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KINETIC STUDY OF SELF-ESTERIFIED PALM-BASED C_{12} FATTY ACID AND DIETHYLENE GLYCOL USING CONVENTIONAL AND MICROWAVE HEATING

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ABSTRACT

Diethylene glycol dilaurate (DEG-DL), which is derived from palm oil, may be produced using either esterification or a transesterification technique. Moreover, either a catalytic or non-catalytic reaction can help the process, along with or without the use of a solvent. However, currently the production of DEG-DL is still using the conventional method with a longer time to produce a good quality ester. In this work, the DEG-DL production was done using a solvent-free microwave heating method in the absence of a catalyst. The solvent-free microwave heating method exhibited itself as an effective method to produce DEG-DL with a shorter reaction time from 22 hr to 2 hr compared to conventional heating. The DEG-DL produced has been characterised using FTIR and ^{1}*H-NMR as well as its acid value to observe the trend. The effects of kinetic and thermodynamic parameters of the ester were investigated and compared between both heating methods. Based on the result obtained, the kinetic reaction fitted the pseudo-first-order well with 24% decreased in the activation energy and the pre-exponential factor increased by 93% when comparing conventional and microwave heating methods. The DEG-DL produced is a potential ingredient to be used as coalescent aid in latex paint formulations.*

Keywords: coalescent aid, diethylene glycol dilaurate, faster heating rate, microwave, thermodynamic properties.

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INTRODUCTION

In 2021, Malaysia is a major prominent exporter of palm oil, as reflected by 18.3% of the global oils and fats (17.37 million tonnes) while contributing to 34.3% of the total palm oil trade (Parveez *et al.*, 2021). For the oleochemical industry, it was one of the world's largest producers of oleochemicals accounting for 20% of the world's basic oleochemical products (Parveez *et al.*, 2020). The said industry was almost totally dependent on palm oil/ palm kernel oil as a major feedstock and it played a vital role in supporting the local palm oil industry as well as adding significant value to palm products. Among the chemical industries, there is an increasing trend toward new processes that should meet the stringent environmental or energy requirements such as the generation of nearly zero waste chemicals, less energy, and sufficient uses of product chemicals in various applications (Parveez *et al.*, 2020). Esters are an important class of chemicals and have many applications in a variety of fields. Foods, personal care products, paper, water treatment, metal working fluids, rolling oils, synthetic lubricants, and oil and grease are all made from esters of fatty acids with complex alcohols (Yaakob and Bhatia, 2004).

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Conventionally, the esterification process was performed in the presence of a strong homogeneous catalyst. Direct esterification can occur spontaneously depending on the miscibility of the reactants, the temperature, and the acidity of the carboxylic acid (Hoydonckx *et al*., 2004). However, there were some drawbacks in the use of a homogeneous acid catalyst (Zhong *et al*., 2015). At a high reaction temperature, the homogeneous catalyst may form toxic carcinogenic esters with the alcohols as shown in *Figure 1*. A study reported that catalytic esterification had been performed between lauric acid and diethylene glycol aided by a p-TSA catalyst (Abas *et al*., 2020a).

It was confirmed that the formation of a catalyst ester peak after the sample had been analysed using GC-FID (Abas *et al*., 2020b). Furthermore, an additional step is required to remove the catalyst impurities from the products which may lead to an increase in the final production cost even though the reaction rate is fast (Zabeti *et al*., 2010).

In terms of heating systems, conventional synthesis usually involves the use of an oil bath or a hot plate which heats the walls of the reactors by convection or conduction (*Figure 2*). The core of the sample takes a much longer time to achieve the target temperature. This is a slow and inefficient method of transferring energy into the reacting system as it involves tedious apparatus setup, which results in a higher cost of the process and the excessive use of solvents/reagents. During these processes, there are many problems of health and safety for workers in addition to the environmental problems caused by their use and disposition as waste (Ajmer *et al*., 2013).

On the other hand, in microwave assisted synthesis the microwaves penetrate inside the material and heat is generated through direct microwave-material interaction (*Figure 2*). Microwave-assisted synthesis has several advantages over conventional reactions in that the microwaves allow for an increase in reaction rate, rapid reaction optimisation, and rapid analogue synthesis (Lidström *et al*., 2002).

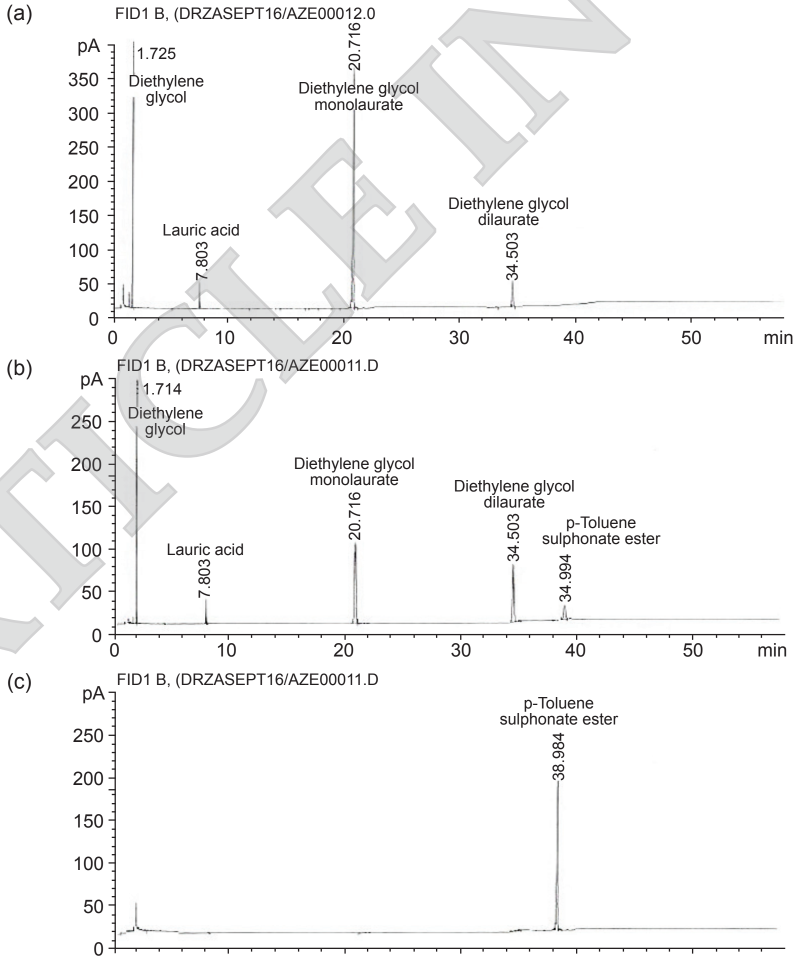


Figure 1. GC chromatogram for esterification of lauric acid and diethylene glycol for different processes (a) autocatalytic reaction; (b) catalytic reaction with p-TSA catalyst; (c) standard p-Toluene sulphonate ester.

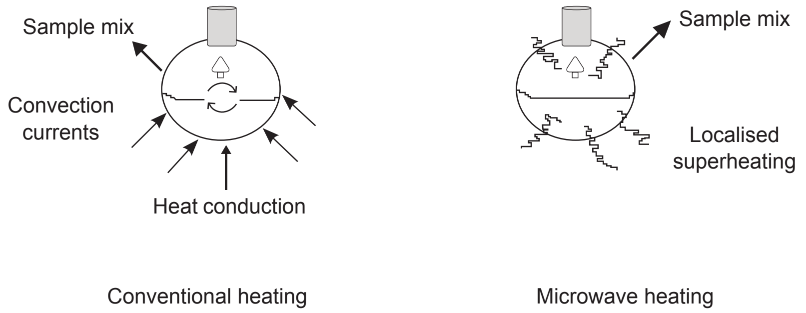


Figure 2. Different heating mechanisms for conventional and microwave heating.

Several chemists have switched from conventional heating method to microwave assisted chemistry because it also consumes both less energy and solvent and it permits challenging compound synthesis that economically leads to the synthesis of many organic compounds (Algul *et al.*, 2008). Developing an autocatalytic esterification reaction which will produce high quality esters is one of the aims. An alternative method to conventional heating is the use of microwave heating which is a clean and green chemistry (Abas *et al.*, 2020a). To minimise the use of catalyst in order to produce green and clean palm-based glycol esters, the self-esterification process was proposed to develop standard esterification reactions in the absence of catalyst that resulting in simple purification, clean and green processes (Abas *et al.*, 2020b).

The use of microwave technology is an effective activation method that reduces the potential barriers and a thermodynamic product was produced easily. This was due to the interaction between the microwave energy and dipole moments of the starting materials (Hayes, 2002). The interaction of matter with the electromagnetic field of radiation causes the movement of ions and the rotation of molecules with induced and permanent dipoles. This explained how the microwave principle of heating liquids works (Meredith, 1998). Some advantages of this technology are such as it is simple to use, produces faster heating, lower duration required and energy saving as compared to oil-bath heating technology (Abas *et al.*, 2020a). Nguyen *et al.* (2020) developed ethyl biodiesel through self-esterification of oleic acid via microwave heating. The process successfully optimised the operating conditions and obtained the highest conversion of oleic acid at 97.62%. It was found that microwave-assisted autocatalytic esterification is eco-friendly and feasible to be used for biodiesel production.

Instead of chemical processing, microwave heating can be a useful tool for extraction and is extensively used in the fragrance, flavour, and pharmaceutical industries (Mahfud *et al.*, 2017). The effectiveness of conventional hydrodistillation (HD) and microwave-assisted hydrodistillation (MAHD) methods in the isolation of essential oils can be compared (Kusuma and Mahfud, 2017). The effects of solvent-free microwave extraction variables such as microwave power, the ratio of raw material mass to distiller volume (F/D), raw material size, and extraction time on essential oil yield were investigated (Kusuma *et al.*, 2018). By using solvent-free microwave extraction (SFME) as a method for "green" extraction of edible essential oil, the method offers significant advantages over conventional hydrodistillation, including shorter extraction times (30 min *vs.* 4.5 hr). Higher yields were obtained which is 0.13% more than conventional system. On the environmental impact, energy cost is appreciably higher for performing conventional hydrodistillation than that required for rapid SFME (Kusuma *et al.*, 2016).

Hong *et al.* (2015) reported on the esterification of palm fatty acid distillate performed under a noncatalytic and high-temperature condition (230°C to 290°C) based on rigorous mathematical modelling. From the reaction rate constants obtained from the proposed kinetic models, the apparent activation energy was estimated to be 43.98 kJ/mol, which is lower than the value obtained from the reaction using heterogeneous catalysts. This low value indicates that the reactants and products behave as an acid catalyst at relatively high operating temperature and constant pressure.

A kinetic study was also conducted for the extraction, and a semi-empirical model was fitted based on the experimental kinetic results. The experimental investigation also revealed that, when compared to classical HD, the operation time for MAHD was shorter for the same product quantity (Kusuma and Mahfud, 2018).

Based on the results obtained, higher yield results from higher extraction rates by microwave could be due to a synergy of two transfer phenomena; mass and heat acting in the same way. With increasing energy consumption and the drive to improve efficiency, industries and research institutions are challenged to find ways which can simplify the operation procedure to meet low-cost requirements and achieve good quality. Moreover, in order to reduce the extraction time and possibly improve the extraction yield, enhance the quality of the extracts and reduce the operation costs, new approaches such as microwave-assisted extraction (MAE) have also been sought (Kusuma and Mahfud, 2017a).

However, to the best of the authors' knowledge, the use of microwave heating in the production of glycol ester from palm fatty acid was still limited. Hence, the objective of this study is to investigate the potential of microwave heating to offer the possibility for better production of ester of lauric acid with diethylene glycol compared to conventional heating. The results demonstrated that the kinetic parameters such as rate constant, activation energy and pre-exponential factor follow the Arrhenius equation. Data on thermodynamic properties of activation are collected as referred to in Eyring equation.

MATERIALS AND METHODS

Materials

Palm-based lauric acid was obtained from Emery Oleochemical (M) Sdn. Bhd. (Edenor C_{12}, ≥98% purity). The commercial-grade of diethylene glycol (Sigma-Aldrich, 99.9%) was purchased from Bumi Pharma Sdn. Bhd. The chemicals were used as received.

Conventional Heating

Esterification of lauric acid (0.5 mol, 100 g) with diethylene glycol (0.25 mol, 26.5 g) was performed in a 250 mL three-neck round bottom flask equipped with a reflux condenser. The autocatalytic reactions were performed by varying the temperature ranging from 170°C to 230°C at atmospheric pressure. The autocatalytic esterification between lauric acid and diethylene glycol produced glycol di-ester as a major product, with water as the by-product.

Samples were taken at the indicated intervals to monitor the AV reduction trend. The agitator speed and mole ratio of lauric acid to diethylene glycol were held constant at 300 rpm and 2:1, respectively. Experiments were performed in triplicate and the data averaged.

Microwave Heating

Similar procedures of self-esterification were carried out using a microwave batch reactor (MARS SYNTHESIS, CEM Corporation USA). The unit is equipped with two magnetrons (1800 W), a glass reactor, magnetic stirrer, reflux condenser, temperature sensor and thermometer. In the microwave cavity, the vessel was attached to the rotor mechanism. Reaction temperature was varied at 170°C, 190°C and 230°C with continuous stirring rate of 300 rpm. The reaction mixture was heated between 10 min to 2 hr. The completed reaction was then left to cool at 50°C. Samples were withdrawn at the specified intervals to analyse for their acid values in order to monitor the reaction progress. Other reaction conditions were: initial molar concentration of acid groups (C_a) of 4.07 mol/L, initial molar concentration of hydroxyl groups (C_b) of 2.03 mol/L. Experiments were performed in triplicate and the data averaged.

Optimisation of reaction parameters was performed with continuous magnetic stirring that varied from 300 to 1200 rpm. Other variables investigated were reaction temperature, reactant mole ratio, reaction time and microwave power. *Table 1* displays a summary of the variable parameters investigated in the reaction (Abas *et al.*, 2020b).

TABLE 1. SUMMARY OF THE VARIABLE LEVELS INVESTIGATED IN THE REACTION

Parameter	Conventional heating	Microwave heating
Reaction temperature (°C)	150, 170, 190, 210 and 230	150, 170, 190, 210 and 230
Mole ratio (LA: DEG)	1: 1, 1: 1.5, 2: 1, 2: 1.5 and 2: 2.5	1: 1, 1: 1.5, 2: 1, 2: 1.5 and 2: 2.5
Stirring rate (rpm)	300, 600, 900 and 1 200	300, 600, 900 and 1 200
Reaction time (hr)	1.0, 1.5, 3.0, 6.0, 8.0, 12.0 and 20.0	1.0, 1.5, 3.0, 6.0, 8.0, 12.0 and 20.0
Microwave power (W)	-	400, 800, 1 000, 1 500

Note: *LA - lauric acid; DEG - diethylene glycol.
Source: Abas *et al.*, 2020a.

Analysis and Characterisation Methods

Acid value (AV) was measured in accordance to the AOCS Official Method Te 1a-64 to monitor the reaction performance over time, whereas AOCS Official Method Cd 13-60 is used to determine the hydroxyl value (OHV). The amount of moisture present in the sample withdrawn at the specified intervals was determined using a Mettler Toledo C30 Karl Fischer Compact Titrator.

Proton nuclear magnetic resonance (^{1}H-NMR) and Fourier transform infrared (FTIR) techniques were carried out to analyse the plausible product. In the determination of structure confirmation, samples were dissolved in $CDCl_3$ (as deuterated solvent) and recorded on a 600 MHz JEOL NMR Spectrometer (Japan).

Structural analysis by FTIR was performed to verify the transformation of the functional group at a range of 4000 cm^{-1} to 700 cm^{-1}. A Perkin Elmer FTIR spectrometer (USA) equipped with attenuated total reflectance (ATR) was used to acquire the IR spectra.

Product Identification

The expected product, diethylene glycol dilaurate (DEG-DL) was analysed by Nuclear Magnetic Resonance ^{1}H (600 MHz) recorded on a JEOL NMR spectrometer with $CDCl_3$ as a deuterated solvent. The NMR spectra will give information on the structure of DEG-DL produced from the reaction. The formation of an ester group was proved by the signal as follows:

^{1}H NMR (600 MHz, $CDCl_3$- d): δ 0.875 (t, J= 11.1 Hz, 3H, CH_3-C), 1.24 (s, 16H, -(CH_2)-), 1.61 (s, 2H, R-CH_2-CH_2-COO-), 2.31 (t, J= 7.8 Hz, 2H, R-CH_2-CH_2-COO-), 3.68 (t, J=4.8 Hz, 2H, HO-CH_2-CH_2-OOC-R) and 4.22 (q, J= 4.8Hz, 2H, HO-CH_2-CH_2-OOC-R)

In the Fourier Transform Infra-Red (FTIR) spectra, the band at 3346 cm^{-1} corresponded to a peak of OH stretching for diethylene glycol. However, the peak disappeared in the spectra of palm-based DEG-DL. The C-O stretching peaks were obtained at wavenumber 1352 and 1429 cm^{-1} in the spectra of DEG-DL. Molecular bioassay indicates the introduction of glycol into palm-based fatty acid ester products. The lauric acid spectra revealed a stretched carboxylic group at wavenumber 1696 cm^{-1} and an ester group at wavenumber 1737 cm^{-1}.

Electric Consumption

Electric energy consumption is the form of energy consumption that uses electrical energy. The electric consumption for the conventional oil-bath heating and microwave heating was calculated based on the influence of power consumption and esterification time. The general equation for electric consumption is described in the Equation (1) (Kusuma and Mahfud, 2017b).

$$E_c = \frac{P \times t}{1000} \tag{1}$$

where, E_c is the electric consumption (kWh); P is the power consumption (W); t is time. The relative electric consumption of the different heating methods could be expressed by the Equation (2):

$$E_c{}^* = \frac{E_c}{m} \tag{2}$$

where, E_c^* is the relative electric consumption (kW.h/g); m is the mass product obtained.

Self-esterification of lauric acid and DEG using the conventional method (oil-bath heating) is conducted using a hot plate (IKA C-MAG HS 10) and a reaction time of 20 hr, while another similar reaction was performed using the microwave batch reactor (MARS SYNTHESIS, CEM Corporation USA) and a reaction time of 2 hr. The difference in the reaction time caused the required cost and energy of esterification process to be greater when using the conventional method compared to the microwave method (Kusuma *et al.*, 2019).

Biodegradability Test

A biodegradation test was conducted on the DEG-DL produced to obtain biodegradation data for this product. This study assessed the biodegradation of the above-mentioned test item by inoculating the test item with a small number of microorganisms. Media preparation and the biodegradation test were conducted according to the Organisation of Economic Cooperation and Development (OECD) standard method. The test item was tested with the test method OECD 301F Manometric Respiratory Test. The test period was 34 days, which included a pre-conditioning period for the inoculum (6 days) and the actual test (28 days).

RESULTS AND DISCUSSION

The reaction was conducted, and product samples were weighed on an electronic balance, then the weight value was used to compute the percent yield. The starting materials used were 100 g lauric acid and 26.5 g diethylene glycol to produce a theoretical yield of DEG-DL of 117. 68 g. The isolated yield of DEG-DL produced using conventional heating weighed 105.4 g, and the isolated yield of DEG-DL produced via microwave heating weighed 112.34 g. The percentage yield for both heating systems was determined to be 89.56% and 95.46%, respectively.

The trend for acid value reduction was plotted for the reaction using conventional and microwave heating at three different reaction temperatures *i.e.*, 170°C, 190°C and 230°C and is shown in *Figure 3* and *4*. Based on the plot obtained, it indicated that increasing reaction temperature led to a faster reduction of the acid value. For example, after an hour of reaction, the acid value measured at 230ºC for conventional heating was 78.6 mg KOH/g, compared to 98.5 mg KOH/g and 115.3 mg KOH/g at 170ºC and 190ºC, respectively. The same trend was observed in *Figure 4*, lower acid value was obtained at a higher temperature, 230°C.

In terms of the heating system aspect, when the reaction was performed via microwave heating under the same operating parameters *i.e.*, at an hour reaction course, it gave an acid value of 41.3 mg KOH/g which was a half reduction from the conventional method. A study reported by Aranda *et al.* (2008) highlighted that the time to heat up the sample to the set point temperature under conventional heating was much longer than the heating time using microwave irradiation. Therefore, it revealed that by using microwave heating, the reaction proceeded more quickly.

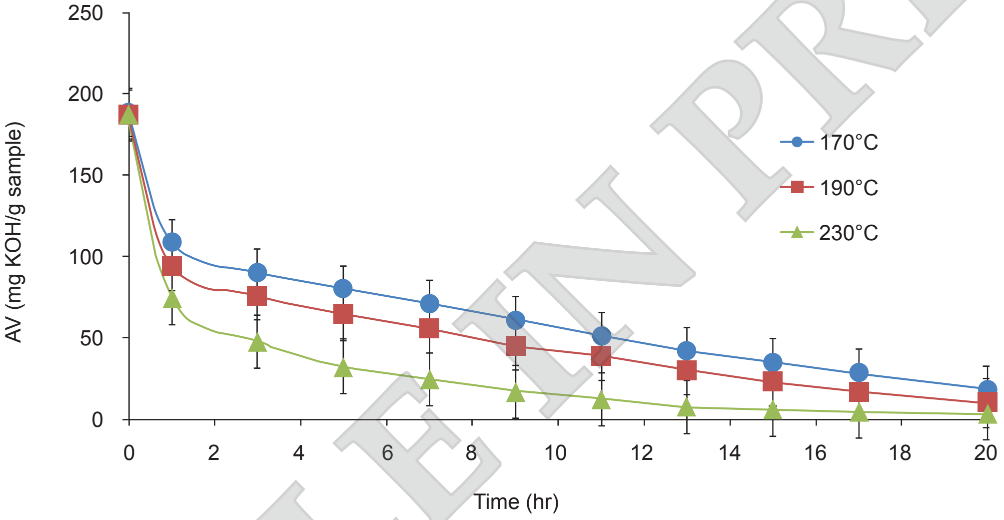


Figure 3. Effect of acid value over time at different reaction temperatures for non-catalytic esterification using conventional heating.

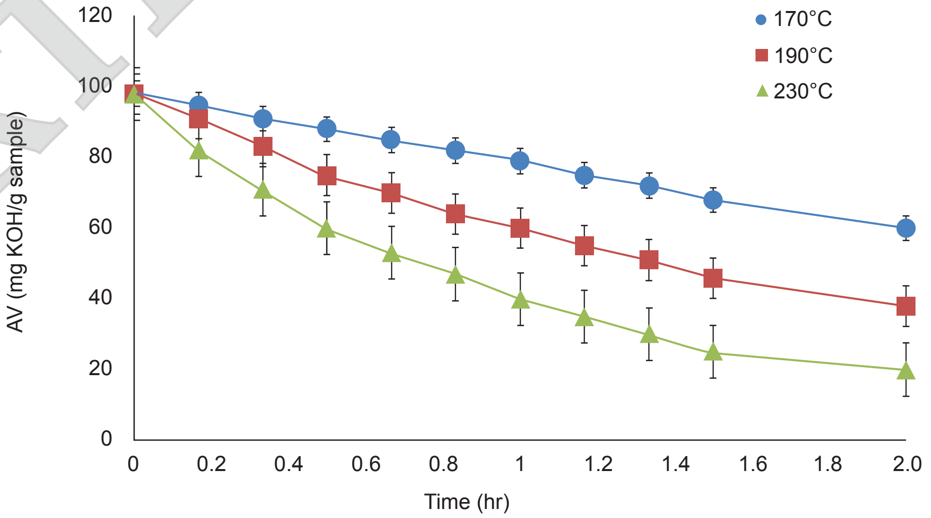


Figure 4. Effect of acid value over time at different reaction temperatures for non-catalytic esterification using microwave heating.

This schematic reaction in *Figure 1* depicts the reaction between lauric acid and diethylene glycol (Equation 3).

lauric acid (A) + diethylene glycol (B) $\rightarrow$ diethylene glycol dilaurate (C) + water (D) (3)

To observe the effect of microwave heating for this reaction, a few assumptions were made to facilitate the calculation of reaction rate and energy efficiency. The concentration of both reactants affected the reaction rate. The reaction fitted well with the pseudo-first-order for both carboxylic acid group (C_A) and the glycol group (C_B) by following the Arrhenius equation. The reaction was assumed to be irreversible as the water was completely removed.

The reaction rate, r is written as;

$$r = kC_A.C_B \tag{4}$$

The differential mass balance equation is as shown in Equation (5) with the assumption the water was not removed from the system.

$$r = C_{AO}\frac{dn}{dt} \tag{5}$$

where, n represents the lauric acid conversion, C_{AO} is the initial molar concentration of acid groups and t is the reaction time.

Skrzypek *et al.* (1994) reported that during the reaction course, the mass of the system decreases due to water removal and can be simplified as in Equation (6). Hence, the lauric acid conversion, n can be defined as:

$$n = \frac{Avo - Avf\,((56{,}100 - 18Avo/56{,}100 - 18Avf))}{Avo} \tag{6}$$

where A_{vo} is the initial acid value and A_{vf} is the final acid value.

Equation (4) is then integrated to obtain Equation (7) which includes a concentration ratio of acid to diol, $M = C_{AO}/\ C_{BO}$ where $M \neq 1$.

$$ln\frac{M - n}{M\,(1 - n)} = C_{AO}\,(M - 1)\,kt \tag{7}$$

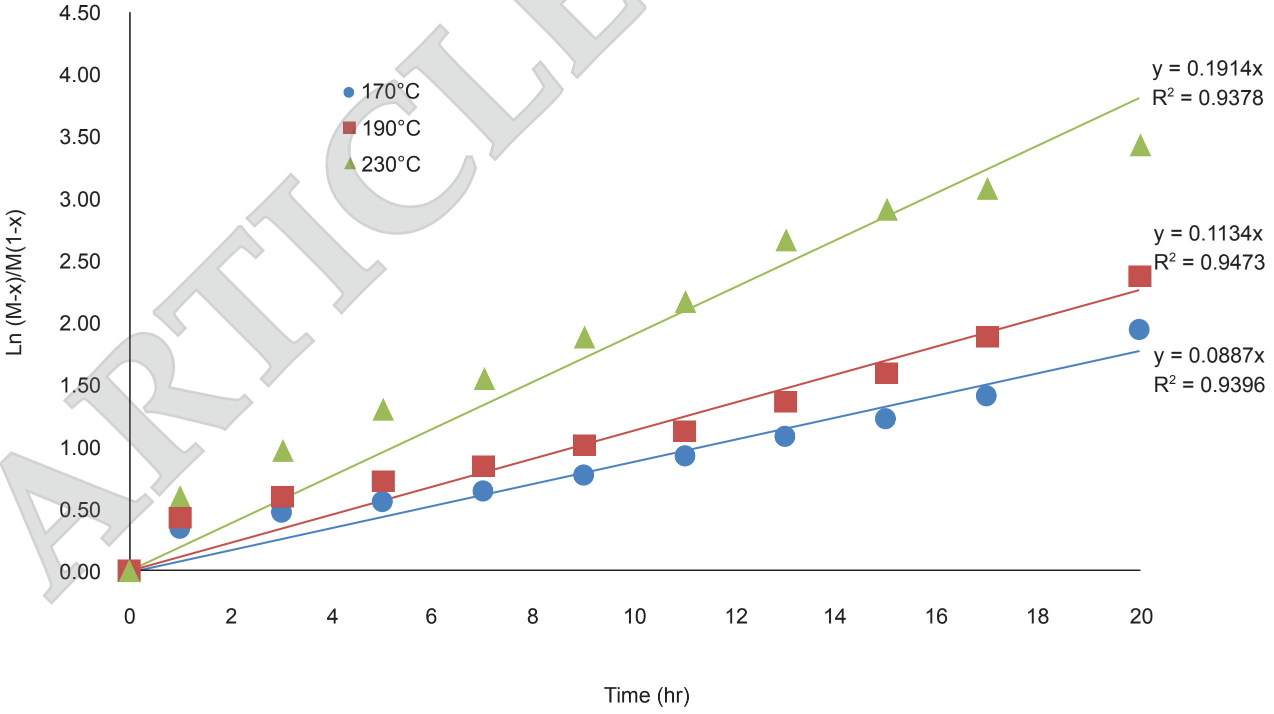


Figure 5. Kinetic modelling of the non-catalytic esterification reaction by conventional heating.

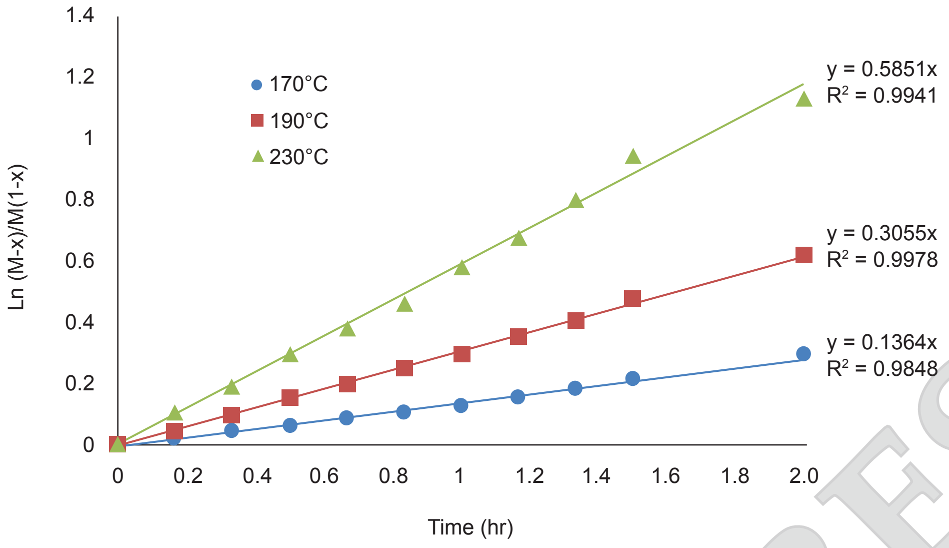


Figure 6. Kinetic modelling of the non-catalytic esterification reaction by microwave heating.

Based on Equation (7), a linear trend plotted at different range of reaction temperature over time was obtained for both conventional and microwave heating, respectively as shown in *Figure 5* and *6*. They fitted a good plot to justify a practical kinetic assumption to be made. According to acid-group and hydroxyl-group proportionality, the reaction followed a first-order kinetics. The rate constant, *k* was obtained and is summarised in *Table 2*. The results showed that the microwave rate constant exceeded conventional heating. The use of microwave may be beneficial compared to the classic method due to several causes. Microwave heating can rapidly reach a given temperature, with only a short induction period.

As a result, rather than gradually warming from room temperature, the reaction quickly reaches the desired temperature. Furthermore, unlike heating in an oil bath, where the glass is heated and then the solution is heated, the microwave heats the solution directly and uniformly (Kappe and Stadler, 2005). Arrhenius' equation describes the temperature dependence of chemical reaction rates and is expressed in Equation (8). Activation energy, Ea, and a pre-exponential factor correlated to the rate constant, *k*, can be calculated for this reaction by using microwave heating.

$$k = \mathrm{A} \times \mathrm{e}^{-\mathrm{Ea}/\mathrm{RT}} \tag{8}$$

where, A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant and T is an absolute temperature.

A plot of the linear trend for both Arhenius equations using conventional heating and microwave heating can be observed in *Figure 7*. The slopes of the line were used to calculate the activation energies, and the intercepts to determine a pre-exponential factor. The activation energy decreased from 24.25 to 18.41 kJ/mol after switching the system from an oil-bath to microwave heating as summarised in *Table 2*. In chemical kinetics, an equation that describes changes in the rate of reaction as a function of temperature is defined as an Eyring equation. It indicates the determination of thermodynamic reaction parameters based on statistical mechanical justification. Eyring equations tend to resemble Arrhenius equations in general terms (Equation 9).

$$k = \frac{k\,k_{\mathrm{B}}T}{\mathrm{h}}\,\mathrm{e}^{-\frac{\Delta G\ddagger}{RT}} \tag{9}$$

It can be rewritten as:

$$\mathrm{k} = \frac{k\,k_{\mathrm{B}}T}{h}\,e^{\frac{\Delta S^{\neq}}{R}}\,e^{\frac{\Delta H^{\neq}}{RT}} \tag{10}$$

This equation can be put in the following form:

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{11}$$

$$\mathrm{In}\,\frac{k}{T} = \frac{-\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \mathrm{In}\,\frac{k\,k_{\mathrm{B}}T}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{12}$$

where, *k* is the reaction rate constant, T is the absolute temperature, *k* = 1, k_B is the Boltzmann's constant, *h* is the Planck's constant, R is the gas constant, ΔG is the Gibbs energy of activation, ΔH is the enthalpy of activation and ΔS is the entropy of activation.

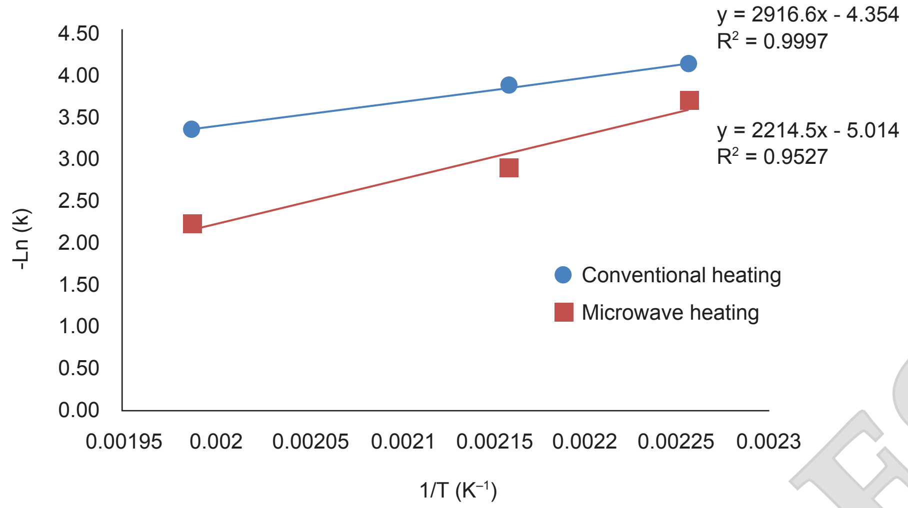


Figure 7. A plot of Arrhenius equation via conventional heating and microwave heating.

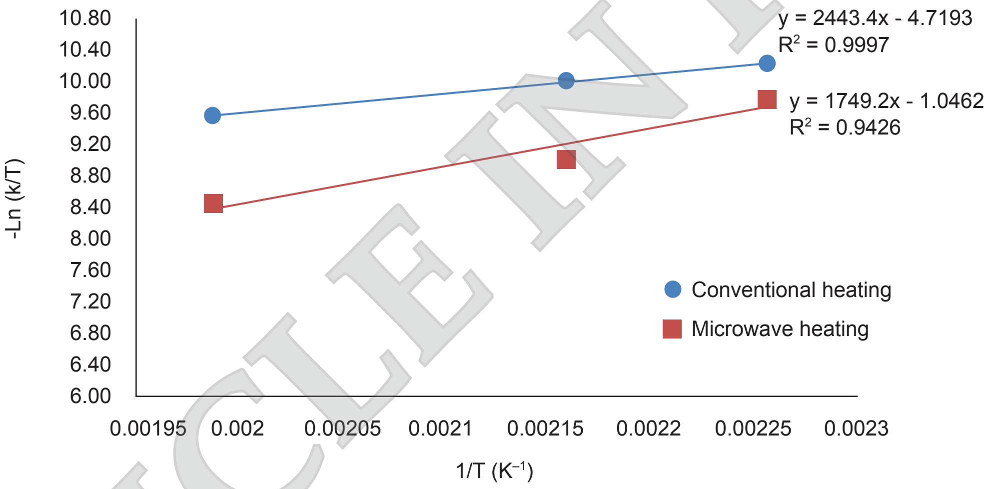


Figure 8. A plot of Eyring equation via conventional heating and microwave heating.

TABLE 2. TEMPERATURE-DEPENDENT KINETICS AND THERMODYNAMICS OF THE NON-CATALYTIC ESTERIFICATION VIA CONVENTIONAL AND MICROWAVE HEATING

Parameter	**Temperature (°C)**	**Heating Method**	
		Conventional	**Microwave**
Rate constant, k (L/mol. hr)	170	0.016	0.249
	190	0.021	0.056
	230	0.035	0.107
Activation energy, Ea (kJ/ mol)		24.25	18.41
Pre-exponential factor, A (L/ mol. hr)		77.79	150.51
Entalphy of activation, ΔH ≠ (kJ/ mol)		20.31	14.54
Entropy of activation, ΔS ≠ (kJ/ mol. K)		-0.24	-0.21
Gibbs energy, ΔG ≠ (kJ/ mol)		126.67	107.60

A graph of ln (k/T) versus (1/T) can be simplified as written in Equation (12). Based on *Figure 8*, the enthalpy of activation is a slope ($-\Delta H^{\neq}/R$) whereas the entropy of activation is derived from an intercept ($\ln (k\, k_B T/h) + (\Delta S^{\neq}/R)$) . $\Delta G^{\neq}$ then can be calculated by using Equation (11). The summary of the thermodynamic reaction parameters for both conventional and microwave heating, respectively, are tabulated in *Table 2*. It reveals that the activation energy decreased by 24% whereas the pre-exponential factor increased by 93%. As a result, it confirmed that very fast heating rates were observed, emphasising one of the main advantages of microwave heating, which provides faster heating than conventional convection heating. Analysis of electric consumption in esterification processes to produce diethylene glycol dilaurate (DEG-DL) using different heating methods was investigated. In esterification of lauric acid and DEG, by using microwave heating, the processing time was relatively fast, which was an advantage when compared to the conventional method. This is due to the esterification reaction time being related to the required cost and energy (Ismanto *et al*., 2017; Putri *et al*., 2017).

Figure 9 shows a bar chart of the consumed energy for esterified lauric acid and DEG with respect to the power consumption of the microwave approach. In this study, the electric consumption requirement for DEG-DL production by the microwave method was 3.0 kWh while for conventional oil-bath heating system was 30 kWh. Therefore, it can be said that using the oil-bath heating method requires 10 times more electricity consumption than microwave heating. A similar trend is shown for the relative electric consumption to obtain 1 g of ester from esterification, whereas the conventional heating requires 9.76 times higher electric consumption when compared with microwave method.

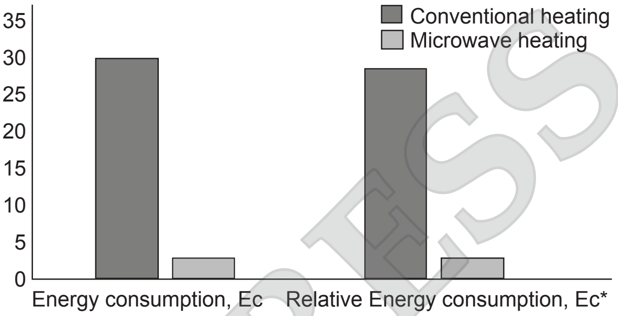
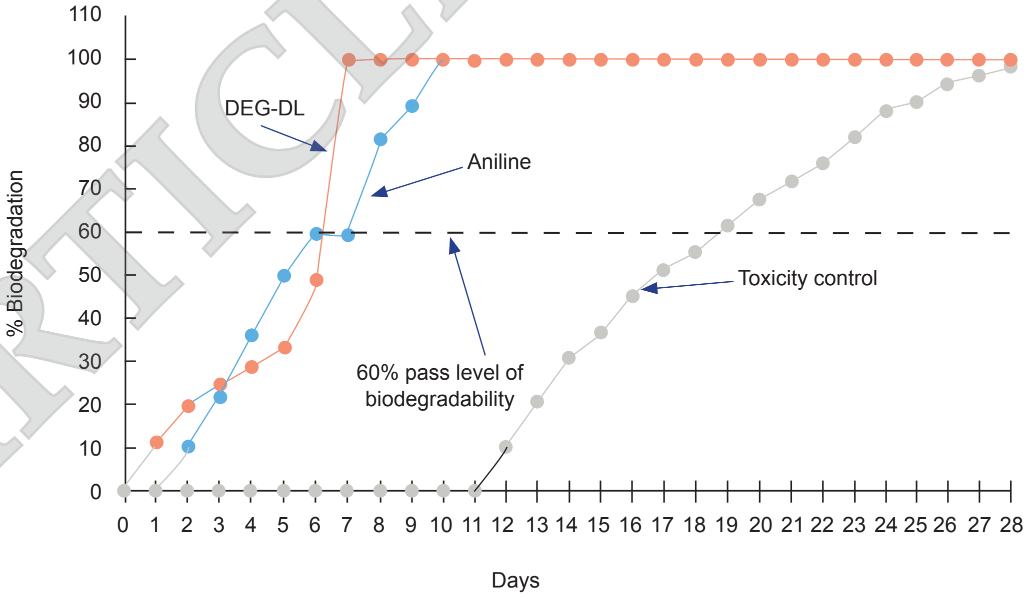


Figure 9. Electricity consumption in self-esterification of lauric acid and diethylene glycol Using conventional heating and microwave heating methods.

A biodegradability study is designed to determine the biodegradability of materials under a given or intended use condition. Based on the curved line produced from the test, as shown in *Figure 10*, the DEG-DL was found to be readily biodegradable with a minimum of 6 days to pass the 60% level and reaches 100% biodegradability in less than 10 days within the period of incubation (28 days).



Note:

1. Aniline, a readily degradable substance is used as a reference.
2. Toxicity control was performed to determine the toxicity of the test substance against the inoculum. The test substance should reach 25% biodegradation within 14 days to ensure it does not inhibit the inoculum.

Figure 10. Biodegradation curve of diethylene glycol dilaurate (DEG-DL); aniline and toxicity control.

CONCLUSION

In this work, the esterification of lauric acid and diethylene glycol in the absence of a catalyst under conventional heating and microwave heating were investigated. The reaction temperature was varied from 170°C, 190°C and 230°C. Based on the results obtained, increasing the reaction temperature resulted in a faster reduction of acid value regardless of the type of heating system used. The temperature-dependent kinetics was the main factor used in order to determine the reaction rates and thermodynamics parameters between both systems. The kinetic reaction fitted well with the first-order for both systems, with activation energies of 24.25 kJ/mol for conventional heating and 18.41 kJ/mol for microwave heating, respectively. According to the activation energy of the chemical reaction law, the lower the activation energy, then the faster the chemical reaction would be. Therefore, between these two methods, it revealed that there was about 24% reduction in the activation energy between conventional and microwave methods of heating. The esterification reaction under microwave heating yielded better results compared to the conventional method with 95.46% and 89.56%, respectively. When compared to conventional heating, the solvent-free microwave heating method produced an effective method for producing DEG-DL with a shorter reaction time and a higher yield of 11 times.

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