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SYNTHESIS OF GLYCEROL TRILEVULINATE ESTER: EFFECT OF REACTION PARAMETERS

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ABSTRACT

Derivatisation of glycerol (Gly) with levulinic acid (LA) to produce glycerol trilevulinate (Gt-LE) was studied. The reaction parameters affecting synthesis of Gt-LE were investigated. Catalytic and non-catalytic reactions between Gly and LA were carried out. Effects of reaction time and temperature on non-catalytic reaction were observed. Conversely, for catalysed reaction, reaction parameters studied were type of catalyst, mole ratio, catalyst loading and reaction time. Result analysis indicated that for the catalyst-free reaction, increment of reaction time and temperature will further reduce the acid value of reaction product. On the other hand, for catalytic reaction, p-*TsOH accelerated the reaction much faster than montmorillonite, Amberlyst-15 or Amberlyst-46. Result analysis also showed that the best mole ratio and catalyst loading to obtain high composition of Gt-LE without having to go through cumbersome purifying process was 1:6 with 8% catalyst loading. For reaction conducted with mole ratio of 1:6 (Gly:LA), the optimum reaction time and temperature was found to be 8 hr and 140°C, respectively, in which GC analysis showed that product contained about 84.5% of Gt-LE.*

Keywords: glycerol, levulinic acid, biodiesel by-product, levulinate ester.

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INTRODUCTION

Most of the carbon-based compounds currently manufactured by the chemical industry are derived from petroleum. The rising cost and dwindling supply of mineral oil has prompted researchers worldwide to divert attention to possible routes in making chemicals, fuels, and solvents from biomass. The situation also initiated an array of research efforts in converting glycerol (Gly) to value-added platform molecules such as glycerol carbonate, 1,3-propanediol, epichlorohydrin, acrolein and few other chemicals (Kenar, 2007).

Currently, Malaysia is the second largest producer of palm oil in the world, which accounted for 40% of total global demand for crude palm oil (CPO) and this strategically position the nation as a significant player in the global dynamics of biodiesel production (Lam *et al*., 2009). The global biodiesel production in 2017 was 35.19 million tonnes and 30.6% was palm biodiesel (Kushairi *et al*., 2018). In Malaysia, 720 410 t of palm biodiesel were produced in 2016 of which 235 291 t were exported mainly to the European Union (EU), 358 586 t were used for local B7 blending and the remaining 126 533 t were used as oleochemicals (Unnithan, 2018; Kushairi *et al*., 2018).

Glycerol is the major by-product of biodiesel production. One tonne of biodiesel yields about 110 kg of crude glycerol or about 100 kg of

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pure glycerol. Finding new uses of glycerol besides the typical consumptions is one of the crucial steps to be taken in order to ensure the sustainability and continuance of the biodiesel industry.

The palm oil industry generates a large quantity of oil palm biomass. It was estimated that 67.69 million tonnes of palm oil mill effluent (POME) and 22.22 million tonnes of empty fruit bunches (EFB) were generated in 2017 (Kushairi *et al.*, 2018). Levulinic acid (LA) is another value-added chemical that can be obtained from lignocellulosic biomass. LA and its derivatives have been used as building blocks for the preparation of many types of new compound that includes levulinate esters, α-valerolactone, acrylic acid, 1,4-pentanediol, β-acetylacrylic acid, α-angelica lactone, 2-methyl THF, and δ-amino levulinic acid (Bozell *et al.*, 2000; Rackemann and Doherty, 2011; Girisuta and Heeres, 2017). These new compounds found uses in many applications such as in biofuel, polymers and plasticisers. Besides that several researchers have reported on extraction of LA from oil palm biomass such as from frond (Khan *et al.*, 2018), empty fruit bunch (Ramli and Amin, 2014) and mesocarp fibre (Tiong *et al.*, 2018). Gly and LA have been known as top value-added chemicals from biomass by scientists (Werpy *et al.*, 2004).

LA and its derivatives have been used as building blocks for the preparation of many types of polymers. The LA derivatives include levulinate esters, c-valerolactone, acrylic acid, 1,4-pentanediol, β-acetylacrylic acid, α-angelica lactone, and 2-methyl THF (Girisuta and Heeres, 2017).

Reaction between Gly and LA has been reported by several researchers recently to give several types of structures with different targeted usage. As an example, Bloom (2007) has reported on synthesis of glycerol trilevulinate (Gt-LE) as part of the content of patent US 2010/0216915 A1. His study revealed that Gt-LE has a potential to be used as plasticiser and coalescent solvents in polymer compositions. In the patent, comparative data shows that paint formulations containing Gt-LE have improved resistance to scrub (resistance towards abrasion caused by a brush, sponge, or other means) (ASTM, 2017), block (the condition wherein coated surfaces adhere to each other (ASTM, 2016) and freeze-thaw. Other than forming Gt-LE, the reaction between Gly and LA can form oligo (levulinic acid-co-glycerol) by using acid catalyst as described by (Amarasekara and Hawkins, 2011). These levulinic acid-glycerol oligomers may possess three types of terminal units: keto, glycerol-ketal, and glycerol-ester in the form of linear oligomers (*Figure 1*). These oligomers were reported to be useful as a plasticiser, and as a raw material for block co-polyester synthesis.

This present work focuses on the esterification of glycerol with LA to produce Gt-LE. This compound ideally will have three ketone (tri-ketones) and three ester functionalities (*Figure 2*).

Triketones derivatives also have long been known for their extensive application as biologically active substances. For instance, nitisinone and sethoxydim (*Figure 3*) has been used as a therapeutic agent for the treatment of tyrosinaemia (Lindstedt *et al.*, 1992). Other than that, triketone derivatives such as sulcotrione and mesotrione (*Figure 3b*) are examples of commercial triketones that found uses as bleaching herbicide. The bleaching herbicide is used to impede essential compound that promote formation of crucial biochemical that is important in normal growth of plant (Da-Wei *et al.*, 2015).

Thus, comprehending the synthesis process and structural development of this multipurpose compound can be considered crucial for further developments of this important versatile molecule. Development of this molecule also indirectly will catalyse the expansion of oleochemical industry, where oleochemical industry serves as the backbone of many end-market industries such as agriculture, automotive, construction, household

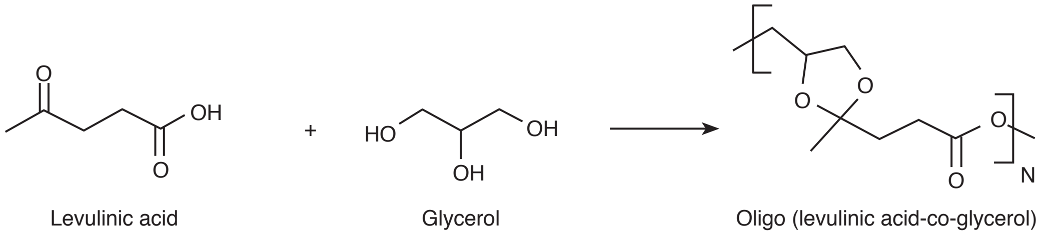


Figure 1. Synthesis of oligo (levulinic acid-co-glycerol).

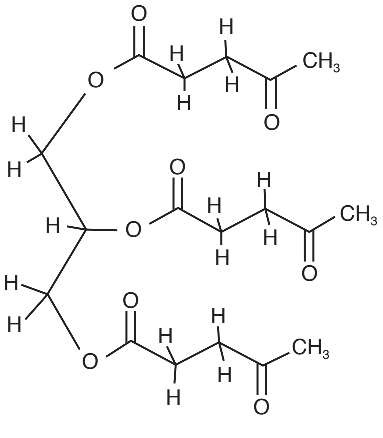
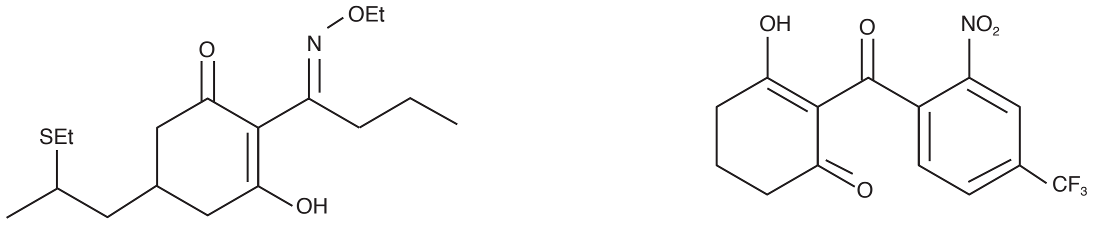


Figure 2. Structure of Gt-LE of glycerol and levulinic acid.



Sethoxydim Nitisinone

Figure 3a. Structure of sethoxydim and nitisinone.

Sulcotrione Mesotrione

Figure 3b. Structure of sulcotrione and mesotrione.

and consumer products (Kushairi *et al.*, 2017). Therefore, the objective of this article is to report the reaction parameters affecting the synthesis of Gt-LE from Gly and LA.

MATERIALS AND METHODS

Materials

Refined Gly (99.8% purity) was obtained from Fluka, USA. LA and *p*-toluene sulphonic acid (*p*-TsOH) were obtained from Sigma Aldrich, USA. Montmorillonite was purchased from Merck, Germany. All the reagents were used without further purification.

Methods

Synthesis of Gt-LE ester. Reactions were carried out in 250 ml two-necked round bottom flask equipped with a magnetic stirrer, a Dean and Stark apparatus attached to a condenser to trap and monitor water discharged from the reaction. Gly, LA, catalyst and toluene were placed in the flask and heated to the desired temperature. For catalyst-free reaction, only the raw material and solvent were used. An oil bath equipped with thermometer was used to maintain the reaction temperature. The amount of reagents was calculated according to the desired molar ratio for each reaction. The reaction was monitored through acid value and thin-layer chromatography analysis. After the reaction was completed, the crude product was analysed using gas chromatography (GC), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

Purification of crude Gt-LE. After the reaction was completed, the sample was washed with saturated sodium carbonate in order to neutralise the acid catalyst. This was followed by addition of toluene to extract Gt-LE and addition of water to remove unreacted Gly and LA. These steps were repeated several times in a separating funnel. After the washing steps were completed, the non-aqueous layer was concentrated under vacuum using rotor-evaporator to obtain the highest possible purity of Gt-LE.

Analysis and Characterisation of Gt-LE Ester

FTIR. A convenient analytical method for determining the functional groups of the Gt-LE was conducted using Spectrum 100 FT-IR Spectrometer Perkin Elmer. Samples were scanned between 4000-650 cm^{-1} wave numbers.

GC analysis. Quantitative analysis of the reaction mixture was conducted using GC. The GC (Agilent System 6890N Network GC System) was equipped with a ZB-5HT INFERNO (30 m x 250 μm x 0.2 μm) capillary column and flame ionisation detector. The following temperature programming was used:

oven temperature, 80°C; initial temperature, 80°C; heating rate at 10°C min^{-1}; final temperature, 315°C; injector temperature, 300°C; detector temperature, 325°C; carrier gas, helium at 40.0 ml min^{-1}. The composition of products was determined according to the percent area under the respective peak in the GC chromatogram.

^{1}H and ^{13}C NMR analysis. Proton (^{1}H) and carbon (^{13}C) NMR spectroscopy were recorded on JOEL JNM-ECZ600R at 600 MHz and 150 MHz respectively at 298 K with approximately 10% w/v solutions in deuterated NMR solvents. Chemical shifts are quoted in ppm relative to internal standard tetramethylsilane (TMS) and reference to the residual solvent. All coupling constant are quoted in hertz (Hz). The ^{1}H and ^{13}C NMR assignments were routinely confirmed by ^{1}H-^{1}H (COSY) and ^{1}H-^{13}C (HMQC) data.

Acid value determination. Acid value (AV) of Gt-LE was analysed according to the AOCS Official Methods and Recommended Practices of the American Oil Chemists' Society, Acid Value (Te 1a-64).

RESULTS AND DISCUSSION

Catalyst Free Reaction: Prescreening of Reaction Time and Temperature

Results in *Figure 4* revealed that the AV decreased as the reaction temperature increased as predicted. AV also decreased as the reaction time increased for all reaction temperature studied. In general, as reported by Dange and Rathod (2017), weak catalytic activity requires high reaction temperatures and long reaction time; result from this theory also can be implemented to the catalyst-free reaction. Other than that, as predicted and in parallel with findings in referred literatures, this result demonstrated that the reaction rate increased with the increment of reaction temperature and time, therefore will increase the rate of glycerol-ester of LA formation (Ashworth *et al.*, 2012; Go *et al.*, 2014). *Table 1* shows the composition of glycerol mono-levulinate ester (Gm-LE), glycerol di-levulinate ester (Gd-LE) and Gly tri-levulinate ester (Gt-LE) in the reaction products as analysed by GC. The results showed that, the percent composition of Gm-LE, Gd-LE and Gt-LE were higher when the reaction temperature was increased. For reaction conducted at 180°C, the composition of Gm-LE, Gd-LE and Gt-LE did not show any increment as compared to reaction conducted at lower temperature. Formation of compound with larger molecular weight was observed for reaction conducted at 180°C. For study at 180°C, the reaction was terminated at 32 hr because beyond that time the reaction product charred. Studies on catalyst-free reactions revealed that the esterification reaction between Gly and LA to obtain high composition of Gt-LE is affected by reaction time and temperature, which determine the cost effectiveness of the process. Several studies on non-catalytic esterification reactions (Ashworth *et al.*, 2012; Sanz *et al.*, 2002; Pöpken *et al.*, 2000) showed that self-catalysed esterification of short chain mono-carboxylic acid such as maleic acid, lactic acid and acetic acid with methanol was found to be catalysed by proton ion (H^{+}) generated by the ionisation of the corresponding acid.

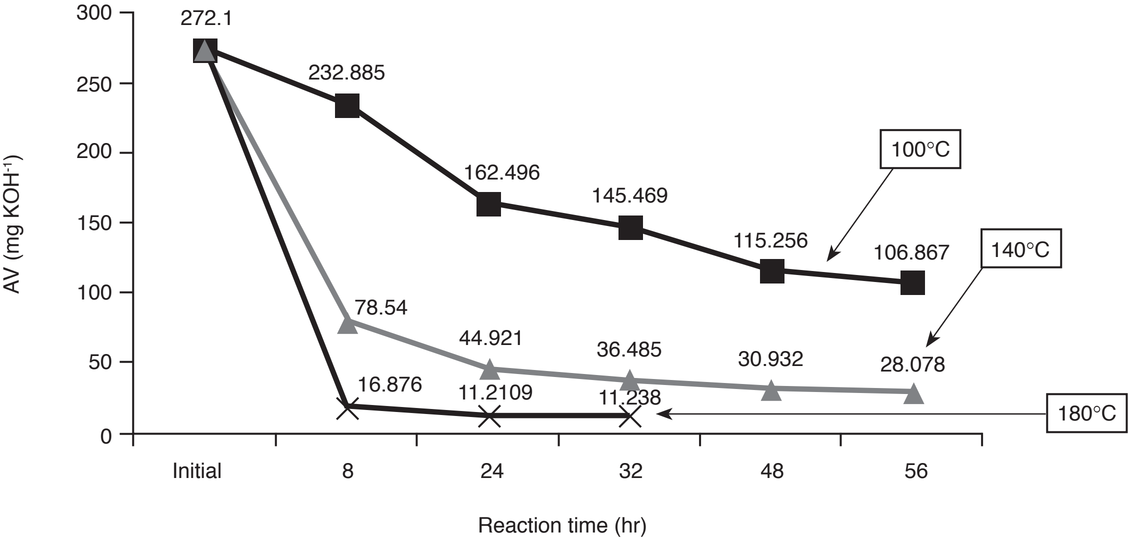


Figure 4. Acid value of the samples at 8, 24, 32, 48 and 56 hr of reaction for each stated reaction temperature. The duration of reaction was kept at 56 hr except for reaction which was conducted at 180°C which was terminated at 32 hr.

TABLE 1. OPTIMISATION OF CATALYST-FREE REACTION: EFFECT OF REACTION TEMPERATURE

Retention time (min)	Area% (reaction at 8 hr)			Remarks
	100°C	140°C	180°C	
12-13	35.9	25.62	19.13	Gm-LE
17-18	13.26	21.62	22.04	Gd-LE
21	6.24	15.9	20.8	Gt-LE
Total ester	55.4	63.14	61.97	-
24 & 29	2.46	13.51	24.17	Larger molecular weight compound

Note: Gm-LE - glycerol mono-levulinate.
Gd-LE - glycerol di-levulinate.
Gt-LE - glycerol tri-levulinate.

Catalysed Reaction

Effects of catalyst compound. In this study, four different acid catalysts (*p*-TsOH, amberlyst A-46, amberlyst A-15, and montmorillonite) were used. *Table 2* shows the AV of product and amount of water collected at the end of reaction for each catalyst. The results revealed that *p*-TsOH was the best catalyst for the reaction followed by Amberlyst-15, Amberlyst-46 and montmorillonite. Lowest AV and highest water collected in Dean Stark apparatus was obtained when *p*-TsOH was used as catalyst. The *p*-TsOH, a heterogeneous catalyst, has showed better catalytic activity. This result finding is in agreement with a study reported by Mohammed and Jabbar (2015), their study disclosed that homogeneous catalyst gave better performance than heterogeneous catalyst in esterification reaction of alcohol such as methanol with fatty acid with lower catalyst loading needed and higher product obtained. Other than that, generally homogeneous catalyst gave higher conversion than heterogeneous catalyst. This may be due to better contact between reactants and homogeneous catalyst in the entire volume of reaction, while for heterogeneous catalyst, the reactants have limited contact on the active sites only (Mohammed and Jabbar, 2015). Therefore, *p*-TsOH will be used for the next study.

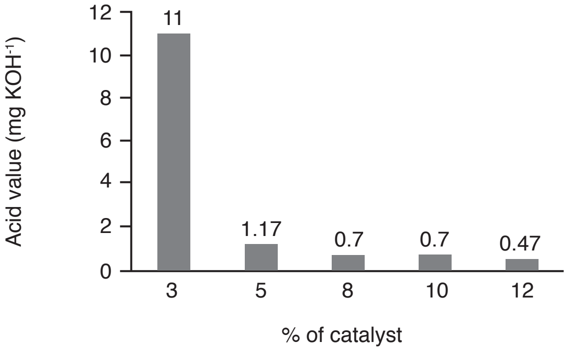
TABLE 2. ACID VALUE (AV) OF PRODUCT AND AMOUNT OF WATER COLLECTED FOR EACH CATALYST

Type of catalyst	Final AV mg (KOH g^{-1})	Amount of water collected (theoretical amount = 5.4 ml)
Amberlyst A-46	28.11	4.7
Amberlyst A-15	12.03	5
p-TsOH	1.98	5.3
Montmorillonite	156.39	3.5

Note: All experiments were carried out at 140°C for 8 hr using 8% catalyst amount.
p-TsOH - *p*-toluene sulphonic acid.

Effect of catalyst loading. The amount of catalyst used is a crucial economics factor for successful industrial application. Therefore, a study on the effect of using various percentage of *p*-TsOH ranging from 3%, 5%, 8%, 10% and 12% based on weight percent of Gly was carried out. As shown in *Figure 5*, reactions conducted with 8% or higher catalyst loading gave AV of less than 1 mg KOH g^{-1}. Further loading of *p*-TsOH up to 12% resulted in a marginal decrease of AV. An increase in the catalyst loading leads to an increase of the reaction rate due to an increase in the total number of active catalytic sites (Delgado *et al.*, 2007). These observations will help to determine the optimum amount of *p*-TsOH required to make the process viable with maximum composition of Gt-LE formed. Further experiments were conducted with 8% of catalyst loading to study other operating conditions.

Molar ratio between Gly and LA. The effects of reactant mole ratios on the formation of Gt-LE were investigated. The mole ratios of Gly:LA were varied from 1:3, 1:4, 1:5 and 1:6 mole while keeping the rest of the experimental conditions similar. The results obtained are presented in *Figure 6*. Generally, the composition of Gt-LE increased when the reactant mole ratio was increased. This is made evidence by the increase of Gt-LE composition from 21.7%



Figre 5. Effect of catalyst loading on acid value of product. Reaction was carried out at 140°C for 8 hr using 1:3 (Gly:LA) mole ratio.

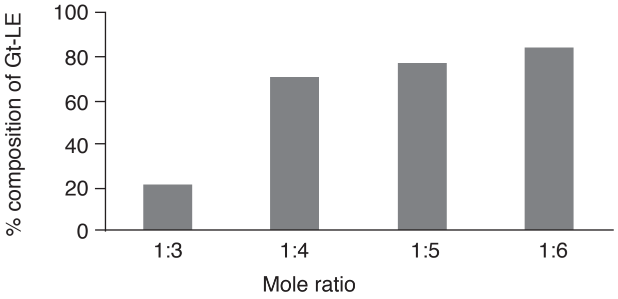


Figure 6. Effect of mole ratio between glycerol and levulinic acid on the reaction on the formation of glycerol trilevulinate (Gt-LE).

to 84.5% when the mole ratio between Gly:LA was increased from 1:3 to 1:5. The analysis result shows that mole ratio of 1:6 gave the highest percent composition of Gt-LE. According to Le-Chatelier's principle (Clark, 2013) in a chemical reaction, excess amount of one reactant drives the reaction in the forward direction. Therefore, mole ratio of 1:6 (Gly:LA) is preferred to maximise the formation of Gt-LE for the next study.

Effect of catalyst loading using mole ratio of 1:6 (Gly:LA). The effect of *p*-TsOH catalyst loading on the reaction at mole ratio of 1:6 (Gly:LA) was studied. The catalyst amount was varied from 1% to 5% and the result was compared with 8% catalyst. *Figure 7* shows that reaction conducted with lower amount of catalyst (1% - 5%) have yielded lower percent composition of Gt-LE as compared to reaction conducted with 8% *p*-TsOH which generated 84.5% of Gt-LE. The result revealed that higher amount of catalyst loading will generate product with higher composition of the desired Gt-LE. The results prove that the optimal *p*-TsOH loading is 8%.

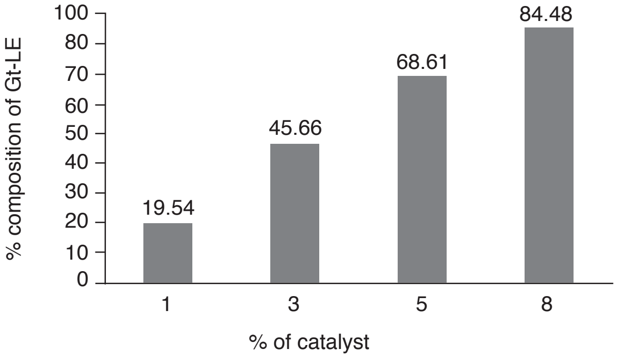


Figure 7. Effect of catalyst loading on the formation of glycerol trilevulinate (Gt-LE) when mole ratio of glycerol to levulinic acid was at 1:6.

Effect of reaction time on the product. The reaction was conducted at mole ratio of 1:6 (Gly:LA) with 8% *p*-TsOH catalyst loading. The reaction was monitored by AV analysis and by measuring the amount of water collected from the reaction in the Dean and Stark apparatus (*Figure 8*). The reaction was conducted for 8 hr. It was observed that the theoretical amount of water to be collected (5.4 ml) was achieved after 5 hr of reaction. After 7 hr of reaction, the amount of water increased to 5.6 ml and remained the same after 8 hr of reaction. The excess amount of water obtained may come from moisture in Gly. Result for AV analysis as shown in *Figure 9* also supports this finding. After 5 hr of reaction, the AV had reached a plateau. Therefore, the optimum reaction time for above corresponding reaction parameter was 5 hr.

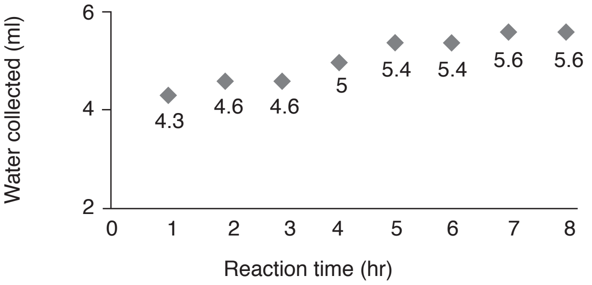


Figure 8. Amount of water collected against time for reaction condition of 8% p-*tolune sulphonic acid (*p-*TsOH) with 1:6 mole ratio of Gly:LA at 140°C reaction temperature.*

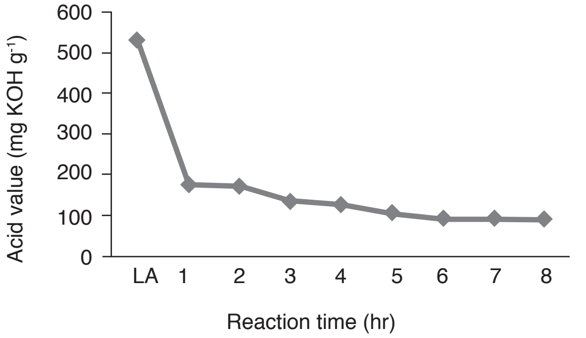


Figure 9. Effect of reaction time on acid value for reaction condition of 8% p-*tolune sulphonic acid (*p-*TsOH) with 1:6 mole ratio of Gly:LA at 140°C reaction temperature.*

Characterisation of Gt-LE

FTIR spectra. FTIR spectra of both Gly and LA were compared with the product in order to prove that the esterification reaction between Gly and LA has taken place. In the FTIR spectrum (*Figure 10*), the absorption band at 1702 cm^{-1} assigned to C=O stretching of ketone carbonyl group of LA has shifted to 1714 cm^{-1} and the presence of ester carbonyl peak at 1736 cm^{-1} indicated the esterification between Gly and LA has occurred. Other than that, the C-O stretching of carboxylic acid of LA at 1162 cm^{-1} has shifted to a sharp peak at 1147 cm^{-1}, which affirmed the esterification reaction has transpired.

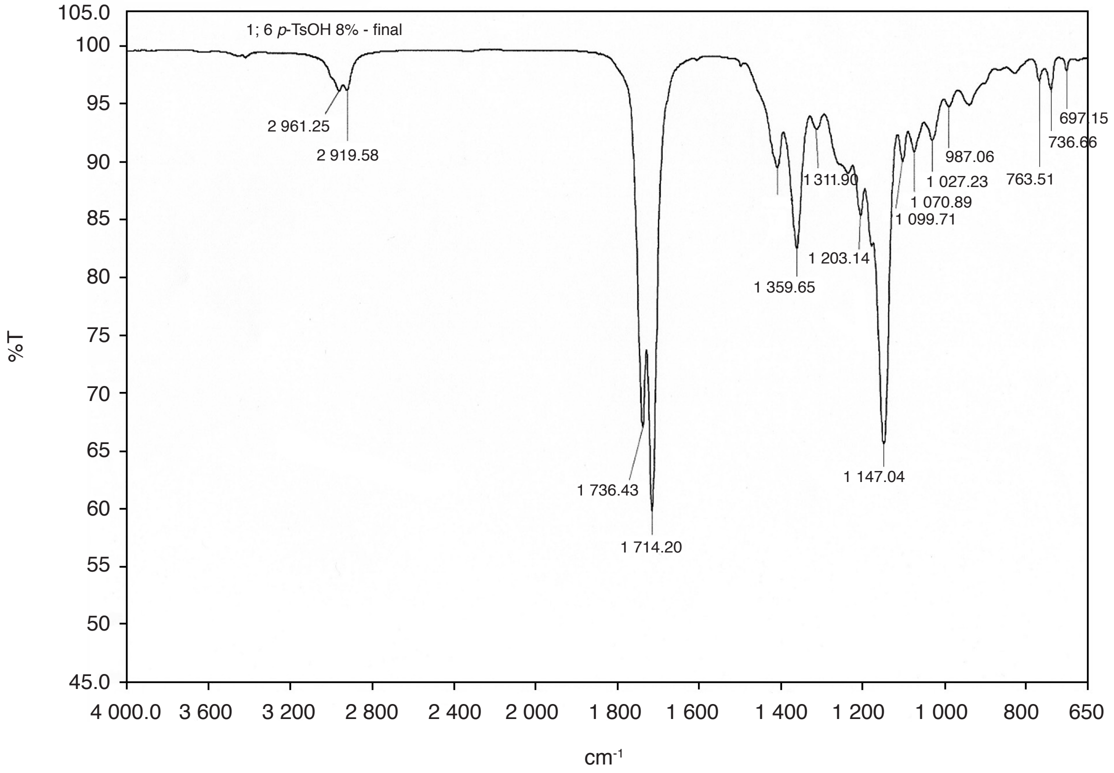


Figure 10. Fourier transform infrared (FTIR) spectrum of glycerol trilevulinate (Gt-LE) obtained from p-*tolune sulphonic acid (*p-*TsOH)-catalysed esterification between glycerol (Gly) and levulinate acid (LA) at 1:6 mole ratios and at 140°C for 8 hr.*

***^{1}H and ^{13}C NMR analysis**. Figure 11* shows the ^{1}H and ^{13}C NMR spectra of Gt-LE. The chemical shift at 2.173 ppm in ^{1}H-NMR spectrum (*Figure 11a*) correspond to the terminal methyl groups (-CH_3) of the levulinate ester chain. The protons attached adjacent to ketone-carbonyl and ester-carbonyl were featured at 2.748 ppm and 2.586 ppm respectively. Peaks at 4.173-4.252 ppm and 5.223-5.240 ppm were related to the protons of -CH_2- and central carbon in the glyceride unit correspondingly. For the ^{13}C-NMR spectrum (*Figure 11b*), the carbonyl groups (-CO-) of ketone and ester appeared at 206 and 172 ppm, respectively. The glyceride carbons present in -CH_2- groups and central carbon can be observed at 62 and 69 ppm, respectively. In addition, peaks at 27 ppm and 37 ppm correspond to the -CH_2- group next to ester and ketone group, respectively. While peak 29 ppm relates to -CH_3 group of the levulinate ester.

GC of Gt-LE. The formation of Gt-LE was confirmed qualitatively via GC analysis. The GC chromatogram confirmed that the synthesised product contains high percent composition of Gt-LE (85%) as represented by a peak at retention time at 22.12 min (*Figure 12*). The chromatogram also indicated the existence of two other minor products with low percent composition namely Gm-LE and Gd-LE, which appeared at 13.904 min and 17.897 min.

CONCLUSION

Non-catalytic reaction conducted at 140°C for 5 hr yielded product with 63.14% composition of total glycerol levulinate ester (GLE). On the other hand, *p*-TsOH the heterogeneous catalyst was the preferred catalyst for catalysed reaction as compared to montmorillonite, Amberlyst-15 or Amberlyst-46. From this study, Gt-LE was successfully synthesised using *p*-TsOH as catalyst at 140°C for 5 hr. The best mole ratio to obtain high composition of Gt-LE without having to go through cumbersome purifying process was 1:6 with 8% catalyst loading. The GC, FTIR and NMR analysis confirmed that the synthesised product contains Gt-LE with the yield of 65% and 85% purity. The optimised reaction procedure to synthesise Gt-LE may gave opportunity to industrial player in specialty chemical to produce at larger scale where this indirectly increase the uses of glycerol and chemical derived from biomass.

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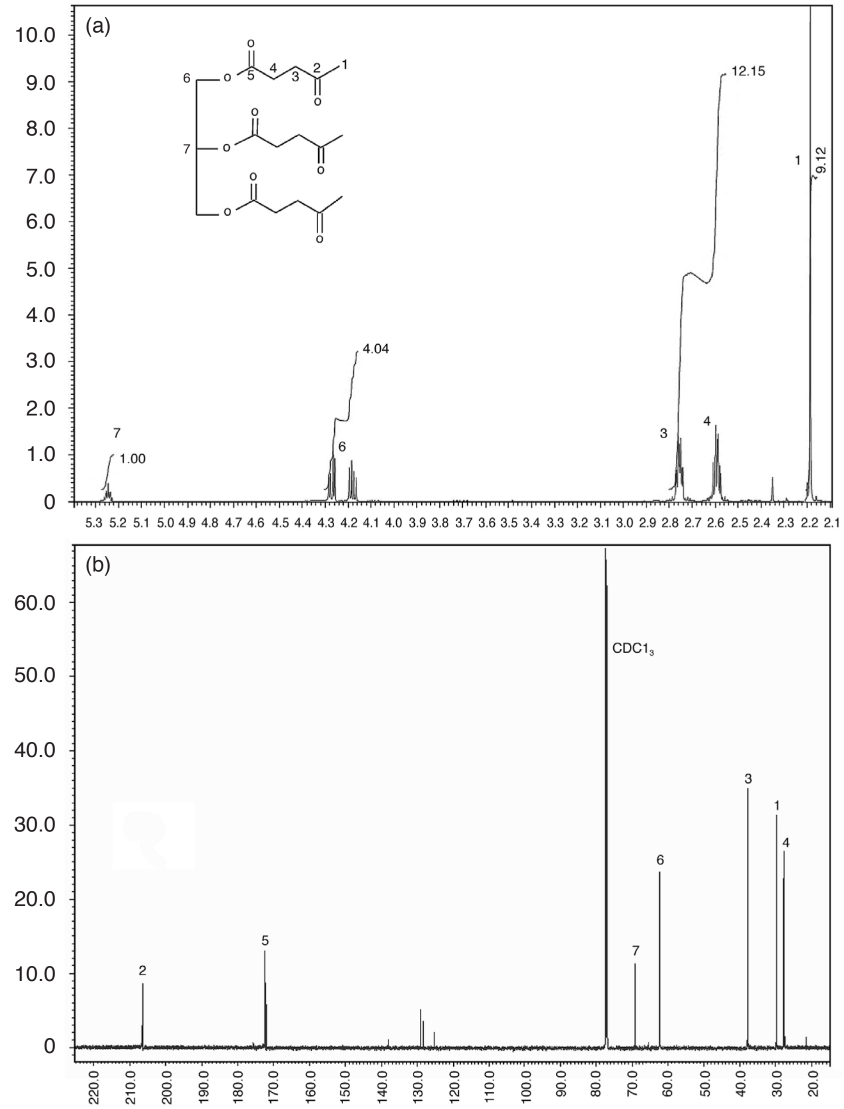

Figure 11. The ^{1}H nuclear magnetic resonance (NMR) (a) and ^{13}C-NMR (b) spectrum of glycerol trivulinate (Gt-LE) obtained from p*-toluene sulphonic acid (*p*-TsOH)-catalysed esterification between glycerol (Gly) and levulinate acid (LA) at 1:6 mole ratios and at 140°C for 8 hr.*

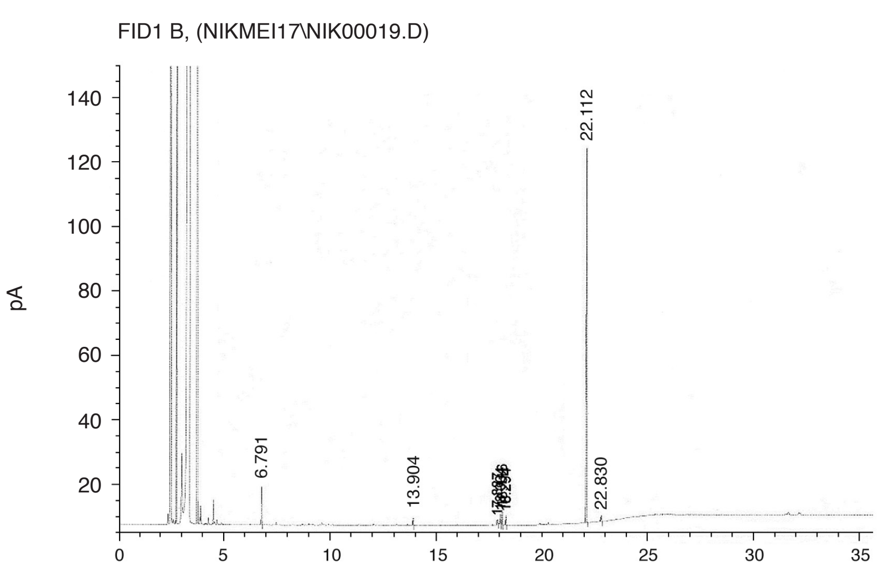

Figure 12. Gas chromatography (GC) chromatogram of glycerol trivulinate (Gt-LE) obtained from p*-toluene sulphonic acid (*p*-TsOH)-catalysed esterification between glycerol (Gly) and levulinate acid (LA) at 1:6 mole ratios and at 140°C for 8 hr.*

REFERENCES

Amarasekara, A S and Hawkins, S A (2011). Synthesis of levulinic acid-glycerol ketal-ester oligomers and structural characterization using NMR spectroscopy. *European Polymer J., 47*: 2451-2457.

Ashworth, I W; Bush, E; Chan, L C; Cherryman, J; Cox, B G; Muir, J; Korupoju, S R and Keshwan, J (2012). Where has my acid gone? Understanding the self-catalyzed esterification of maleic acid in methanol during salt formation. *Organic Process Research & Development, 16*: 1646-1651.

ASTM (2016). *Standard Test Method for Pressure Mottling and Blocking Resistance of Organic Coatings on Metal Substrates*. West Conshohocken, PA, USA: ASTM International. 3 pp.

ASTM (2017). *Standard Test Methods for Scrub Resistance of Wall Paints*. ASTM International. 4 pp.

Bloom, P D (2007). Levulinic acid ester as rective plasticizers and coalescent solvents. French patent application 2007094922A2.

Bozell, J J; Moens, L; Elliott, D C; Wang, Y; Neuenscwander, G G; Fitzpatrick, S W; Bilski, R J and Jarnefeld, J L (2000). Production of levulinic acid and use as a platform chemical for derived products. *Resources, Conservation and Recycling, 28*: 227-239.

Clark, J (2013). Le chatelier's principle. https://www.chemguide.co.uk/physical/equilibria/lechatelier.html, accessed on 26 June 2018.

Da-Wei, W; Hong-Yan, L; Run-Jie, C; Ze-Zhong, M; Tao, C; Ge-Fei, H; Wen-Chao, Y and Guang-Fu, Y (2015). Design, synthesis and herbicidal activity of novel quinazoline-2,4-diones as 4-hydroxyphenylpyruvate dioxygenase inhibitors. *Pest Management Science, 71*: 1122-1132.

Dange, P N and Rathod, V K (2017). Equilibrium and thermodynamic parameters for heterogeneous esterification of butyric acid with methanol under microwave irradiation. *Resource-efficient Technologies, 3*: 64-70.

Delgado, P; Sanz, M T and Beltrán, S (2007). Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst. *Chemical Engineering J., 126*: 111-118.

Girisuta, B and Heeres, H J (2017). Levulinic acid from biomass: Synthesis and applications. *Production of Platform Chemicals from Sustainable Resources* (Fang, Z; Smith, J R L and Qi, X eds.). Springer, Singapore. 475 pp.

Go, A W; Tran Nguyen, P L; Huynh, L H; Liu, Y-T; Sutanto, S. and Ju, Y-H (2014). Catalyst free esterification of fatty acids with methanol under subcritical condition. *Energy, 70*: 393-400.

Kenar, J A (2007). Glycerol as a platform chemical: Sweet opportunities on the horizon? *Lipid Technology, 19*: 249-253.

Khan, A S; Man, Z; Bustam, M A; Nasrullah, A; Ullah, Z; Sarwono, A; Shah, F U and Muhammad, N (2018). Efficient conversion of lignocellulosic biomass to levulinic acid using acidic ionic liquids. *Carbohydrate Polymers, 181*: 208-214.

Kushairi, A; Loh, S K; Azman, I; Hishamuddin, E; Ong-Abdullah, M; Izuddin, Z; Razmah, G; Sundram, S and Parveez, G K A (2018). Oil palm economic performance in Malaysia and R&D progress in 2017. *J. Oil Palm Res. Vol. 30 (2)*: 163-195.

Kushairi, A; Singh, R and Ong-Abdullah, M (2017). The oil palm industry in Malaysia: Thriving with transformative technologies. *J. Oil Palm Res.Vol. 29 (4)*: 431-439.

Lam, M K; Lee, K T and Mohamed, A R (2009). Life cycle assessment for the production of biodiesel: A case study in Malaysia for palm oil versus Jatropha oil. *Biofuels, Bioproducts and Biorefining, 3*: 601-612.

Lindstedt, S; Holme, E; Lock, E A; Hjalmarson, O and Strandvik, B (1992). Treatment of hereditary tyrosinaemia type I by inhibition of 4-hydroxyphenylpyruvate dioxygenase. *The Lancet, 340*: 813-817.

Mohammed, W T and Jabbar, M F A (2015). Comparison between homogeneous and heterogeneous esterification reactions for biodiesel production using reactive distillation. *International J. Current Engineering and Technology, 5*: 3439-3447.

Pöpken, T; Götze, L and Gmehling, J (2000). Reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis. *Industrial & Engineering Chemistry Research, 39*: 2601-2611.

Rackemann, D W and Doherty, W O (2011). The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioproducts and Biorefining, 5*: 198-214.

Ramli, N A S and Amin, N A S (2014). Catalytic hydrolysis of cellulose and oil palm biomass in ionic liquid to reducing sugar for levulinic acid production. *Fuel Processing Technology, 128*: 490-498.

Sanz, M T; Murga, R; Beltrán, S; Cabezas, J L and Coca, J (2002). Autocatalyzed and ion-exchange-resin-catalyzed esterification kinetics of lactic acid with methanol. *Industrial & Engineering Chemistry Research, 41*: 512-517.

Tiong, Y W; Yap, C L; Gan, S and Yap, W S P (2018). Kinetic study on oil palm biomass conversion to levulinic acid via indium trichloride-ionic liquids. 2nd International Conference on Energy and Environmental Science. Kuala Lumpur.

Unnithan (2018). Palm biodiesel industry - Navigating through the storm. Lauric Oils Price Outlook Conference & Exhibition. Kuala Lumpur.

Werpy, T; Petersen, G; Aden, A; Bozell, J; Holladay, J; White, J; Manheim, A; Eliot, D; Lasure, L and Jones, S (2004). Results of screening for potential candidates from sugars and synthesis gas. *Top Value Added Chemicals from Biomass*. Department of Energy, Washington DC, USA. 76 pp.