

PRODUCTION OF PALM-BASED GLYCOL ESTER VIA AUTOCATALYTIC ESTERIFICATION

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ABSTRACT

The self-esterification of the lauric acid (LA) with diethylene glycol (DEG) to produce diethylene glycol dilaurate (DEG-DL) was conducted under atmospheric via conventional method. The effects of reaction temperature, reactant molar ratio and stirring speed rate were studied. Results showed that the composition of DEG-DL was increased with the increase in reaction temperature and reactant molar ratio. The reaction rate was observed independent of stirring speed rate. A high conversion of LA (>90%) was obtained based on one-factor-at-time (OFAT) method of designing experiments. At the reaction temperature of 230°C and molar ratio of LA: DEG was varied from 1:1 to 2:1, the composition of DEG-DL was increased from 50.1% to 97.2%. Nuclear magnetic resonance (NMR) spectra confirmed a compound produced was DEG-DL based on structural result. The acid value of LA was reduced from 182 to 3.09 mg KOH g⁻¹ LA. The autocatalytic esterification is a clean reaction as it omits the separation step of catalyst and solvents. The hydrophilic lipophilic balance (HLB) index calculated for DEG-DL was 7.5 and potentially functioned as a water-in-oil or oil-in-water emulsifier for cosmetic applications.

Keywords: palm-based glycol ester, surfactant, clean process, HLB index.

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INTRODUCTION

Malaysia is blessed with the abundant supply of palm oil and palm kernel oil. In 2017 alone, a total of 5.81 million hectares of land were planted with oil palm which produced an average yield of fresh fruit bunch (FFB) of 17.89 t ha⁻¹. Subsequently, the oil palm fruitlets yield 3.53 t ha⁻¹ of crude palm oil (CPO) from the mesocarp and 0.88 t ha⁻¹ of palm kernel oil (PKO) from the kernel seed (Kushairi *et al.*, 2018). Today, oleochemical industries market in Malaysia accounted for 20% of world's basic oleochemical capacity. The industry emerged rapidly as 2.76 million tonnes of oleochemicals are exported to Europe and this contributed to additional revenue over the basic value of the commodity oils (Razmah, 2017).

Esters are derived by the reaction of a carboxylic acid and an alcohol with water as a by-product (Kantlehner, 1991). Direct esterification can be catalysed or even can proceed in a spontaneous fashion, depending on the reactants properties, the temperature and the acidity of the carboxylic acid reaction partner to produce esters (Hans *et al.*, 2004). Conventionally, the esterification process is performed in the presence of either homogeneous or heterogeneous catalyst. However, there were some drawbacks on the use of homogeneous acid catalyst (Zhong *et al.*, 2015). Strong mineral acids may form toxic and carcinogen esters with the alcohols, if the reactions were conducted at very high temperatures and some issue related to corrosion and separation problems.

It is difficult to separate the catalyst in the product mixture and that requires additional steps of purification in order to produce product with high purity (Mazo *et al.*, 2012). The carbon chain length of carboxylic acid, the alcohol feedstock, the reaction temperature and the design of the reactor system are parameters influencing the conversion of fatty acid (Kalaru *et al.*, 2009).

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The incorporation of biocatalyst (enzyme) as heterogeneous catalyst in esterification consumes less energy than chemical process, produces a clean ester with excellent properties, biodegradable and low toxicity (Jothiramalingam and Wang, 2009). Nevertheless, enzymatic reactions are quite difficult to handle because they are highly sensitive to changes in physical and chemical conditions surrounding them. Besides, the biocatalyst is easily denatured by even a small increase in temperature and is highly susceptible to poisons and changes in pH. Another drawback of this type of heterogeneous catalyst is the high cost of enzyme isolation and purification that discourages their use (Robert, 1997).

Hence, to minimise on the use of catalyst in order to produce green and clean palm-based glycol ester, the self-esterification process was proposed subsequently to develop the standard esterification protocol. There were few studies published on both esterification reactions in the absence of catalyst that result in simple purification, clean and green processes (Yujaroen *et al.*, 2009; Yamazaki *et al.*, 2007; Maeda *et al.*, 2008).

Hyun *et al.* (2012) conducted autocatalytic esterification of palm fatty acid distillate (PFAD) with methanol at high temperature in order to obtain acid value less than 0.5 mg KOH g⁻¹ sample. The effect of process parameters like reaction time, temperature and reactant molar ratio was investigated in non-catalytic esterification of free fatty acids (FFA) in jathrophia with methanol. The optimal conditions were found to give a maximum conversion of 95.1% at 5 hr reaction time (Karna *et al.*, 2016).

There are various ester applications such as in food and beverages, cosmetic and personal care, wastewater management, paper and coating, metal working fluids, rolling oils and synthetic lubricants (Yaakob and Bhatia, 2004). Previous study reported on the use of soyabean-based glycol ester as coalescent aid in water-based paint formulation. The compositions of soyabean-based glycol ester and their physical properties were determined according to the application (Jiratumnukul and

Van Der Mark, 2000). Therefore in this work, the influence of operating condition such as reaction temperature, reactant mole ratio and stirring speed rate for production of diethylene glycol dilaurate in the absence of catalyst were studied.

MATERIALS AND METHODS

Materials

Lauric acid (LA) (≥ 98% purity) was obtained from Emery Oleochemical (M) Sdn Bhd, Malaysia. Diethylene glycol (≥ 98% purity) was purchased from Bumi Pharma Sdn Bhd, Malaysia. The reagents were used without any purification and stored as recommended by manufacturers.

Reaction Procedure for Autocatalytic Esterification of Lauric Acid

LA was reacted with diethylene glycol (DEG) in a 250 ml three-necked flask fitted with a magnetic stirrer, thermometer and a water condenser. The reaction temperature was varied at 150°C, 170°C, 190°C, 210°C to 230°C in the absence of catalyst. The LA to DEG molar ratio was set for 1:1, 1:1.5 and 2:1. The experiments were carried out under atmospheric pressure and the stirring speed rate of the solution was varied from 300-1200 rpm. The reactants are mixed and heated to the desired reaction temperature. After reaction, the excess reactants were removed by vacuum distillation.

Analyses and Properties Evaluation of Palm-based Glycol Ester

The progress of the reactions was monitored by acid value (AV) determination from samples withdrawn every hourly intervals as referred to AOCS Official Method Te1a-64. The percentage of unreacted DEG was measured by the hydroxyl value (OHV) analysis according to AOCS Official Method Cd13-60. The amount of moisture content

TABLE 1. CLASSIFICATION OF SURFACTANT FUNCTION BASED ON HYDROPHILIC-LIPOPILIC BALANCE (HLB) INDEX

Solubility characteristic	HLB index	Function
Hydrophobic (oil soluble)	0	-
	2-3	Anti-foaming agents
	3-6	w/o emulsifying agents
Water dispersible	7-9	Wetting and spreading agents
Hydrophilic (water soluble)	8-16	o/w emulsifying agents
	13-15	Detergents
	15-18	Solubilising agents

Note: Calculation of HLB values of non-ionic surfactants.
Source: Griffin (1954).

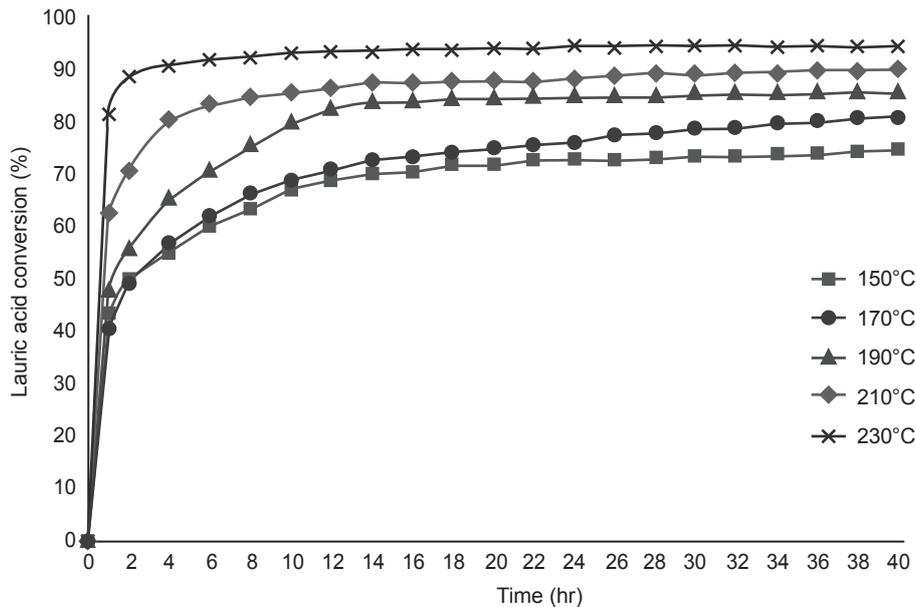


Figure 3. Conversion of lauric acid (LA) over time for esterification of LA and diethylene glycol (DEG) at different reaction temperatures using molar ratio of LA:DEG = 1:1 at 300 rpm.

Effect of Stirring Speed Rate

The external mass transfer rate between bulk phases of the reactants will increase by increasing the stirring speed rate. The effect of stirring speed on conversion of LA was investigated. The speed of magnetic stirrer was varied at 300 rpm, 600 rpm, 900 rpm and 1200 rpm at reaction temperatures of 150°C and 210°C. Based on the conversion trend obtained in Figure 2, there was no influence of reaction rate in stirring speed. At the reaction temperature of 150°C, the conversion of LA increased slightly from 88.5% up to 89% with the increase of stirring speed rate from 300 rpm to 1200 rpm. Similar trend was observed when the reaction was performed at reaction temperature of 210°C.

The conversion of LA was 93.4% at 300 rpm and not much increase when the stirring speed was varied up to 1200 rpm. This indicated that the effect of stirring speed rate on LA conversion was minimal and has no influence on reaction rate. Hence, the optimum stirring speed rate chosen was 300 rpm to ensure complete mixing.

Effect of Reaction Temperature

The effect of reaction temperature on the esterification was studied at 150°C, 170°C, 190°C, 210°C and 230°C. Other process parameters were fixed at molar ratio of LA/DEG of 2:1 and 300 rpm as shown in Figure 3. From the plots, it can be observed that the LA conversion increased with temperature. At lower temperature of 150°C, a minimal

conversion was obtained with 72% LA converted throughout 20 hr duration. After 22 hr reaction, the reaction reached equilibrium with a maximum LA conversion of approximately 74%. A slightly higher conversion was observed when performing the reaction at 170°C than that obtained at 150°C, with maximum conversion of 82%. At temperature of 190°C, the conversion of LA increased rapidly to more than 80% within 10 hr reaction and started to plateau after 12 hr reaction course.

Increasing the temperature to 230°C resulted in an apparent increased conversion in the beginning with maximum LA conversion of more than 90% and it approached a plateau after 4 hr reaction time as it reached equilibrium thereafter. Hence, 230°C was found to be the best temperature to perform the esterification due to the limitation of the boiling point of DEG reported at approximately 245°C in material safety data sheet (MSDS).

Effect of Reactants Molar Ratio

To study the effect of molar ratio of LA to DEG (LA:DEG) on product composition, three molar ratios were investigated, *i.e.* 1:1, 1:1.5 and 2:1. Figure 4 shows that as the molar ratio of LA to DEG was increased from 1:1 to 2:1, DEG-ML content decreased and DEG-DL content increased. At molar ratio of 1:1, a maximum percentage composition of DEG-ML obtained was 42.9% with DEG-DL content of 49.5%. After 20 hr reaction course, the compositions of DEG-ML and DEG-DL content were at constant due to no excess of DEG to forward the reaction.

AV determined was $8.5 \text{ mg KOH g}^{-1} \text{ LA}$ with conversion of LA was 93.4%. By excessing of DEG in the reaction, the molar ratio of LA:DEG was set at 1:1.5 resulted in the increase of DEG-DL content of 54.9% with traces amount of unreacted LA detected. Nevertheless, as the LA was fully consumed in the reaction, the excess of DEG content in the product mixture required further step of separation for DEG removal.

The autocatalytic esterification then was performed between two moles of LA reacted with a mole of DEG with the aim to increase the production DEG-DL at lowest AV. The other parameters

remained constant. Based on plot of the trend composition of the DEG-ML and DEG-DL as shown in Figure 5, LA was reacted further with DEG-ML to form the DEG-DL. The DEG-ML composition was reduced with the increment of DEG-DL content in the reaction mixture. The observation was also in accordance with the diminishing of DEG detected in the reaction product. The lowest AV measured was $3.09 \text{ mg KOH g}^{-1} \text{ LA}$ and OHV was $11.8 \text{ mg KOH g}^{-1} \text{ LA}$. A maximum composition of the mixtures of the DEG-ML and DEG-DL obtained were 0.78% and 97.2%, respectively. Therefore, the molar ratio of 2:1 was chosen as the optimum ratio.

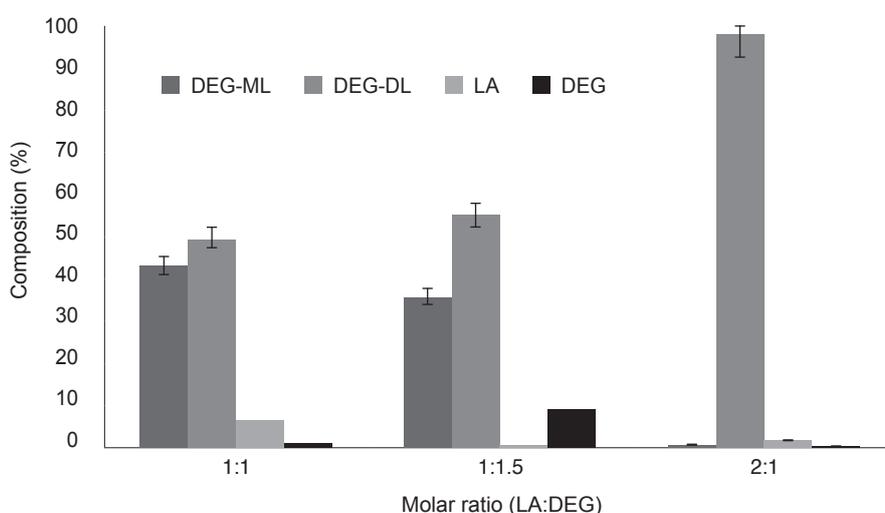


Figure 4. Effect of molar ratio (lauric acid: diethylene glycol) on diethylene glycol (DEG) monolaurate (DEG-ML) and DEG dilaurate (DEG-DL) compositions. Reaction conditions: 230°C , 1 atmospheric (atm), 300 rpm and duration of 20 hr.

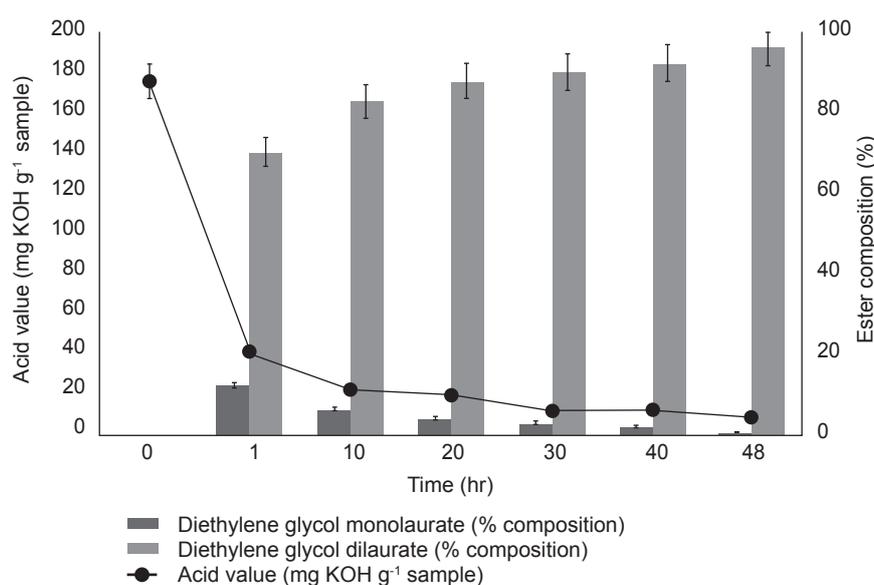


Figure 5. Acid value and product percentage composition profile for self-esterification of 2 moles of lauric acid (LA) and 1 mole of diethylene glycol (DEG) at temperature of 230°C for 48 hr reaction time.

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