_1 + 0.2269\,X_2 + 0.3518\,X_3 - 1.1442\,X_1^2 - 0.7977\,X_2^2 - 0.6530\,X_3^2 - 0.5966\,X_1X_2 - 0.1254\,X_1X_3 - 0.3479\,X_2X_3$$

Where, X_1, X_2, X_3 are the stirring speed, catalyst concentration, and temperature respectively. The stirring speed and reaction temperature affected the conversion of FAME, with the p-value of 0.002 and 0.051 respectively, whereas a square of stirring speed, catalyst concentration, and the temperature is not significantly influenced the conversion.

Table-2: Results of the Experimental Design Performed to Achieve Higher Conversion.

Term	Coefficient	P
Constant (Y)	97.5684	0.000
Stirring speed (X_1)	0.8588	0.002
Catalyst concentration (X_2)	0.2269	0.160
Temperature (X_3)	0.3518	0.051
Stirring speed (X_1)* Stirring speed (X_1)	-1.1442	0.002
Catalyst concentration (X_2)* Catalyst concentration (X_2)	-0.7977	0.011
Temperature (X_3)* Temperature (X_3)	-0.6530	0.023
Stirring speed (X_1)* Catalyst concentration (X_2)	-0.5966	0.028
Stirring speed (X_1)* Temperature (X_3)	-0.1254	0.547
Catalyst concentration (X_2)* Temperature (X_3)	-0.3479	0.134
R-Sq = total squared = 95.74%		
R-Sq(adj) = squares due to treatment = 88.06%		

The mutual interaction between stirring speed and catalyst concentration can be interpreted from the response contour plot diagram (Fig.-4), which indicated that that alkyl-diethanolamide production is related to both stirring speed and catalyst concentration. At higher stirring speed the conversion increase with the increase in catalyst concentration. Based on Fig.-4 the optimum conversion is obtained by stirring speed of 350 rpm with a catalyst concentration of around 4% (w/wFAME).

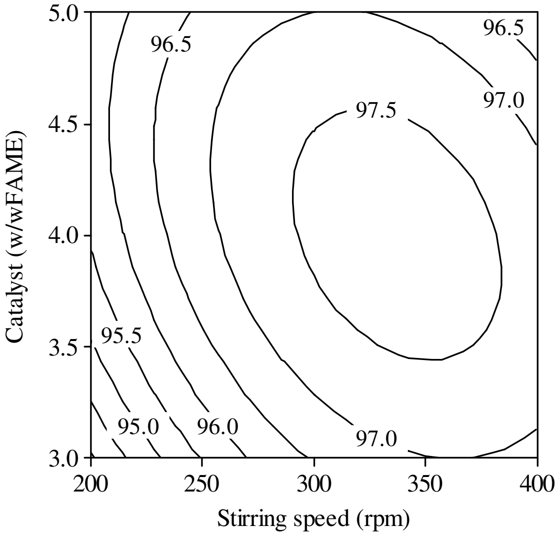

Fig.-3: The Relation Between Stirring Speed and Conversion.

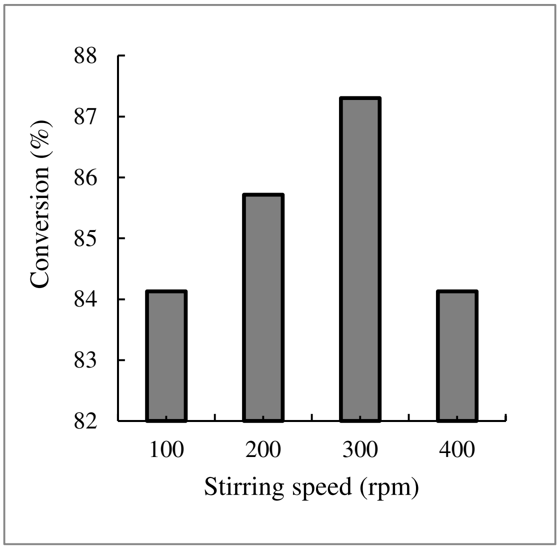

Fig.-4: The Interaction Between Stirring Speed and Catalyst Concentration.

The amidation reaction produces a side reaction in the form of methanol, which will affect the conversion of the resulting reaction. The amidation reaction, which takes place at a stirring speed of 400 rpm is likely to produce more side reactions than the reaction that takes place at 300 rpm. In addition, even though the

reaction is an irreversible reaction, there is still a possibility of a reverse reaction that will affect product conversion because it is known that there is no irreversible or reversible reaction.
Figure-5 represent the effect of varying temperature and stirring speed at a catalyst concentration of 4%, substrate molar ratio 6/1 (DEA/FAME), solvent ratio 2/1 (v/wFAME) at reaction time 3 hour. A high percentage of conversion can be achieved by employing a wide range of temperatures from 65-80ºC. In stirring speed of less than 300 rpm, an increase in temperature does not significantly increase the yield of alkyl-diethanolamide, but an increase in stirring speed up to 375 rpm can increase conversion if the temperature range is in the range of 65-75ºC. The best percentage of FAME conversion is obtained at the center of the circle, which is at stirring speed 350 rpm and temperature 70-75ºC.
The temperature of the reaction that is too high can cause the reaction results to decrease. The amount of loss, is believed to be caused by evaporation of methanol during the reaction.[24-25]At temperatures above 75ºC, the conversion of methyl ester to alkyl-diethanolamide tends to decrease. This is caused by the reaction temperature where is close to the boiling point of isopropanol. Where some isopropanol evaporates so the reaction is not optimal.
Figure-6 shows the effects of temperature and catalyst on concentration and their mutual interaction at a constant stirring speed (300 rpm), substrate molar ratio (6/1 DEA/FAME) and the solvent ratio (2/1 v/wFAME). At the lowest temperature and catalyst concentration, the conversion was less than 96%. The conversion increase when the temperature and catalyst concentration increased and the maximum conversion was obtained at a temperature of 70-75ºC and catalyst concentration of 4% (w/wFAME). Further increase in catalyst concentration did not significantly change the reaction rate.[15]

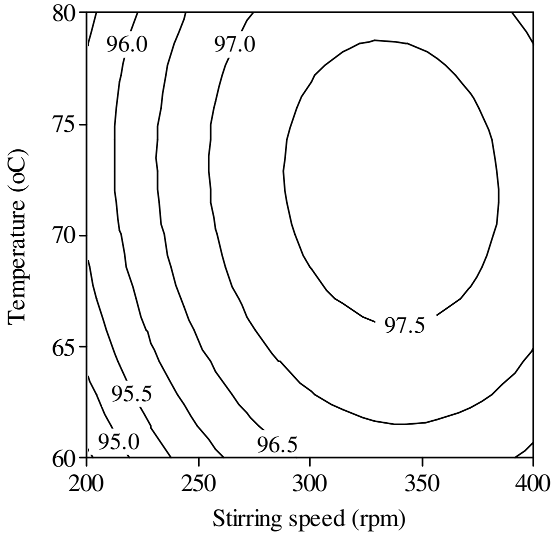

Fig.-5: The Interaction Between Temperature and Stirring Speed.

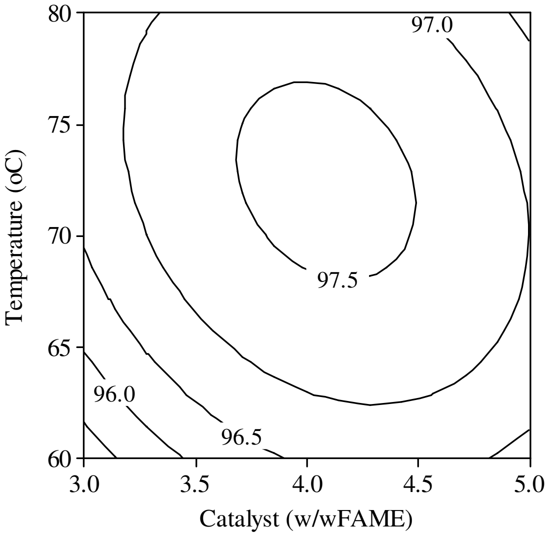

Fig.-6: The Interaction Between Temperature and Catalyst Concentration.

The reaction rate will generally increase when the catalyst concentration increases. In the first stage, FAME and amine will be absorbed on the surface of the CaO by electronic donations, in which groups of amines and esters are activated. This causes the electron pair to attack the ester group. Based on specific nucleophilic substitution reactions, amides will form and then be released from CaO, which will take part in the next catalysis cycle.[20]CaO itself has been used as a solid catalyst because of its high catalytic activity, can work under mild reaction conditions, and also long life and low-cost catalyst.[15,26]

Identification Using FT-IR

The results of the alkyl-diethanolamide spectrum obtained are shown in Fig.-7. Amide absorption stretches in the spectral region 1600-1700 cm^{-1} which correspond to C=O peptide relationship span. The N-H bond for the amine is at the wave number 3500-3100 cm^{-1}. The C-O bond for the esters is at wave number 1300-1000 cm^{-1}. O-H for alcohol is at the wave number 3650-3600 cm^{-1}. From the results of the sample FTIR spectrum test, the absorption peak at the wave number area of 1619.30 cm^{-1} indicates of a C=O region of this wave number which indicates a sample containing an amide group. While recharge at wave number 3308.84 cm^{-1} indicates of N-H groups for amines. The N-H group on this wave shows the amines namely diethanolamine (DEA). Infiltration peak at wave number 1040.90 cm^{-1} shows the C-O groups for ester compounds namely residual methyl ester and wave absorption 3649.13 cm^{-1} shows the presence of O-H groups for alcohol compounds namely methanol as a side reaction.

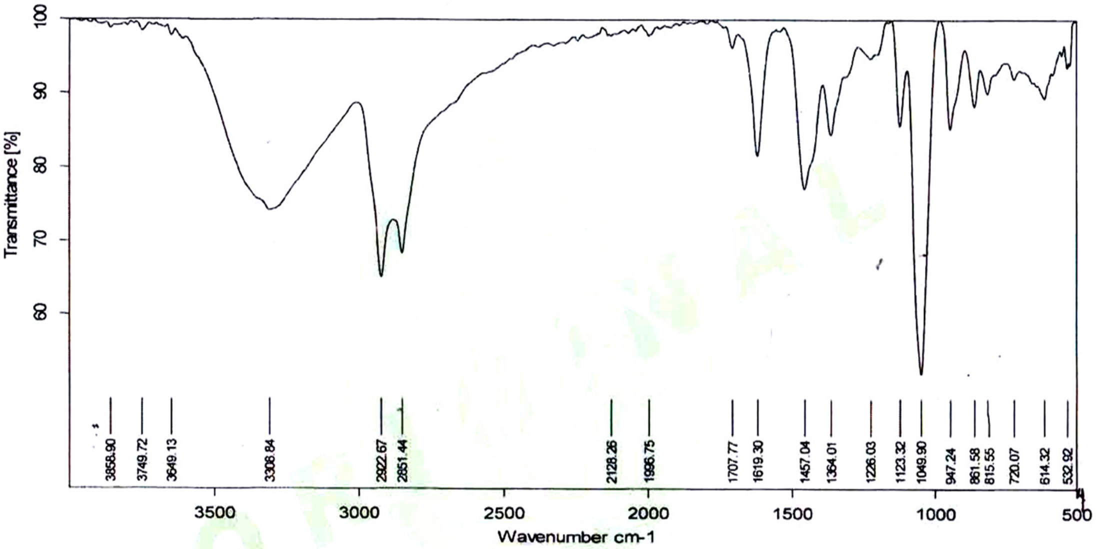

Fig.-7: The Results of the Alkyl-Diethanolamide Spectrum.

CONCLUSION

Alkyl-diethanolamide is one of the most interesting fatty acid amides. Alkyl-diethanolamide was synthesized by transesterification of coconut oil and methanol to fatty acid methyl esters, followed by amidification of FAME with diethanolamine to alkyl-diethanolamide. To optimize the reaction condition of amide production, Box Behnken design with RSM was used, and the interaction effect of stirring speed, temperature and catalyst concentration on alkyl-diethanolamide synthesis can be obtained. The analysis of variance is also implied that the model satisfactory represented the relationship between variables and fatty acid conversion.

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