RASĀYAN *J. Chem.*
Vol. 16 | No. 1 |391-397| January - March | 2023
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

NON-CATALYTIC SYNTHESIS OF FATTY ACID ALKANOLAMIDES FROM PALM FATTY ACID DISTILLATE AND MONOETHANOLAMINE UNDER MICROWAVE IRRADIATION

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ABSTRACT

The non-catalytic synthesis of fatty acid alkanol amide (FAA) from the amidation of palm fatty acid distillate (PFAD) and monoethanolamine (MEA) under microwave irradiation has been investigated. Parameters of the molar ratio of PFAD to MEA, reaction time, and microwave power were determined using the response surface method and the Box-Behnken experimental design. The optimum conversion of FAA of 98.89% was obtained under reaction conditions of ratio molar PFAD to MEA of 1:1, a reaction time of 18.5 minutes, and a microwave power of 100%. The formation of FAA compounds was confirmed with FT-IR which showed stretching vibration of C-N groups at a wavenumber of 3301.89 cm^{-1} supported by the appearance of stretching vibrations of C-N-H and C-N at wavenumbers 1557.03 cm^{-1} and 1466.08 cm^{-1}. The GC-MS spectrum showed the confirmation of the formation of FAA compounds where several alkanol amide derivatives are N-(2-hydroxyethyl)-Octanamide, N-(2-hydroxyethyl)-Decanamide, N-(2-hydroxyethyl)-Dodecanamide, N-(2- hydroxyethyl)-Hexadecanamide and N-(2-hydroxyethyl)-Octadecanamide were identified to be formed.

Keywords: Alkanolamide, Palm Fatty Acid Distillate, Microwave Irradiation, Amidation, Non-Catalyst.
RASĀYAN *J. Chem.*, Vol. 16, No.1, 2023

INTRODUCTION

FAA compounds are widely used for household products, cosmetics, and pharmaceuticals. FAA is classified as a non-ionic surfactant with the main function being to stabilize foam, increase viscosity and act as an emulsifier.[1,2] The physicochemical properties of these FAA vary based on the length of the fatty acid carbon chain.[3,4] Commercially, FAA can be produced from the amidation of fatty methyl esters with ethanolamine at reaction conditions of 180 – 200°C and 3 – 7 bar pressure.[5] However, some unwanted side products were obtained and the extreme reaction condition leads to higher production costs. Another method is through the reaction of triglycerides or fatty acid methyl esters or fatty acids with ethanolamine or diethanolamine using a base catalyst. Kolancilar (2004) concluded that the concentration of sodium methoxide affects the reaction speed of amide formation from laurel oil. The reaction time is getting faster from 9 hours using a 0.2% catalyst concentration to 1 hour with a 2% concentration.[6] FAA can also be made using enzymes as catalysts. Zoete *et al*. (1996) reported a 90% conversion of oleamide using Novozym 435 lipase at 60°C reaction temperature and 72 hours reaction time.[7] Another researcher reported a yield of 77% oleamide using the *Candida rugose* lipase under reaction conditions of 40°C and 72 hours.[8] Furthermore, the reaction rate could be accelerated in the addition of a co-solvent. A conversion of 100% of oleoylethanol amide with a purity level of 97% can be obtained under the reaction conditions of 30% lipase enzyme concentration, 3 hours reaction time, 65°C temperature, and 1.5 ml hexane volume.[9] However the high price of lipase enzyme limited its uses as a biocatalyst in the synthesis of alkanolamides.[10] Currently, environmentally friendly methods with lower process costs to gain more attention in the synthesis of alkanol amides. Utilization of heterogeneous compounds as catalysts can be an alternative method because they are environmentally friendly, do not mix with the products, and can be easily separated and reused.[11] Heterogeneous catalysts, both acidic and basic, have been widely used as catalysts in the transesterification reaction into fatty acid methyl esters or biodiesel with high conversion rates and yields.[12-15] Heterogeneous catalysts have also been used in amide formation reactions. Kumar and Ali (2015) used NaOH-impregnated CaO as a catalyst in the synthesis of alkanol amides from used

http://doi.org/10.31788/RJC.2023.1618188

cooking oil which contains a high amount of free fatty acids (FFA) with diethanolamine. Alkanol amide conversion of 99% was obtained in 45 minutes at a temperature of 110°C with a catalyst concentration of 5% and a molar ratio of used cooking oil to diethanolamine of 1:6.[16] To date, all the alkanol amides syntheses which have been developed use catalysts either in the form of homogeneous, heterogeneous or enzymes. These catalysts have their respective advantages and disadvantages and their application depends on the raw materials used.[11] However, in general, the use of this catalyst has a major drawback which requires a separate process from the product.[17] Therefore, finding a new alkanolamides production method without using a catalyst is necessary to avoid the separation and purification of the product. Das, *et al.* [2017] have proved that FAA content in jatropha oil could be reacting with MEA to form FAA compounds without a catalyst. Even though the conversion of 98% was achieved at 34°C reaction temperature and 550 rpm speed agitation, a 6 hours reaction time was required to obtain it.[5] The use of microwaves to accelerate chemical reactions has been developed and proven could accelerate reactions with high yields.[18,19] Several studies have shown that the presence of microwave radiation could increase reaction rate with a high degree of purity.[20,21] Rokni, *et al.* (2022) have made biodiesel from camelina oil with a yield of 95.5% using sodium hydroxide catalyst in just 5.85 minutes.[22] Biodiesel with a conversion rate of 99% can also be obtained in 3.56 minutes from *Argemone Mexicana* oil.[23] Based on that, this study aims to synthesize alkanolamide from PFAD and MEA with microwave radiation without using a catalyst. PFAD is generated from palm oil plants as a major by-product. For every tonne of palm oil produced, 30–40 kg of PFAD will be produced as waste from the de-acidification and deodorization processes.[24] Indonesia's palm oil production in 2021 is estimated to reach 46.85 million tons of which 1.87 million tons of by-products in the form of PFAD will also be obtained.[25] Due to very abundant quantities while their use is still limited for hard-textured soap and animal feed thus giving PFAD giving opportunity to be an alternative raw material for producing alkanolamides.[26] Palmitic and oleic acids are the main content of PFAD.[27,28] The domestic microwave household was used with some modification to connected with a condenser and a magnetic stirrer. The influence of different ratio molar of PFAD to MEA, reaction time and microwave power to FAA conversion was optimized using the Box-Behnken design experiment. Further, the formation of FAA was identified using FT-IR and GC-MS.

EXPERIMENTAL

Material and Methods

The PFAD were obtained from a local palm oil plant in Sei Mangkei, Indonesia. All the chemicals were brought from the local chemical distributor and were used as received.

Non-Catalytic Amidation of PFAD and MEA to Produce FAA Under Microwave Irradiation

The amidation reaction of PFAD and MEA (Fig.-1) was carried out using a modified household microwave. The microwave input and output powers were 1400 and 900 watts, respectively. The 125 ml round bottom flask was filled with 15 grams of PFAD, a prescribed amount of MEA and a molecular sieve to attract the water. The reaction was conducted based on investigated reaction time. Upon completion, the product was separated from the molecular sieve and the leftover MEA was evaporated using a rotary evaporator. The FAA conversion was estimated from the acid values obtained for blank samples without enzyme (AV_0) and test samples with enzyme (AV_1) as shown in eqn.-1.

$$FAA\ Conversion\ (\%) = \frac{AV_0 - AV_1}{AV_0} x\ 100\% \quad (1)$$

The acid value was determined using a titrimetric method as reported elsewhere.[5,29]

Statistical Analysis

The optimization amidation PFAD and MEA to produce FAA was performed employing Box-Behnken designs which consist of 3-factors, 3-level, and 1-response. The design consisted of 15 total experiments including 3 center points. Table-1 compiles the coded and actual levels of the Box-Behnken design.

RESULTS AND DISCUSSION

The FFA content in PFAD is 88.9%, mainly consisting of palmitic (50.6%) and oleic acid (31.9%). The high levels of FFA contained in PFAD open the possibility of being reacted with MEA to produce FAA compounds. The schematic reaction of FAA and MEA is presented in Fig.-1.

Table-1: Actual and Coded Levels of the Variable Studied

Variable	Unit	Symbol	Level		
			-1	0	1
Ratio molar PFAD: MEA	-	A	1:1	1:3	1:5
Reaction time	Minutes	B	3	16,5	30
Power microwave	% Watt	C	20	60	100

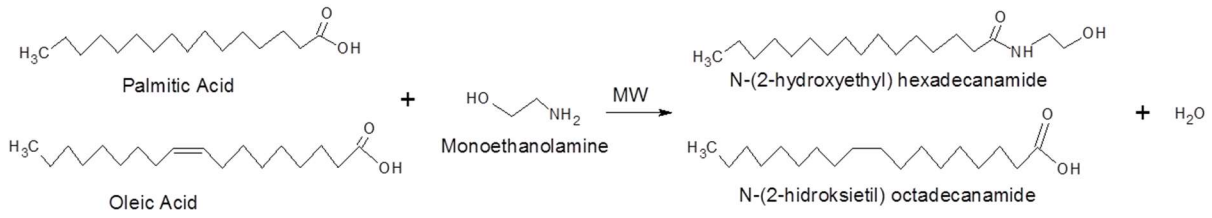

Fig-1: Schematic Representation of Synthesis FAA

Experimental Data Analysis

The amidation of PFAD with MEA to FAA compounds was conducted under microwave irradiation without using a catalyst. Microwave irradiation has been used widely and proven could lessen reaction time compared to the traditional method.[18,20,21] The effect of amidation variables such as ratio molar PFAD to MEA, reaction time, and microwave power was studied using the Box-Behnken design approach. Experimental and predicted FAA conversions are indicated in Table-2. The highest FAA conversion of 95.6% in this study was corresponding to the fatty acid ethanolamide conversion of 91.8% investigated by Wang, *et al.* [2016] from the amidation of sunflower oil with ethanolamine. The effect of amidation parameters on the FAA compounds conversion was proved by the coefficient of determination *R*-squared between experimental and predicted conversion. The regression analysis resulted in an *R*-squared value of 99.16% which concluded that the regression model provides an accurate description of the experimental data explaining positive correlation among the amidation reaction parameters that affect the FAA compounds conversion. The result of probability (p-value) from the ANOVA model is 3.79×10^{-9} presenting a high significance of the variables. The quadratic regression model of the FAA compounds conversion with determined coefficients was given in eqn.-2.

$$\text{FAA Compounds Conversion (\%)} = 76.98 - 2.99A + 8.89B + 6.70C - 3.63AB - 6.33AC + 3.57BC + 3.88AA + 1.18BB + 0.39CC \quad (2)$$

Table-2: The FAA and Predicted Conversion

No	A: Ratio Molar	B: Reaction Time	C: Power	FAA Conversion (%)	FAA Prediction Conversion (%)
1	3	30	100	92,9	95,050
2	1	16,5	100	95,4	94,137
3	1	30	60	95,6	94,712
4	3	16,5	60	51,2	62,067
5	1	3	60	41,4	40,188
6	5	16,5	100	56,9	53,537
7	5	30	60	64,7	65,913
8	3	3	100	38,4	40,875
9	5	3	60	42,1	42,988
10	3	3	20	29,3	27,150
11	1	16,5	20	34	37,362
12	3	30	20	52,9	50,425
13	5	16,5	20	50,7	51,962
14	3	16,5	60	67,7	62,067
15	3	16,5	60	67,3	62,067

According to that regression model, both reaction time and microwave power have a positive effect on FAA compound conversion. Therefore increasing microwave power in a longer reaction time could

increase the conversion. The same result was reported by Thirugnanasambandham, *et al.* [2017] in the optimization of biodiesel production from waste cooking oil under microwave irradiation.

The Effect of Interaction Parameters

Three-dimensional response surface graphs were plotted based on the quadratic regression model equation to determine the interaction between the independent and dependent parameters. The optimum condition of each parameter for maximum FAA compound conversion was established based on the model equation. The influence of the ratio molar and reaction time on FAA compounds conversion is presented in Figure- 2A. It can be seen that the increase in the ratio molar does not affect the FAA conversion. Increasing the ratio molar causes a decrease in FAA conversion. At a lower ratio molar and in increasing reaction time, the FAA conversion was increased. In contrast, an increase in reaction time leads to raising the FAA conversion. Figure-2A shows the optimum conversion of the relation of the molar ratio to the reaction time obtained at a molar ratio of 1:1 and a reaction time of 30 min. The 3D graph of the connection of the molar ratio with microwave power as shown in Fig.-2B has the same pattern as the 3D graph of the relationship between the ratio molar and the reaction time. The increase in the ratio molar appears to have little effect on the FAA conversion. Different things can be seen in the microwave power parameters where an increase in microwave power significantly causes an increase in FAA conversion. Hence, the optimum conversion of FAA compounds is obtained in the range of 1:1 molar ratio and 100% microwave power. Figure-2C shows the interaction effect of reaction time and microwave power. A positive relationship was observed between these two parameters on the FAA compound conversion. This means that increasing reaction time and microwave power significantly affects the FAA conversion.

Optimization and Validation

The predicted optimum FAA compound conversion could be determined based on the regression equation model. The optimum conversion of 99.24% is predicted to be obtained at the ratio molar of PFAD to MEA 1:1, 18.5 minutes reaction time and microwave power of 100%. Furthermore, a validation experiment was conducted to determine the optimum FAA compound conversion based on the predicted optimum level condition established above. The experiment was carried out and the FAA conversion of 98.89% was achieved.

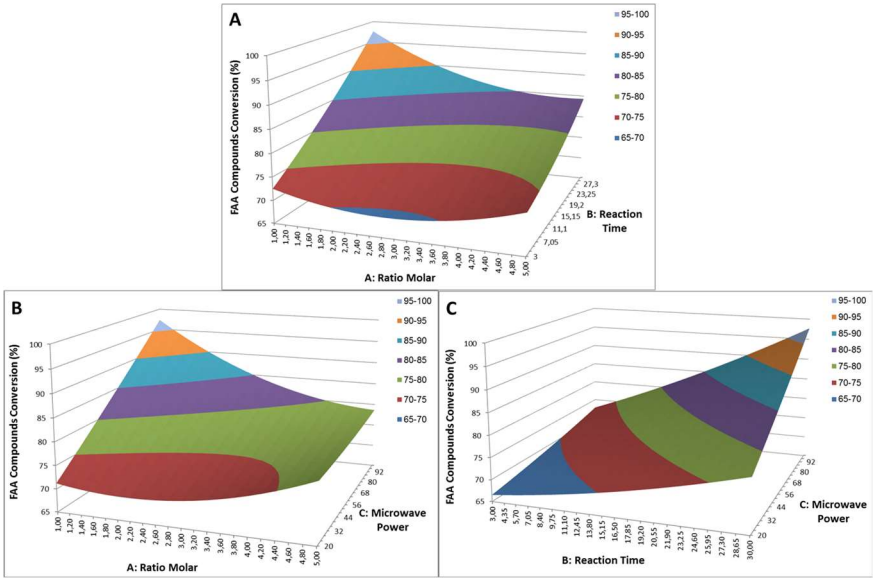

Fig.-2: The Response Surface Graph of the Interaction Effect of (A) Ratio Molar and Reaction Time; (B) Ratio Molar and Microwave Power; and (C) Reaction Time and Microwave Power on FAA Compounds Conversion

This shows that the results of predictions and laboratory experiments are almost the same or only have a deviation of 0.25. Therefore the result shows the acceptability and high predictability of the model.

Furthermore, in comparison with the non-catalytic reflux method[5], this study is time-wise as this microwave-facilitated non-catalytic amidation could save time by 95%.

FAA Compounds Confirmation using FT-IR and GC-MS

The FAA produced from the amidation reaction of PFAD and MEA under microwave radiation was confirmed using FT-IR and GC-MS spectrophotometers. Figure-3 shows the FT-IR spectrum of PFAD and FAA where there is a shift in the wavenumber from 3007.20 cm^{-1} with a broad peak from the OH group to 3301.89 cm^{-1} denoting the stretching vibration of the N-H group with a sharp peak. The formation of FAA compounds was supported by the appearance of stretching vibrations C-N-H and C-N at wavenumbers of 1557.03 cm^{-1} and 1466.08 cm^{-1}. The formation of these FAA compounds was also confirmed using a GC-MS spectrophotometer. Figure-4 shows the GC-MS spectrum of some of the detected FAA derivatives. The compound of N-(2-hydroxyethyl)-octanamide, N-(2-hydroxyethyl)-decanamide, N-(2-hydroxyethyl)-dodecanamide, N-(2-hydroxyethyl)-hexadecanamide, and N-(2-hydroxyethyl)-octadecanamide were identified as the main compound of FAA from amidation of PFAD with MEA under microwave irradiation without a catalyst.

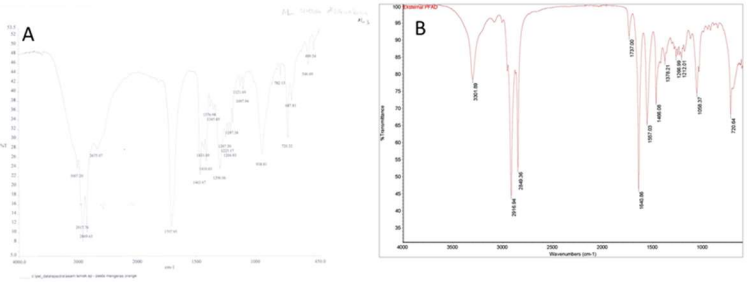

Fig.-3: Spectrum FT-IR of (A) PFAD and (B) FAA Compounds

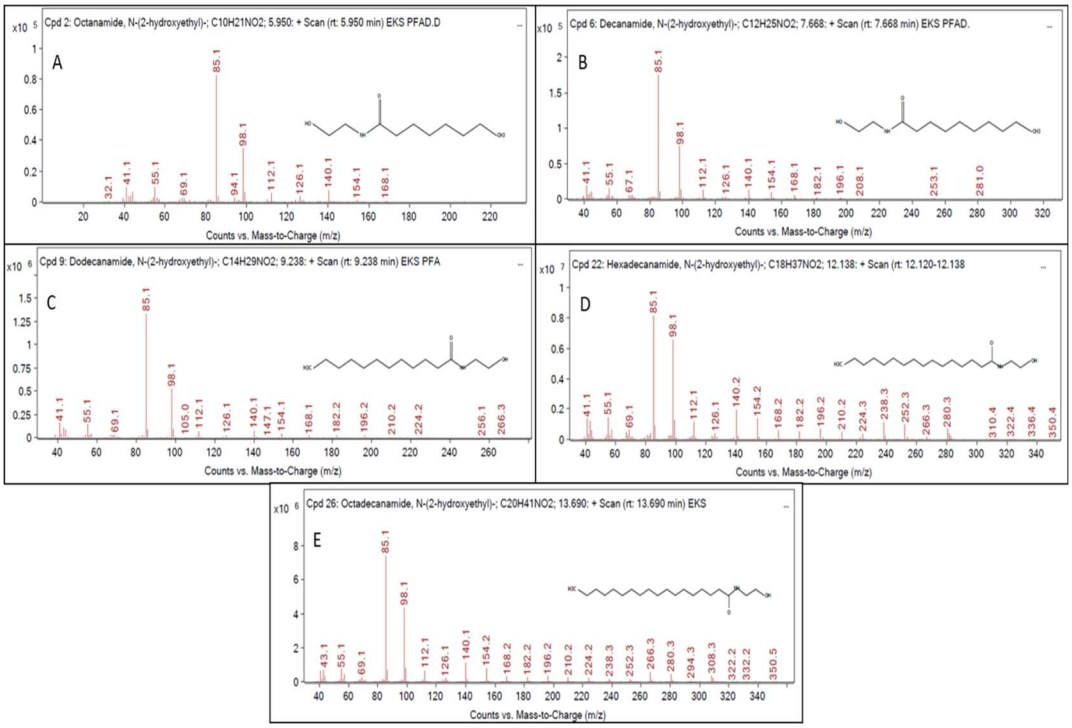

Fig.-4: Spectrum GC-MS of (A) N-(2-hydroxyethyl)-octanamide, (B) N-(2-hydroxyethyl)-decanamide, (C) N-(2-hydroxyethyl)-dodecanamide, (D) N-(2-hydroxyethyl)-hexadecanamide, and € N-(2-hydroxyethyl)-octadecanamide

CONCLUSION

Synthesis FAA compounds under microwave irradiation offer a new method of amidation reaction without a catalyst. The FAA compounds can be synthesized from PFAD and MEA using microwave

irradiation with a maximum conversion of 98.89% obtained under the PFAD to MEA ratio molar of 1:1, 18.5 minutes reaction time, and a microwave power of 100%. Confirmation of the formation of FAA compounds by FT-IR shows the formation of C-N groups at wavenumber 3301.89 cm^{-1} with sharp peaks supported by appearing stretching vibrations of C-N-H and C-N groups at wavenumbers 1557.03 cm^{-1} and 1466.08 cm^{-1}, respectively. The GC-MS spectrum strengthens the confirmation of the formation of FAA compounds where several alkanolamide derivatives are N-(2-hydroxyethyl)-Octanamide, N-(2-hydroxyethyl)-Decanamide, N-(2-hydroxyethyl)-Dodecanamide, N-(2- hydroxyethyl)-Hexadecanamide and N-(2-hydroxyethyl)-Octadecanamide were identified to be formed.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Reactor of Universitas Sumatera Utara for their support and help during the research.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

B.S. Tarigan: methodology, investigation, writing - original draft, writing – review & editing. A. Ginting: methodology & data analysis. E.K. Sitepu: data analysis & writing – original draft.: J.B. Tarigan: supervision, data analysis, writing – review & editing. The ORCID ids of the authors are given below.

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