

Synthesis and Physicochemical Properties of Three Glutaric Acid Diester

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Abstract

Three diesters were prepared through the esterification reaction of diacid (glutaric acid) with 3 different straight chain alcohols with para-toluene sulphonic acid (PTSA) (4%) as a catalyst. The resulting products were confirmed by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) analyses. The oxidative stability, viscosity, flash point and pour point were measured. Dioctyl glutarate and didecyl glutarate showed a liquid form at room temperature. Glutaric acid diesters produced show highoxidativestability, higher than 187°Cand high temperature pour point. Didodecyl glutarate forms solid at room temperature andshowshighflash pointof210°C and viscosity index VI of 194 respectively.

Keywords: biolubricant, esterification, glutaric acid, alcohol

1. INTRODUCTION

Due to the force of environmental legislation and high demand for sustainable energy has triggered the researcher to use bio-based as raw material to the production of lubricant. Previous studies found that the use of vegetable oil as base stock have its disadvantages. The disadvantages of vegetable oil are poor thermal, oxidative and hydrolytic stability [1]. Due to that, it has triggered the usage of syntheticoleochemical ester as a base stock for biolubricant. This is because,oleochemical ester is similar to natural oil that has been modified and possessed much better thermal, oxidative and hydrolytic stability as well as cold temperature fluidity.

Less stable to oxidative and hydrolytic and limitation to low temperature fluidity are the major problems in oil that need to be solved. Instead of using vegetable oil as a base stock, chemical modification of plant oil can be done to prevent the oil to become oxidation. The synthetic oleochemical ester is now commonly has been used as a based stock to produce lubricants.

Ester based lubricant possessed excellent lubrication properties due to the C=O functional group that make the compound polar. More polarity the molecules will adhere to positively charged metal surfaces and finally creating protective films which slow down the wear and tear of the metal surface. Therefore, to increase the polarity of such molecules, the synthesis of diester is an effective way to solve the problems. Furthermore, by increasing the polarity, it tends to produce a lubricant that less volatile and has a much higher flash point and much lower vapor pressure.

Synthetic ester is used in the production of lubricant oil due to the biodegradable characteristic and renewable. A previous study has produced diester from oleic acid with several fatty acids. The result showed that the increasing chain length of mid chain ester and end chain ester has improved the low temperature properties of diester. However, several researchers found out that by increasing the mid-chain ester group length, it improved the low-temperature properties but give a negative effect on oxidative stability. Lower pour point will affect the use of oil at low operating temperatures [2]. A method to improve the low-temperature properties is to introduce branching side to the diacid that significantly improved low-temperature flow characteristics and friction-wear properties [3]. Diester can be synthesized by esterification of dicarboxylic acid with alcohol.

Medium chain carboxylic acid has a good oxidative stability and good low temperature properties [4]. The diester was used as a base stock due to the polarity which caused the lubricant stick to the metal. In this paper, we focused on effect of physicochemical glutaric acids diester with different types of alcohol used to the side chain of diacid after being esterified. Production of diester was achieved by the esterification reaction of diacid with 3 different alcohols catalyzed by homogenous catalyst such as para-toluene sulfonic acids (PTSA).

2. MATERIALS AND METHODS

The raw material used to prepare the samples were glutaric acid, three different alcohols (octanol, decanol and dodecanol) and catalyst (PTSA) were used for synthesis diester for based stock lubricant. Another chemical used were sodium bicarbonate, diethyl ether, sodium chloride which was used for purification after the esterification process. The esterification was carried out by using reflux condenser and was performed by using 500 mL three necked round bottom flask equipped with a magnetic stirrer and thermometer. The reaction was carried out three times with same temperature on 120-130°C, time for 6-7 hours, molar ratio acid: alcohol 1:2.5 but different types of alcohol. 9.26 g (0.07 moles) of glutaric acid, 22.75 g (27.3 mL, 0.175 moles) octanol and about 1.29 g (4%) of catalyst PTSA were placed in the flask and heat for 6 hours with constant stirring provided by the magnetic stirrer. Molar ratio 1:2.5 were used which is excess alcohol used compared to acid with 4% of catalyst was added to increase the rate of reaction. During the reaction, molecular sieve was added in order to absorb the remaining water. After completing the reaction, the solution was washed and neutralized by using diethyl ether and based solution to remove the catalyst. The solvent was removed by using a rotary evaporator under reduced pressure at 80° C. The structure of the title product was confirmed by FTIR, ¹H NMR and ¹³C NMR spectra.

3. RESULTS AND DISCUSSION

3.1 Diesters Synthesis

Glutaric acid and 3 different alcohols were mixed at molar ratio 2.5:1 with the presence of PTSA as a catalyst to a 500 mL reactor at 180°C. A temperature controlled oil bath was used to control the reaction temperature and the reaction was mixed using an overhead stirrer at 700-800 rpm. In this research, we focused on the side chain of ester group which is to monitor the effect of different types of alcohols used the standard measurement of lubricant.

The nucleophilic attack by alcohol molecule to the diacid of glutaric acid resulted in the formation of dioctyl glutarate, didecyl glutarate and didodecyl glutarate, as shown in Fig. 1. Here, the alcohols acted as a branching agent. The reaction was stopped by separating the catalyst from the reaction mixture by filtration over a glass filter and subsequently washed or neutralized the acid with sodium bicarbonate. Next, the sodium chloride solution used to remove any emulsion that formed. Lastly, put sodium sulphate to the oil to remove any excess water left. The oil was filtered by using filter paper and sample was confirmed through FTIR and NMR analysis. The yield of each sample was 43% (dioctyl glutarate), 37% (dodecyl glutarate) and 52% (didodecyl glutarate). Too much of oil loses during the filtrations caused the yield is less enough when compared to previous research.

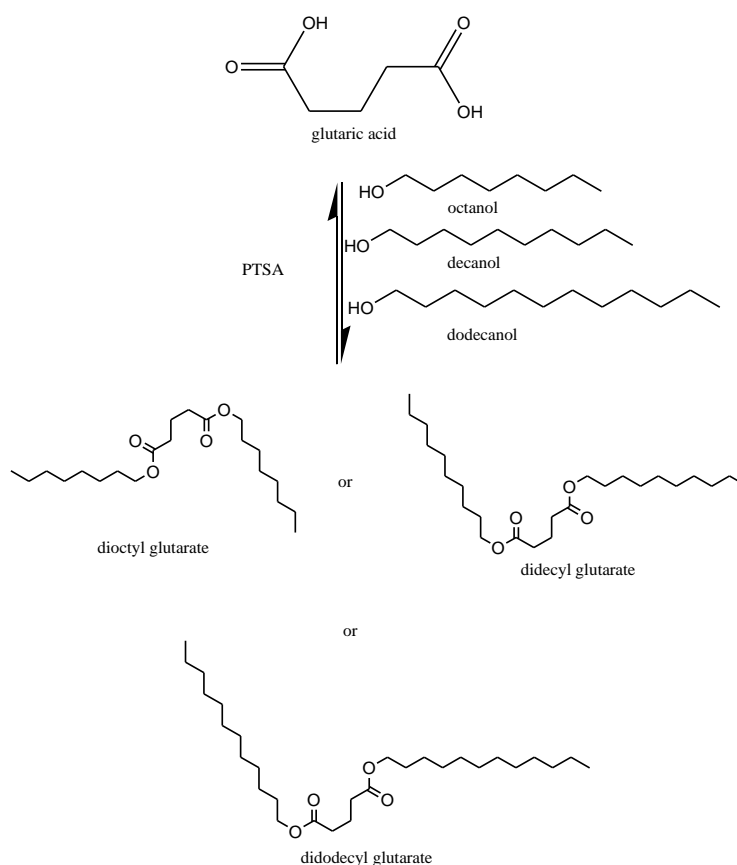


Figure 1: Chemical reaction for the production of diesters

3.2 Characterization

3.2.1 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was used to determine the presence of ester group of dioctyl glutarate, didecanyl glutarate and didodecyl glutarate. Each spectrum showed the formation of functional group of the ester. The wavelengths which present the formation of carbonyl ester group for the three samples were produced at 1737 cm^{-1} and 1738 cm^{-1} . The spectrum also showed the formation of C-O ester at wavelength 1173 cm^{-1} while at wavelength 2955 cm^{-1} and above showed the alkane stretch (sp^3). Table 1 showed the data obtained from FTIR.

Table 1: FTIR data for glutaric acid diesters

Functional group	Wavelength no. cm^{-1}	Explanations
1. C=O	1732	Carbonyl ester
2. CH ₃	1393	CH ₃ bend
3. CH ₂	1458	CH ₂ bend
4. CH ₂ sp^3	2955	Strong and sharp peak indicate high repeat unit
	2927	
	2856	
5. C-O	1173	C-O bond in ester
	1062	

3.2.2 Nuclear Magnetic Resonance (NMR)

^1H and ^{13}C NMR spectra were recorded using JEOL JNM-ECP 400 spectrometer operating at a frequency of 400.13 and 100.77 MHz and using deuterium chloroform as a solvent. The data spectrum of ^1H NMR and ^{13}C NMR were shown in Table 2 and 3. The result showed the formation of signals of methylene protons, $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ which is the important signals in this study. In this study, ^{13}C NMR also very important which can detect the signals that represents the functional group of ester carbonyl. Pavia et al., 2010, the formation of ester carbonyl is at signal 170-185 ppm. In this study, ester carbonyl forms at signal of 173 ppm. Carbon at this area are not being shielded due to the hybridization of sp^2 and already bound to oxygen atom that has an electronegativity to the functional group of carbonyl. Furthermore C-O signal was in the range 40-80 ppm while Hwang & Erhan 2006, this signal form at peak of 60 ppm and 63 ppm [5]. Data showed that the signal form at peak 65 ppm.

Table 2: Data interpretation of ^1H NMR for glutaric acid diesters

Functional group	Chemical shift (ppm)	Explanations
1. CH_3	0.83-0.86	Methyl group at end of chain
2. CH_2	1.24-1.27	Methylene protons of the chain
3. CH_2CH_3	1.56-1.58	Methylene protons beside CH_3
4. $\text{CH}_2\text{CH}_2\text{C}=\text{O}$	1.89-1.93	$\beta\text{-CH}_2$ of $\text{C}=\text{O}$
5. $\text{CH}_2\text{C}=\text{O}$	2.31-2.35	$\alpha\text{-CH}_2$ of $\text{C}=\text{O}$
6. COOCH_2	4.01-4.04	Methylene protons beside OCOR bond

Table 3: Data interpretation of ^{13}C NMR for glutaric acid diesters

Functional group	Chemical shift (ppm)	Explanations
1. CH_3	14.19	Methyl carbon at end of chain
2. $\text{CH}_2\text{CH}_2\text{C}=\text{O}$	20.33	-
3. CH_2CH_3	22.76	-
4. CH_2	26.04-29.33	Carbon of near to methyl group
5. $\text{CH}_2\text{CH}_2\text{CH}_3$	31.91	Methylene carbon in the chain
6. $\text{CH}_2\text{CH}_2\text{C}=\text{O}$	33.46	Methylene carbon bond to carbonyl
7. COOCH_2	64.74	Carbon bond to $-\text{OC}=\text{O}$
8. CH_2CO	173.2	Carbon of Ester carbonyl

3.3 Physicochemical of Glutaric Acid Diester

By using the alcohols as a branching agent has improved the oxidative stability. Based on Table 4, oxidative stability and flash point increased with carbon chain which coincides with the increasing of molecular weight. Resistance to oxidative stability will decrease the formation of sludge, contaminants and by-product of oil [6]. Oxidative stability will increase with the decrease of the double bond in the carbon chain. Biolubricant produced in this study has a straight molecular chain. The more carbon number, the higher the flash point of the oil [7].

Table 4: Comparison of characterization of glutaric acid diesters

Characterization	Dioctyl glutarate	Didecyl glutarate	Didodecyl glutarate
Oxidative stability (°C)	187	187	190
Pour point (°C)	16	26	-
Viscosity	-	-	194
Flash point (°C)	150	170	210

The higher the degree of unsaturation of ester, it will have low pour point [8]. In this study, the side chain of glutaric acids diester which consists of medium straight chain alcohol (C:8), (C:10), (C:12) showed the pour point as low as 10°C for dioctyl glutarate and 26°C for dodecyl glutarate while for didodecyl glutarate solid at room temperature. Based on this result, it showed that glutaric acid diester was less suitable to be implemented at low temperature. Low degree of unsaturation caused the glutaric acids diester has high pour point with a medium length chain.

Table 5 below shows the data obtained for viscosity. An increasing number of carbon chain is directly proportional to value of viscosity index (VI) obtained. This high VI can prevent excessive thickening when the engine is cold and encourage the rapid onset and rapid flow. Molecule with larger molecular weight has high viscosity. In addition, the polar nature of the molecules influenced the viscosity. The polar molecule will have higher viscosity [9]. In this study, the compounds had two ester groups in each molecule and this directly showed the increasing of the molecular weight. Molecular weight for dioctyl glutarate was 324g/Mol, dodecyl glutarate is 380g/Mol and didodecyl glutarate was 436g/Mol. The viscosity index for dioctyl glutarate and dodecyl glutarate cannot be calculated. This is because of the kinematic viscosity at 100°C was too low and to be out of the range of the viscosity index table.

Table 5: Viscosity data for diester glutaric

Sample	Viscosity at 40°C	Viscosity at 100°C
Dioctyl glutarate	4	1
Didecyl glutarate	5	1
Didodecyl glutarate	7	2

4. CONCLUSION

Three diester glutaric derived from acid glutaric with 3 types of straight chain alcohol were successfully prepared by esterification. Addition of alcohol to the side chain of diacid increased the oxidative stability and flash point. The straight chain saturated of different alcohol affect the oxidative stability of oil by increasing the carbon number of chain alcohol. The diester can be prepared easily with high yield.

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