

# SYNTHESIS OF DIMERATE ESTERS BY SOLVENT-FREE METHOD

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## ABSTRACT

Dimerate ester is normally used as lubricant base stock. Herein, we highlighted the preparation of several C<sub>36</sub> dimerate esters derived from C<sub>36</sub> dimer acid and medium chain length alcohols, i.e. 1-octanol, 1-hexanol and 2-ethylhexanol without the need for either solvent or catalyst but drying agent, 3Å molecular sieve (3Å MS) having acid value as low as 0.06 mg KOH g<sup>-1</sup> of sample. Optimisation of various reaction parameters such as temperature, molar ratio, reaction time and water removal set-up was also carried out. The most affecting factors in synthesising low acid value C<sub>36</sub> dimerate ester are reaction temperature and efficiency of water removal. The esterification was carried out under optimum conditions by refluxing at 200°C for 24 hr using 1:4.5 molar ratio of C<sub>36</sub> dimer acid/alcohol in the presence of 15% w/w of 3Å MS.

**Keywords:** C<sub>36</sub> dimer acid, C<sub>36</sub> dimerate ester, lubricant base stock, esterification, self-catalysed esterification, acid value.

**Date received:** 2 September 2016; **Sent for revision:** 6 September 2016; **Received in final form:** 18 October 2016; **Accepted:** 22 November 2016.

## INTRODUCTION

Dimer acids are commonly derived from unsaturated fatty acids mainly consist of oleic and linoleic acids such as tall oil and high oleic tallow (Elsasser and McCargar, 2001). Some dimer acids are produced from erucic acid, a monounsaturated omega-9 fatty acid of rapeseed oil (Morway *et al.*, 1954). Palm oil or so-called golden crop, that contains oleic acid as one of the major fatty acid (37.1%) as well as linoleic acid (8.1%) (Tan and Nehdi, 2012) can be used as a renewable feedstock for production of dimer acid. This dimer acid appeared as very viscous light yellow liquid and is widely used as raw material in the polymeric synthesis of fatty polyamides for

application as resins (Mohammad *et al.*, 2013) and hot melt adhesives (Ghasem, 2014). It is a useful polymer building block because they are able to impart the highly desirable properties of flexibility, elasticity and high impact strength to many polymer products. Besides polyamides, C<sub>36</sub> dimerate esters which commonly used as chain oils, 2T and 4T oils (Randles, 2006) can be derived by esterification of C<sub>36</sub> dimer acid and alcohol.

Dimerate esters generally have good thermal and oxidant stability which make them an excellent lubricant. Furthermore, the stability can be improved by hydrogenation of the double bonds. This diester is commonly used in two-stroke, predominantly in marine application as it provides low smoke properties and good biodegradability for spilled or combusted oil. The degree of biodegradability of esters are generally higher than corresponding hydrocarbons (Buenemann *et al.*, 2003). Several patents have been filed on the use of dimer esters for many non-polymer industrial chemicals such as synthetic lubricants (Henry and Tierney, 1962; Matuszak and Craven, 1958; Tierney, 1960) and lubricant additives (Rutkowski and Szykowski, 1976).

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Esterification is a commonly used synthetic reaction which require presence of acid catalyst either homo- or heterogeneous catalyst to drive the reaction forward. Mandake *et al.* (2013) showed the acceleration of reaction rate in the presence of 10% w/w of Amberlyst 15<sup>®</sup> which afforded 54% conversion in 3 hr in contrast to only 14% conversion for non-catalytic esterification of acetic acid and methanol (1:3 molar ratio) within the same period of time. Conventionally, the esterification reaction is carried out in the presence of homogeneous inorganic catalyst such as sulphuric (Kale *et al.*, 1991; Zeki *et al.*, 2010), sulphonic and hydrochloric acid. To date, this trend has shifted towards the use of heterogeneous catalysts due to their several advantages over homogeneous catalysts. Numerous studies had been carried out for esterification reaction catalysed by various types of solid catalysts such as ion-exchange resin, *i.e.* Amberlyst 15<sup>®</sup> (Kirbaslar *et al.*, 2001; Toor *et al.*, 2011) and Tulsion<sup>®</sup> (Patil and Kulkarni, 2014). Several studies on acid-catalysed preparation of C<sub>36</sub> dimerate with various short-chain alcohols (Burg and Kleiman, 1991; Kale *et al.*, 1991) and their applications have been reported in several publications and patents (Henry and Tierney, 1962; Tierney, 1960) which showed the importance of the dimerates as versatile products such as lubricants, lubricant additives, surface-active agents and corrosion and rust inhibitors. Kale *et al.* (1991) had previously described preparation of C<sub>36</sub> dimer ester in the presence of 1% (w/w) of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) in benzene as an azeotropic solvent. However, no studies of the spontaneous esterification of C<sub>36</sub> dimer acid have been reported. In the world of organic synthesis, greener methods of chemical synthesis is an attractive field of research. The concept of green chemistry is the design of chemical products and/or processes that reduce or eliminate the use or generation of hazardous substances. In this study, we emphasised several principles of green chemistry (Anastas and Warner, 1998) in the synthesis of C<sub>36</sub> dimerate ester using renewable feedstock under mild conditions without the need for either solvent or catalyst.

## MATERIALS AND METHODS

### Materials

Hydrogenated C<sub>36</sub> dimer acid was purchased from supplier of Sigma Aldrich. 1-Butanol and 1-octanol were purchased from Fischer Scientific (United Kingdom) while 2-propanol was purchased from Friendemann Schmidt and 3Å MS (powder form) was obtained from Sigma Aldrich. All of the reagents were used as supplied, without any purification and stored according to the manufacturer's recommendations

### Methods

**Acid value determination.** The acid value is defined as number of milligrams of potassium hydroxide (KOH) required to neutralise the fatty acids in 1 g of sample and was determined using MPOB Test Method c2.7. This method is applicable to all fatty acids and polymerised fatty acids (MPOB, 2005a).

The acid value is expressed as

$$\text{Acid value} = \left( \frac{56.1 \times V \times M}{m} \right) \text{mg KOH g}^{-1}$$

where,

*V* is the volume in millilitres (ml) of standard volumetric KOH used;

*M* is the exact concentration in mole per litre of the standard volumetric KOH solution used;

and

*m* is the mass in grams of the test portion.

For accuracy in the determination of acid value, the sample size used is varied, as recommended in MPOB Test Method p2.5 (Table 1).

Decrease in acid value is a good indicator of reaction progress for the reaction with C<sub>36</sub> dimer acids as the limiting reactant (Mohammad *et al.*, 2013).

**Infra-red (IR) spectroscopy.** Infrared spectra were recorded as neat samples using a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. All IR data were manipulated using Spectrum v6.3.5 software.

**Nuclear magnetic resonance (NMR) spectroscopy.** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in Fourier transform mode on a 400 MHz Bruker Avance III using the specified deuterated solvent. All spectra were processed using MestR-C Nova software. The chemical shift for both <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in ppm and were referenced to the residual solvent peak or TMS peak. Multiplicities in the NMR are described as: *s* = singlet, *d* = doublet, *t* = triplet, *td* = triplet of

TABLE 1. RECOMMENDED SAMPLE SIZE

Acidity (FFA)	Weight of sample (±10%), g	Weighing accuracy (± g)
0 to 1	20.0	0.05
1 to 4	10.0	0.02
4 to 15	2.5	0.01
15 to 75	0.5	0.001
75 and over	0.1	0.0002

Note: FFA - free fatty acid.

Source: MPOB (2005b).

doublets,  $q$  = quartet, sept. = septet,  $m$  = multiplet, br = broad, coupling constants,  $J$  values are reported in Hertz (Hz).

### General Procedure for Non-catalytic Esterification of $C_{36}$ Dimer Acid

Alcohol of 4.5 equiv was added into a single neck 500 ml round bottom flask containing hydrogenated  $C_{36}$  dimer acid (114.0 g, 0.2 mol) and 3Å MS (15% w/w, 17.2 g). This flask was then attached to a Dean-Stark apparatus and the mixture was subjected to heating at 200°C for 24 hr after which the reaction was ceased. The reaction was then cooled down to ambient temperature. The 3Å MS was filtered off and purification of the crude compound was carried out via vacuum distillation for the removal of excess of alcohol and remaining water molecule.

**Hydrogenated  $C_{36}$  dioctyl dimerate.** Prepared according to the general procedure for non-catalytic esterification of  $C_{36}$  dimer acid 1-octanol (142.2 ml, 0.9 mol). The product (Figure 1) was isolated as yellowish oil (143.0 g, 76%) and  $v_{\max}$  (neat)/ $\text{cm}^{-1}$  2925, 2856, 1797, 1470, 1977, 1250, 1170 and 1118;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.04 (t,  $J$  = 7.0 Hz, 4H), 2.27 (t,  $J$  = 7.2 Hz, 4H), 1.60 (br. s, 10H), 1.44 – 1.03 (m, 68H), 0.87 (t,  $J$  = 6.5 Hz, 14H).

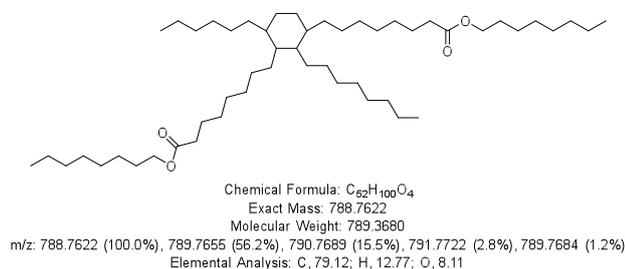


Figure 1. Structure of hydrogenated  $C_{36}$  dioctyl dimerate.

**Hydrogenated  $C_{36}$  di-(2-ethylhexyl) dimerate.** Prepared according to the general procedure from 2-ethylhexanol (0.9 mol, 141 ml). The product (Figure 2) was isolated as yellowish oil (151.9 g, 96%) and  $v_{\max}$  (neat)/ $\text{cm}^{-1}$  2925, 2856, 1797, 1470, 1977, 1250, 1170 and 1118;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.99 –

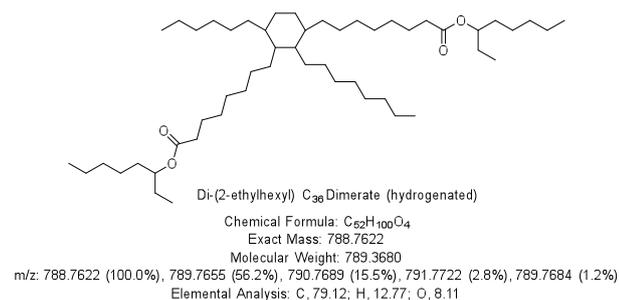


Figure 2. Structure of hydrogenated  $C_{36}$  di-(2-ethylhexyl) dimerate.

3.94 (m, 4H), 2.28 (t,  $J$  = 7.6 Hz, 4H), 1.60 – 1.52 (m, 10H), 1.44 – 1.03 (m, 68H), 0.89 – 0.81 (m, 14H).

**Hydrogenated  $C_{36}$  dihexyl dimerate.** Prepared according to the general procedure from 1-hexanol (0.9 mol, 141 ml). The product (Figure 3) was isolated as yellowish oil (124.7 g, 85%) and  $v_{\max}$  (neat)/ $\text{cm}^{-1}$  2925, 2856, 1797, 1470, 1977, 1250, 1170 and 1118;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.05 (t,  $J$  = 6.6 Hz, 4H), 2.28 (t,  $J$  = 7.6 Hz, 4H), 1.60 (br. s, 10H), 1.44 – 1.03 (m, 60H), 0.87 (m, 14H).

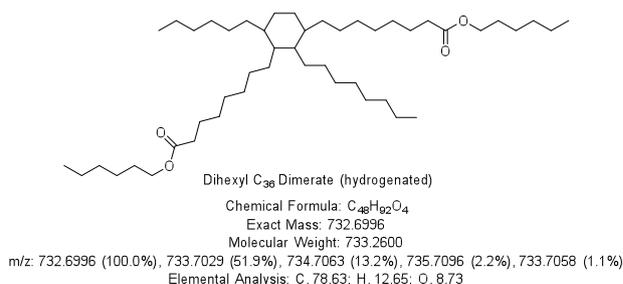


Figure 3. Structure of hydrogenated  $C_{36}$  dihexyl dimerate.

## RESULTS AND DISCUSSION

We aimed to prepare  $C_{36}$  dimerate having acid value less than 1.0 mg KOH  $\text{g}^{-1}$  of sample. Initially, we investigated the synthesis of  $C_{36}$  dimerate ester via esterification of  $C_{36}$  dimer acid with 1-octanol. The reaction was carried out by heating the reaction mixture up to 200°C in 1:4.5 mole ratio ( $C_{36}$  dimer acid/1-octanol), equipped with Dean-Stark apparatus producing the corresponding dioctyl dimerate. This preliminary study showed the capability of the  $C_{36}$  dimer acid to self-catalyse the esterification reaction.

The reaction parameters including temperature, molar ratio and reaction time in the absence of acid catalyst and organic solvent were optimised. Above all, the design of the experimental set-up was also investigated in order to efficiently remove water that would drive the esterification reaction to completion.

### Study of Reaction Conditions and Parameters

**Reaction temperature.** Effect of reaction temperature in the esterification of  $C_{36}$  dimer acid was studied by monitoring the acid value reduction; and four different reaction temperatures were investigated *i.e.* 130°C, 150°C, 170°C and 200°C. As can be seen in Figure 4, the reaction carried out at 200°C gave the fastest rate and the lowest acid value throughout the reaction. In the first hour, reactions at all temperature gave nearly similar reaction rate but at 200°C, the acid number decreased to 54 mg KOH  $\text{g}^{-1}$  of sample, more than 75% reduction from initial acid value of 200 mg KOH  $\text{g}^{-1}$  of sample. After 7 hr of reaction, the

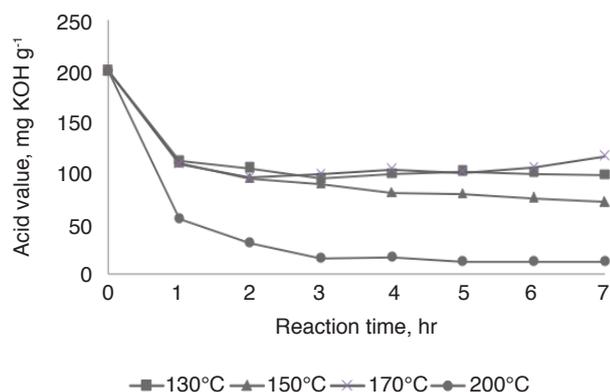


Figure 4. Effect of reaction temperature on acid value at 1:2 ratio of  $C_{36}$  dimer acid/1-octanol.

acid value went down to 12 mg KOH  $g^{-1}$  of sample while reaction at temperature 130°C, 150°C, and 170°C gave end products with acid value of 116, 97, and 71 mg KOH  $g^{-1}$  of sample, respectively.

The maximum temperature for this reaction was set no more than 200°C due to the boiling point of 1-octanol *i.e.* 195°C as it was reported that higher amount of heat would be released at higher reaction temperature which may lead to runaway reaction (Syed *et al.*, 2010). Several studies on esterification of acetic acid with different alcohols showed that the reaction can be accelerated forward with the increment of temperature (Kirbaslar *et al.*, 2001; Mandake *et al.*, 2013; Toor *et al.*, 2011; Zeki *et al.*, 2010), which is an indication of absence of mass transfer effect and this is in accordance with our results.

**Molar ratio and reaction time.** Stoichiometrically, two moles of 1-octanol is required to react on both ends of the  $C_{36}$  dimer acid. Thus, initial reaction was conducted using 1:2 mole ratio of  $C_{36}$  dimer acid/1-octanol. However, the acid value obtained from the reaction was 17.32 mg KOH  $g^{-1}$  of sample after 8 hr, while the desired acid value of the ester product should be less than 1.0 mg KOH  $g^{-1}$  of sample. The reactions were then carried out by increasing the number of mole of 1-octanol used in the reaction ( $C_{36}$  dimer acid/1-octanol); 1:2.2, 1:2.6, 1:3.3 and 1:4.5. After 8 hr of reaction, the acid values obtained were 11.06, 11.40, 10.68, and 6.93 mg KOH  $g^{-1}$  of sample, respectively as illustrated in Figure 5.

The acid value obtained was the lowest in the reaction using 1:4.5 mole ratio of  $C_{36}$  dimer acid/1-octanol, *i.e.* 6.39 mg KOH  $g^{-1}$  of sample. Hence, we decided to use this ratio as the optimum mole ratio for our subsequent reactions.

Increasing the mole ratio of 1-octanol with respect to  $C_{36}$  dimer acid is unfavourable as this may reduce the reaction rate gradually as reported by Kale *et al.* (1991) as the mole ratio of  $C_{36}$  dimer acid to 2-propanol changed from 1:5 to 1:10 and further increment of alcohol used may cause excess

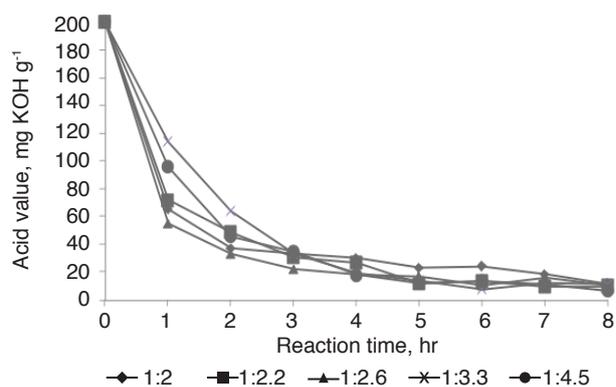


Figure 5. Acid value profile at different mole ratio of  $C_{36}$  dimer acid/1-octanol at 200°C.

dilution of the reaction mixture. All the reactions (having different molar ratios of  $C_{36}$  dimer acid to octanol) were then prolonged to 40 hr and the acid values were tabulated (Table 2). As expected, for all entries, the acid value decreased as the reaction time was extended.

TABLE 2. EFFECT OF DIFFERENT MOLE RATIO OF  $C_{36}$  DIMER ACID/1-OCTANOL ON THE ACID VALUE

Entry	Molar ratio of $C_{36}$ dimer acid/1-octanol	Acid value (mg KOH $g^{-1}$ )	
		8 hr	40 hr
1	1:2.0	17.32	8.40
2	1:2.2	11.06	6.83
3	1:2.6	11.40	6.53
4	1:3.3	10.68	6.96
5	1:4.5	6.93	5.95

**Effect of water in the reaction.** In the esterification reaction, the presence of water due to its occurrence in the raw material and as a side product of esterification can reverse the reaction. Therefore, the removal of water is very crucial for this reaction to bring the reaction forward and thus, obtain high yield of product.

Effect of water on moisture sensitive reaction has been reported in several studies (Elsasser and McCargar, 2001; Ma *et al.*, 1998; Park *et al.*, 2010; Tran *et al.*, 2013). Park *et al.* (2010) reported that in the esterification of oleic acid of soyabean, initial water content as low as 1% of oil is sufficient to accelerate the inverse reaction. In addition, catalyst activity (for example Amberlyst 15®) gradually decreased due to catalyst poisoning and poor accessibility of reactants to acid sites in the presence of water. In transesterification of beef tallow and methanol (MeOH) catalysed by sodium hydroxide (NaOH), water content above 0.06% will significantly reduce the fatty acid methyl esters (FAME) produced (Ma *et al.*, 1998).

In the attempt to efficiently remove water during the reaction including the use of Dean-Stark apparatus, 3Å MS addition into the reaction mixture – under the optimum reaction conditions shall be discussed.

#### a) Dean-Stark apparatus

In this study, the use of Dean-Stark has been proven to significantly improve the efficiency of the reaction as monitored by the reduction of acid value. This is accompanied by several other factors such as experimental set-up design, suitable flask size for amount of starting materials (reactants), and proper heat distribution to ensure efficient water removal.

In the initial design of the experimental set-up, the Dean-Stark apparatus was attached to Claisen adapter and three-neck round bottom flask in which the other two necks were used to fit in the thermometer adapter and nitrogen (N<sub>2</sub>) gas inlet. The reaction was carried out under optimum conditions: temperature of 200°C, 1:4.5 molar ratio (C<sub>36</sub> dimer acid/1-octanol) in 24 hr. This reaction set-up, however, did not give the best results probably due to inefficient water removal.

On the basis of reducing the numbers of adapters/connectors used, the Dean-Stark apparatus was then directly attached to the flask. The single-neck flask also helped to avoid water accumulation at the side ports. With the same reaction conditions, the acid value was further reduced using this set-up.

Table 3 showed the acid values obtained under optimum conditions but at various reaction times for the two Dean-Stark set-ups. The second set-up managed to reduce the acid value to 2.37 mg KOH g<sup>-1</sup> on 24 hr compared to 5.95 mg KOH g<sup>-1</sup> for the initial set-up even after 40 hr reaction.

TABLE 3. ACID VALUE OF DIFFERENT REACTION SET-UP

Reaction set-up	Acid value (mg KOH g <sup>-1</sup> of sample)		
	8 hr	24 hr	40 hr
Initial	6.93	-	5.95
Final	6.39	2.37	-

#### b) Addition of 3Å MS

Molecular sieves are considered as a general-purpose drying agent in both polar and non-polar media. Molecular sieves have been shown to remove water, alcohols (including methanol and ethanol), and hydrochloric acid from such systems as ketimine and enamine syntheses, ester condensations, and the conversion of unsaturated aldehydes to polyenals (Aldrich, 2015).

The purpose of adding 3Å MS into the reaction was to absorb the remaining water molecule in the

reaction mixture. Under the optimal conditions, using 100 ml round bottom flask the amount of 3Å MS loaded into the reaction mixture up to 4.4% w/w affording dioctyl dimerate with acid value of 0.75 mg KOH g<sup>-1</sup> of sample (Table 4). However, when the reaction was up-scaled using 500 ml flask, 15% w/w 3Å MS was required to obtain acid value below 1.0 mg KOH g<sup>-1</sup>.

TABLE 4. EFFECT OF 3Å MOLCULAR SIEVES ADDITION. REAGENTS AND CONDITIONS: 200°C, 24 hr, DEAN-STARK APPARATUS, C<sub>36</sub> DIMER ACID/1-OCTANOL (1:4.5)

Entry	No. of mole of C <sub>36</sub> dimer acid	Size of flask (ml)	Molecular sieves (% w/w)	Acid value (mg KOH g <sup>-1</sup> )
1	0.04	100	-	2.37
2	0.04	100	2.2	1.49
3	0.04	100	4.4	0.75
4	0.20	500	4.4	1.36
5	0.20	500	10.0	1.04
6	0.20	500	15.0	0.54

#### Self-catalysed Esterification of C<sub>36</sub> Dimer Acid with Different Chain of Alcohols

The standard acid-catalysed reaction involves reversible protonation at the carbonyl oxygen followed by the rate-limiting attack of the alcohol upon the protonated carboxylic acid intermediate (Figure 6) (Maskill, 1990).

Profiling the reaction between C<sub>36</sub> dimer acid and 1-octanol has demonstrated esterification of C<sub>36</sub> dimer acid to generate the corresponding mono- and diester product seemingly took place relatively fast. At 4 hr mark, the C<sub>36</sub> dimer acid was fully consumed producing both mono- and diester in a nearly equal amount. In the presence of excess of 1-octanol, the monoesters further react to yield the corresponding diester (Figure 7).

This finding is really unanticipated as the reaction conditions in which we carried out the esterification reaction was really mild and without the presence of any organic solvent or catalyst. High reaction temperature is probably the main factor contributing to 100% conversion of C<sub>36</sub> dimer acid within 4 hr of reaction. At 200°C, water molecules present in the reaction mixture can be removed by evaporation into the Dean-Stark apparatus.

Previously, several non-catalytic esterification of methanol with monocarboxylic acid such as acetic acid (Mandake *et al.*, 2013; Pöpken *et al.*, 2000) and lactic acid (Sanz *et al.*, 2002) had been reported, in which the esterification was found to be catalysed by H<sup>+</sup> generated by the carboxylic acid itself.

According to Ashworth *et al.* (2012), theoretically, self-catalysed esterification will depend upon both on the esterification rate constant and the acid

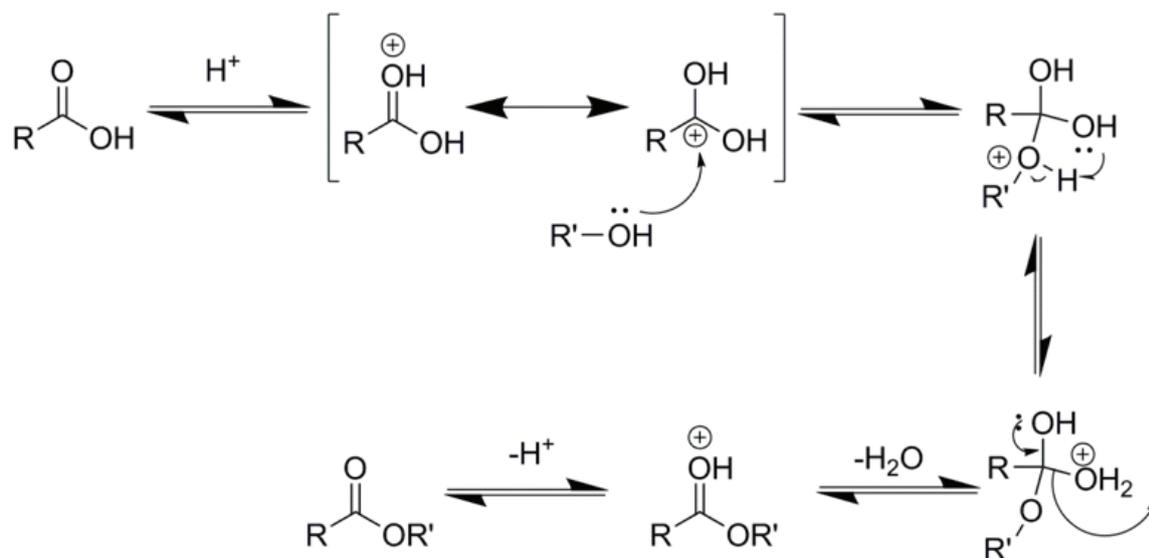


Figure 6. Mechanism of acid-catalysed esterification of carboxylic acids.

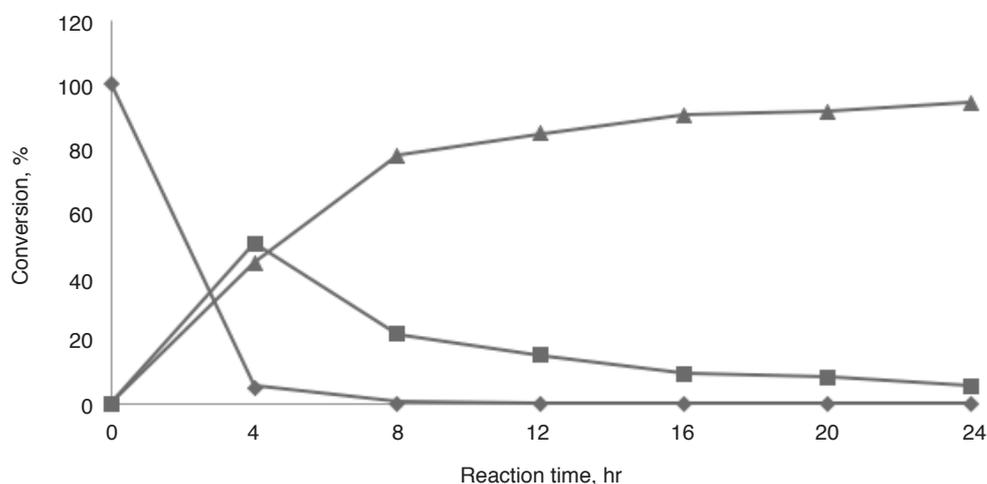


Figure 7. Time course vs. formation. Reagents and conditions: 200°C, C<sub>36</sub> dimer acid/1-octanol – 1:4.5, 24 hr.

dissociation constant,  $K_a$ . In relative to the acidity of the maleic acid in methanol, carboxylic acid with similar or higher acidity will be more likely to self-catalyse following one-and-a-half-order rate law.

Esterification of C<sub>36</sub> dimer acid in 1-octanol is occurring due to dissociation of the dicarboxylic acid producing H<sup>+</sup> to self-catalyse the reaction. This is assisted by efficient removal of water molecule to drive the reaction to completion.

Self-catalysed (or sometimes known as auto-catalysed) esterification is also common in the synthesis of polyester. Polyesters are polymers synthesised from dicarboxylic acid and diol. One of the most common examples of polyester is polyethylene terephthalate (PET), derived from terephthalic acid and ethylene glycol. In the formation of polyester, the diacid monomer acts as its own catalyst for the esterification reaction. A comprehensive discussion on the kinetic studies

of the self-catalysed polyester formation had been published in several books (Chanda, 2006; Duda and Penczek, 2005; Mandal, 2013).

As we accomplished the optimisation of reaction conditions for esterification of C<sub>36</sub> dimer acid and 1-octanol followed by purification, we then applied these conditions and methods on esterification of several other alcohols, *i.e.* 1-hexanol, 2-ethyl-1-hexanol and 1-butanol. Very high acid value for dibutyl dimerate was obtained due to the incomplete conversion of C<sub>36</sub> dimer acid (Table 5) which further confirmed by IR spectrum analysis.

#### Product Purification via Vacuum Distillation

It was determined that the crude product contained 1-octanol, which is used in excess in the reaction by the presence of broad –OH peak according to IR spectrum. Due to high boiling point

TABLE 5. ACID VALUE OF C<sub>36</sub> DIMERATE ESTERS

Alcohols	Acid value, mg KOH g <sup>-1</sup>
1-Octanol	0.54
1-Hexanol	0.06
2-Ethyl-1-hexanol	1.65
1-Butanol	30.10

of 1-octanol, *i.e.* 195°C, the removal of the starting material using simple distillation is not preferable. Hence, the purification of the crude product was carried out via distillation under reduced pressure. A vacuum distillation is used to distill the compound or the solvent off when the boiling point is too high (more than 150°C) without significant decomposition.

The mixture was first heated up to desired temperature, *i.e.* 120°C and the vacuum pump was then started and the pressure was controlled manually and reduced down as low as 6.7 × 10<sup>-2</sup> mbar. The reduction of pressure should be carried out cautiously in order to avoid the product drawn into the receiving flask.

Referring to IR spectra analysis, complete removal of 1-octanol was confirmed by the absence of broad peak of –OH between 3200 – 3600 cm<sup>-1</sup> and C–O peak at 1058 cm<sup>-1</sup> and strong peak of C=O stretching of carboxylic acid at 1707 cm<sup>-1</sup> (refer to Figure 8, red line). The formation of C<sub>36</sub> dimerate ester is further confirmed using NMR analysis.

It was also determined that the compound contained carbonyl groups of ester from the peak at 1737 cm<sup>-1</sup>. The carbonyl stretching of the ester carbonyl group in the C<sub>36</sub> dimerate ester is observed

at slightly higher frequency than carbonyl of carboxylic acid. The complimentary peaks of C–O stretches of the esters appeared at 1244, 1169, and 1118 cm<sup>-1</sup>.

The formation of the dioctyl dimerate can be further confirmed using NMR spectroscopic analysis (Figure 9). The appearance of triplet peak at 4.04 ppm with coupling constant of 7.0 Hz shows the presence of ester.

The IR spectra of three other dimerate esters synthesised, *i.e.* dihexyl dimerate, di-(2-ethylhexyl) dimerate, and dibutyl dimerate have similar absorption showing presence of carbonyl group of ester at 1737 cm<sup>-1</sup> (Figure 10). However, in the product of dibutyl dimerate, the presence of C<sub>36</sub> dimer acid is shown with the absorption at 1710 cm<sup>-1</sup>. This result is an indicator of incomplete conversion of C<sub>36</sub> dimer acid into dibutyl dimerate.

Under the optimised reaction conditions, high reaction temperature, *i.e.* 200°C is probably not suitable for esterification of C<sub>36</sub> dimer acid and 1-butanol as 1-butanol has much lower boiling point, at 117.7°C. Hence, 1-butanol evaporates easily under this reaction conditions. In other word, the optimised reaction conditions we emphasised for esterification of C<sub>36</sub> dimer acid and 1-octanol is not appropriate for alcohol with low boiling point.

### CONCLUSION

The C<sub>36</sub> dimerate ester with acid value below 1.0 mg KOH g<sup>-1</sup> of sample has been successfully synthesised under optimum conditions of at 200°C for 24 hr using 1:4.5 molar ratio of C<sub>36</sub> dimer acid/

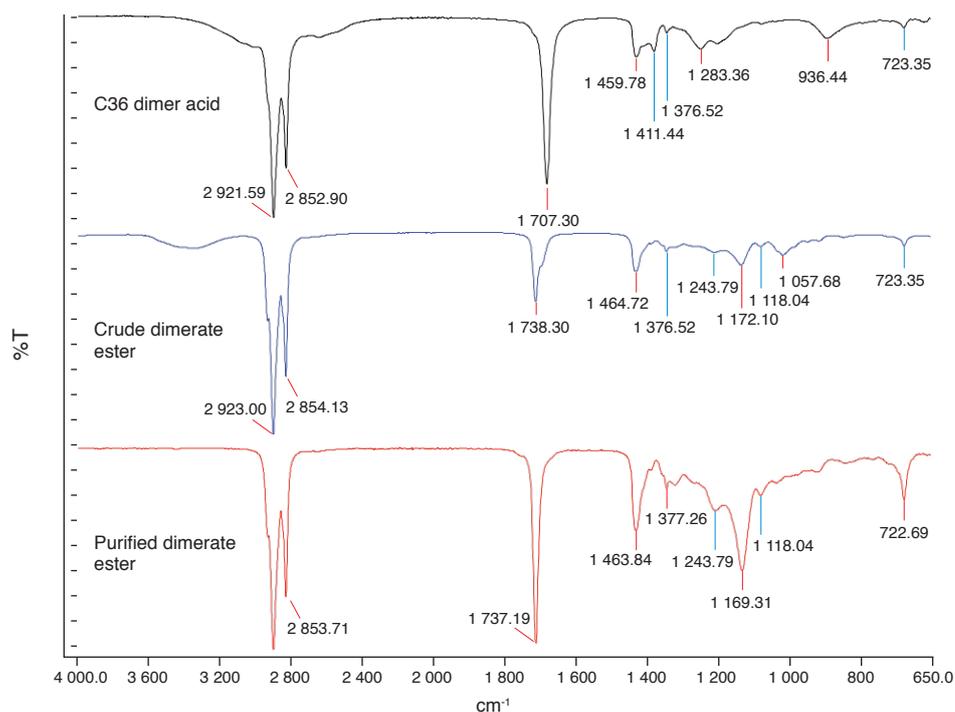


Figure 8. Infra-red spectra comparison of starting material, crude and purified dioctyl dimerate.

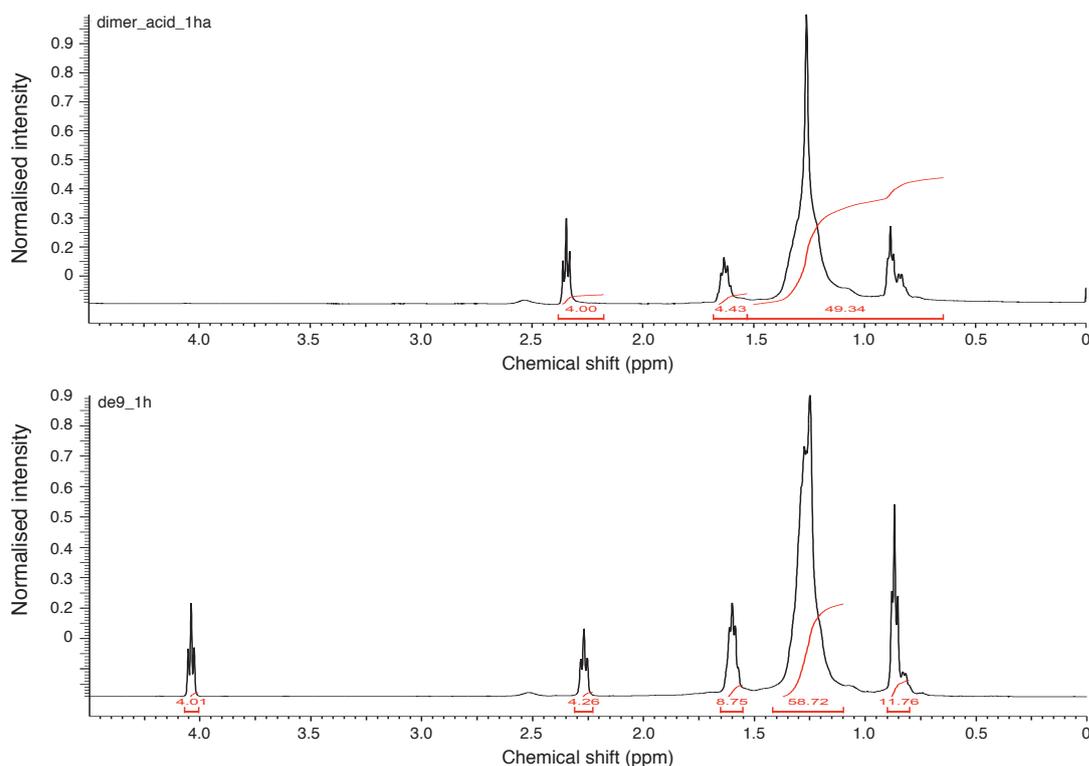


Figure 9. Nuclear magnetic resonance (NMR) spectra of hydrogenated C<sub>36</sub> dimer acid (a) and the corresponding product, dioctyl dimerate (b).

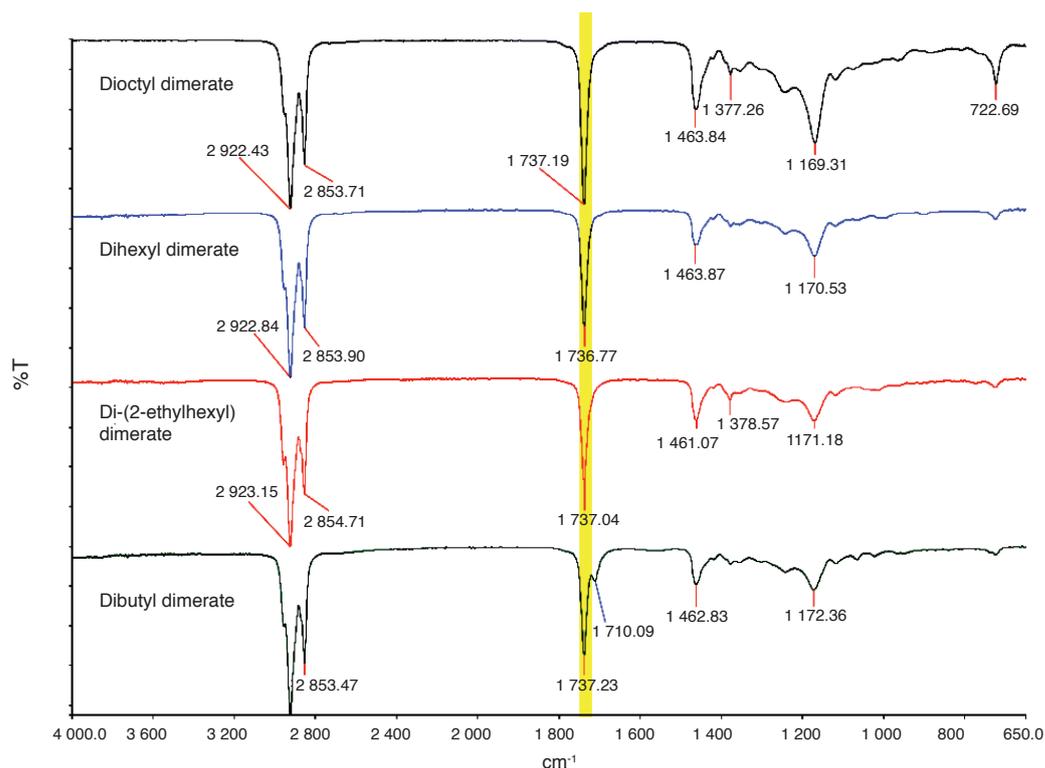


Figure 10. Infra-red overlay of synthesised C<sub>36</sub> dimerate esters.

alcohol. The synthesis was achieved without using any solvent or catalyst but drying agent, 3Å MS (15% w/w). Furthermore, the feedstock is from renewable resource. Hence, green chemistry has been applied successfully as the synthesis process including purification eliminated the release of any chemical waste to air, water and land.

#### ACKNOWLEDGMENT

The authors would like to thank MPOB for the financial support provided throughout the research. The technical assistance provided by Zuraidah Kamarudin and Selasih Abdullah for the synthesis of C<sub>36</sub> dimerate ester and analysis works is greatly

appreciated. We would also like to thank Rosnah Ismail, Senior Research Fellow for her guidance and advice in writing the article.

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