

# The Effect of Long-chain and Branched Alcohol on Lubricity of Dodecanedioic Acid Based Ester

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## Abstract

Thirteen samples of esters based on dodecanedioic acid with different chemical structures were synthesized. Among these were di-2-octyl dodecanedioate, didecyl dodecanedioate, di-2-ethylhexanol dodecanedioate, di-2-ethylbutyl dodecanedioate, dioctyl dodecanedioate, dihexyl dodecanedioate, and dioleil dodecanedioate. Diesters were synthesized through the esterification of dodecanedioic acid with selected long-chain and branched alcohols with acid catalyst of H<sub>2</sub>SO<sub>4</sub>. These esters were tested in terms of their suitability for application as lubricants. The results showed that the lubricity properties, based on their pour point, flash point, and oxidation stability of the esters were significantly affected by the linear and branched alcohols used. An excellent pour point property of di-2-ethylbutyl dodecanedioate and di-2-ethylhexanol dodecanedioate at -55 °C and -50 °C was observed compared to their respective same linear carbon number esters of dihexyl dodecanedioate at 10 °C and dioctyl dodecanedioate at 20 °C. These are due to the presence of the branched group in their molecule vicinity structure. However, the esters flash points were insignificantly affected by the presence of branched structure. The selected esters could be used for biolubricants or engine oil.

## Keywords

Dodecanedioic acid based ester, pour point, flash point, viscosity index

## 1 Introduction

Natural and synthetic esters are essential materials in the chemical industry. They have been most commonly applied in manufacturing of lubricating oils, solvents, plasticizers, paints, food, pharmaceuticals, cosmetics, and liquid fuels.<sup>1</sup> Among those esters, dicarboxylic acid based esters are of particular interest due to their excellent properties, such as low volatility, high flash point, good thermal stability, and low toxicity.<sup>2</sup> The esters based on dicarboxylic acids (containing two carboxyl groups) are organic, oxygen-containing compounds, which result from the reaction of an alcohol with an organic acid. The acid and the alcohol are esterified either thermally or in the presence of catalyst. Their chemical properties vary due to their alcohol and/or acid components.

It is known that long-chain and branched or bulky moieties esters compounds find uses in various commercial products. For instance, for biodiesel,<sup>3</sup> an alternative diesel fuel derived from vegetable oils or animal fats; branched esters such as neat isopropyl or isobutyl esters have been applied as pour point depressants<sup>4</sup> to improve low-temperature properties. For this insight, the use of branched esters is one of the possible solutions for improving the low-temperature properties of biolubricants. Nowadays, the compounds with branched or bulky moieties, such as neopentyl glycol diesters, are commonly used commercial in plasticizers, cosmetics and lubricants.<sup>5</sup>

Physicochemical properties of ester-based lubricant depends upon the balance between hydrocarbon moiety and ester group(s). Hydrocarbon chain length contributes and reflects towards the viscosity, viscosity index, and solubility compatibility, whereas the pour point, oxidation stability, and biodegradability are reflected by the extent of branched groups. Number of ester groups reflects in compatibility and esters acid number, *i.e.*, stearic hindrance reflects in thermal stability and hydrolytic stability. The presence of ester group contributes towards molecule polarity, which reflects in their evaporation, lubricity, and solvency. Therefore, in comparison to mineral oil lubricants, many esters have a series of technical advantages, and at far, for biolubricant application. Such advantages, include having natural high viscosity indexes (over 160), low temperature properties (good cold flowing), pour point < -30 °C, low evaporation losses, and good thermal stability, *i.e.*, high temperature properties, hydrolytic stability, good anti-friction, and anti-wear characteristics, high flash point (> 260 °C), more compatibility, and biodegradability.<sup>6</sup>

High performance esters are used as lubricants in many applications, including automotive engine oils, hydraulic fluids, compressor oils, gear oils, and grease formulations.<sup>7</sup> High performance esters are characterized notably by good biodegradability, low volatility, good lubricity, good thermal stability, and low pour points. The particular properties of ester oils determine their specific application areas, especially as environmentally friendly lubricants.

Over the years, a great deal of effort has been invested into the development of lubricants with optimum qualities

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to meet the ever increasing demands of a new generation of engines.<sup>8,9,10</sup> The impetus always being the same; new innovations in machine design required new innovations in lubricant composition. This development has led to an increased need for esters functional fluids that are both biodegradable and low in toxicity. The most commonly dibasic acid-based esters used in industries are short-chain esters based on adipic, sebacic, and azelaic acids. Their molecular weight is high enough to disregard volatility problems in industrial application temperature such as for lubricants. However, medium and long carbon chain with branched esters are still getting less attention. It is believed that the branching group in the alcohol fragments lead to the esters having a very good low temperature performance, high flash point, high viscosity indexes, and good stability on oxidation process.

The present study focuses on the synthesis of esters based on medium chain acid, dodecanedioic acid. The effect of short and medium chain alcohol carbons number ranging from C2 to C12, and branched structure such as 2-butanol, 2-octanol, 2-methyl-1-butanol, 2ethyl-1-butanol, and 2-ethyl-1-hexanol on the lubrication properties of esters were studied. These include evaluation of the pour point, flash point, viscosity indexes, and oxidation stability of the dicarboxylic acid based esters to suggest their application as biolubricant oils.

## 2 Materials and method

### 2.1 Materials

Dodecanedioic acid, DA (99 %) was obtained from Fisher Scientific. All other chemicals and reagents such as oleyl alcohol, 2-ethyl-1-hexanol, 2ethyl-1-butanol, decanol, octanol, 2-octanol, sec-butanol, cis-3-hexen-1-ol were obtained from Aldrich Chemical, and used directly without further purification. The organic extracts were dried using anhydrous sodium sulphate (Aldrich Chemical).

### 2.2 Method

#### 2.2.1 Ester synthesis

Esters of dodecanedioic acid were synthesized by two esterification methods using appropriate alcohols and dodecanedioic acid as the starting material.

#### a. Dean-Stark distillation setup

The known acid catalytic esterification method with a Dean-Stark distillation setup was used. A mixture of dodecanedioic acid and alcohol (mole ratio 1 : 2) was initially placed into a three-necked round-bottom reaction flask fitted with this setup. An amount of 40–50 ml of toluene was added as a reaction medium. The reaction mixture was heated with stirring in an oil bath to desired reaction temperature at 120–130 °C. A catalytic amount of concentrated H<sub>2</sub>SO<sub>4</sub> (2 wt% of total DA weight) was slowly introduced into the reaction vessel. The reaction was carried out for about 4 h. The water formed during the reaction was continuously distilled off from the system. The progress of the reaction

was monitored by measuring the quantity of water that was collected in a dropping funnel. Reaction was stopped when no water was further distilled off from the reaction vessel.

#### b. Reflux condenser method

The synthesis was performed in a 100 ml three-necked flask equipped with a reflux condenser, and a contact thermometer. The reaction mixture was heated on a magnetic heater and stirrer until it reached the desired temperature at 70 °C; catalyst 2 % of concentrated H<sub>2</sub>SO<sub>4</sub>, and desiccant of molecular sieve (50 wt% of total DA weight) were added to the mixture at that moment. The reaction temperatures were held constant within a range of ±1 °C. A mixture of DA and alcohol (mole ratio 1 : 2) in a 100 ml three-neck flask equipped with a cooler and thermometer was heated for 1 h at 70 °C. During the 1 h reaction, molecular sieve was put in the oven at 180 °C for drying. After 1 h drying, the molecular sieve and 2 % sulphuric acid were added to the mixture. This method was used in the case of ethanol and butanol, because the high temperature caused evaporation.

#### 2.2.2 Purification of dodecanedioic acid esters

After the end of the reaction, the crude reaction product was transferred into a round-bottom flask. Toluene was firstly removed, and the crude product was allowed to cool to room temperature before it was purified and then transferred into a separating funnel. 50 ml of diethyl ether was added into the funnel followed by three times 10 ml of saturated sodium bicarbonate solution to neutralize the catalytic inorganic acid used in the reaction and remove unreacted starting dodecanedioic acid. Saturated sodium chloride solution was then added to avoid any emulsion formation. The aqueous layer was decanted and the diethyl ether layer dried over sufficient anhydrous sodium sulphate, while the hydrated Na<sub>2</sub>SO<sub>4</sub> was filtered off. The dried product was cleaned through a column packed with silica gel 60 to remove any decomposed materials and compounds carbonized with sulphuric acid. The column product was rotary-evaporated to remove the solvent. Trace solvent was further removed under nitrogen gas, and excess alcohol in the mixture was removed using the distillation method. The yield (%) of the diester product was determined. The final diester purity was checked by elemental analysis and identified by IR, <sup>1</sup>H-NMR, and <sup>13</sup>C NMR spectral analyses.

#### 2.2.3 Low temperature operability

The pour point (PP) is defined as the lowest temperature at which a liquid remains pourable (meaning it still behaves as a fluid). This method is used routinely to determine the low temperature flow properties of fluids. PP values were measured according to the ASTM D5949 method (ASTM 2005)<sup>11</sup> using a Phase Technology Analyzer, Model PSA-70S (Hammersmith Gate, Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree were reported. For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Generally, materials with

lower PP exhibit improved fluidity at low temperatures than those with higher PP. Triplicate measurements were made and the average values were reported with standard deviation ( $\pm$ SD).

#### 2.2.4 Flash point

The flash point (FP) is the lowest temperature at which a liquid can give off sufficient vapours to form an ignitable mixture in the air near the surface of the liquid. The flash point is often used as a descriptive characteristic of oil fuel, and is used to describe oils that are not normally applied as fuels. Flash point refers to both flammable oils and combustible oils. The lower the flash point, the easier it is to ignite the material. The flash point was determined by the American National Standard Method using a Tag Closed Cup Tester (ASTM, 2011).<sup>12</sup> Each sample was run in triplicate, and the average values rounded to the nearest whole degree were reported with standard deviation ( $\pm$ SD).

#### 2.2.5 Viscosity index measurements

Viscosity index (VI) is an arbitrary measure for the change of kinematic viscosity with temperature. It is used to characterise the lubricating oil in the automotive industry. Many lubricant applications require performing across a wide range of conditions, e.g., in an engine. Automotive lubricants must reduce friction between engine components when it is started from cold (relative to engine operating temperatures) as well as when it is running (up to 200 °C). Automated multi-range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure the viscosity. The measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 and 100.0 °C. The viscosity and viscosity index were calculated using ASTM method ASTM D 2270-93 (ASTM 2005),<sup>11</sup> respectively. Triplicate measurements were made, and the average values were reported with standard deviation ( $\pm$ SD).

#### 2.2.6 Oxidative stability

Pressurized DSC (PDSC) experiments were accomplished using a DSC 2910 thermal analyser from TA Instruments (Newcastle, DE). Typically, a 2-IL sample, resulting in a film thickness of <1 mm, was placed in an aluminium pan, which was hermetically sealed with a pinhole lid and oxidised in the presence of dry air (Gateway Airgas, St. Louis, MO), which was pressurised in the module at a constant pressure of 1378.95 kPa (200 psi). A 10 °C min<sup>-1</sup> heating rate from 50 to 350 °C was used during each experiment. The oxidation onset (OT, °C) was calculated from a plot of the heat flow (W/g) vs. temperature for each experiment. The sample was run in triplicate, and average values rounded to the nearest whole degree were reported with standard deviation ( $\pm$ SD).

### 3. Result and discussion

#### 3.1 Characterization and yield (%) of ester groups

The esterification of dodecanedioic acid was carried out with selected long-chain (C2-C12) and branched alcohols in the presence of sulphuric acid as catalyst. The esterification reaction conditions were done according to the previous study:<sup>13</sup> Duration of reaction 4 h, temperature at 120–130 °C, and acid/alcohol molar ratio (1 : 2). The amount of catalyst used was 2 % of the weight of the dodecanedioic acid. The example of esterification process to produce di(2-ethylhexyl) dodecanedioate (D2EHD) is shown in Fig. 1.

The diester yield% value is shown in Table 1. The percentage yields are significantly different from one another, depending on the structure of alcohols used and the miscibility between alcohols and the dodecanedioic acid at reaction temperature. The research was not oriented toward optimisation of ester synthesis, and mainly focused on the effect of the long-chain and branched alcohol used.

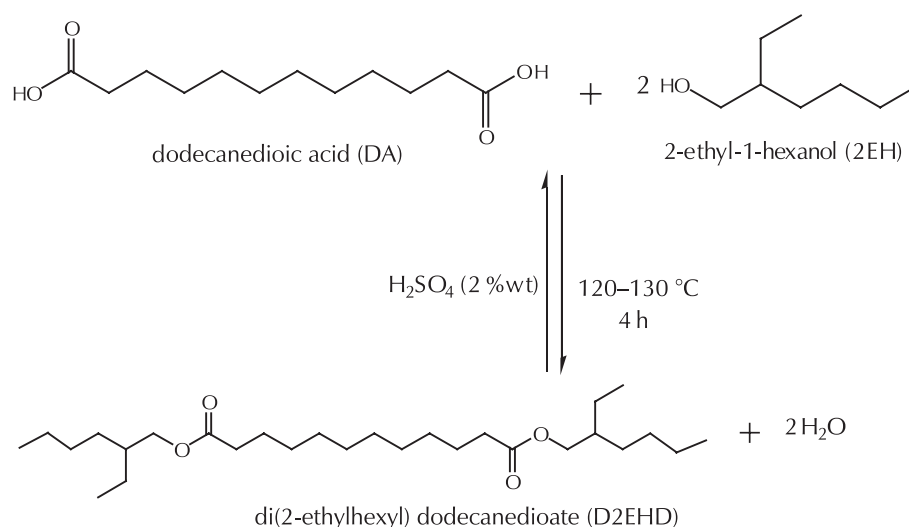


Fig. 1 – Esterification reaction to form di(2-ethylhexyl) dodecanedioate (D2EHD)

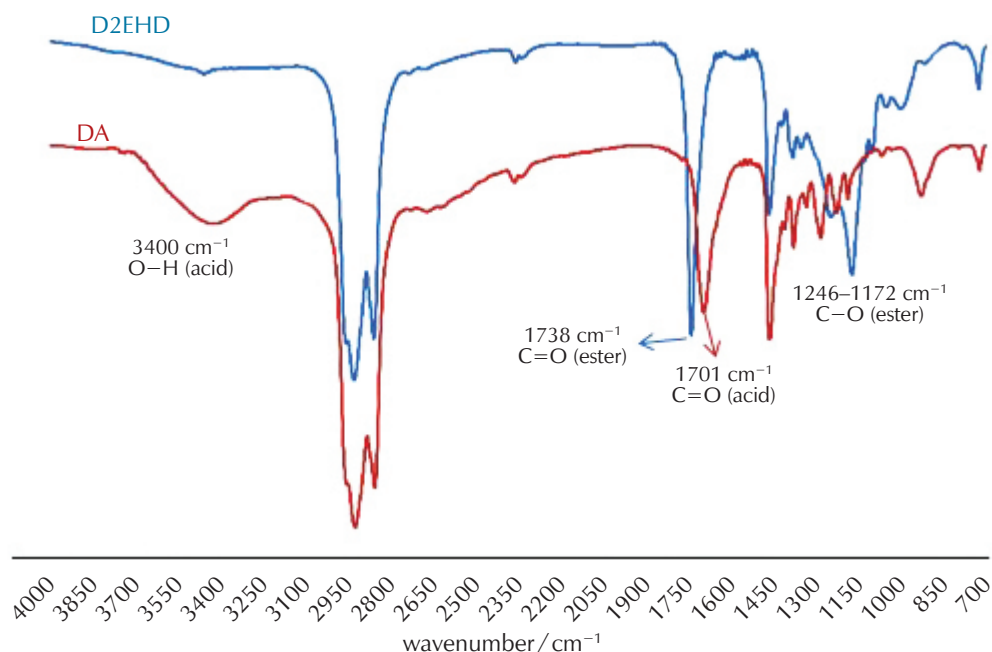


Fig. 2 – FTIR spectra of dodecanedioic acid (DA) and di(2-ethylhexyl) dodecanedioate (D2EHD)

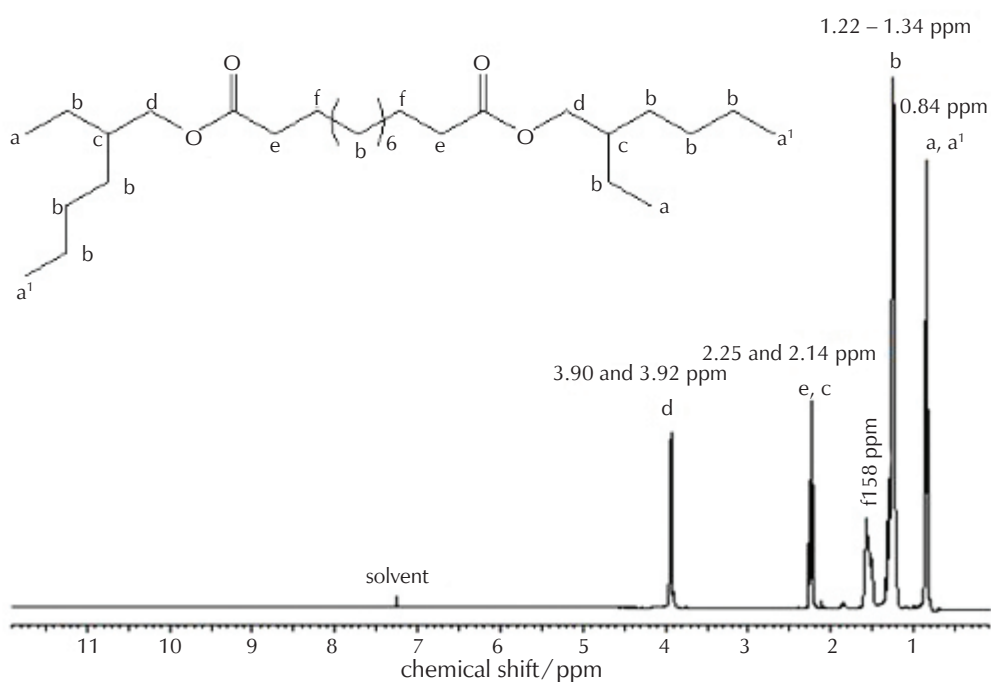


Fig. 3 –  $^1\text{H}$  NMR spectrum of di(2-ethylhexyl) dodecanedioate (D2EHD)

In the FTIR spectra of compound, the absorption bands, due to the aliphatic carboxylic group ( $1710$  and  $1715\text{ cm}^{-1}$ ) were not observed (Fig. 2). This result suggests that dodecanedioic acid undergoes complete esterification under the conditions employed. Production of diesters was characterised with absorption bands of C=O bend of ester at  $1735$ – $1739\text{ cm}^{-1}$ , C–O stretching vibrations of  $1244$ – $1171\text{ cm}^{-1}$  and C–O–C bands in esters of  $965$ – $1101\text{ cm}^{-1}$  for all synthesized diesters.

$^1\text{H}$  NMR spectroscopy is the most valuable form of the technique for compound analysis. The frequency at which any given hydrogen atom in an organic compound resonates is strongly dependent on its precise molecular environment. The  $^1\text{H}$  NMR spectroscopy shows the main signals assignments in some tested diesters, such as D2EHD (Fig. 3). The distinguishable peaks appeared at  $3.90$  and  $3.92\text{ ppm}$  for C=O ester of D2EHD.  $^{13}\text{C}$  NMR spectroscopy as one of the less naturally-abundant isotopes of carbon

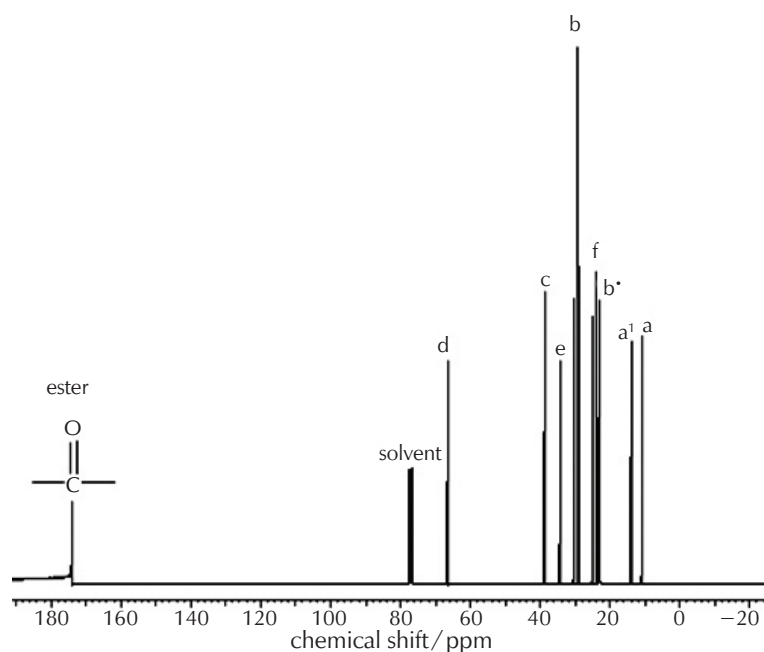


Fig. 4 –  $^{13}\text{C}$  NMR spectrum of di(2-ethylhexyl) dodecanedioate (D2EHD)

also exhibits the phenomenon, but until comparatively recent development in instrumentation and data processing has been made,  $^{13}\text{C}$  NMR spectroscopy is now much more accessible, and since all carbon atoms in the organic compounds give distinctive signals, whether or not they are linked to the protons, a great deal of structural information can be obtained from the spectra.

The  $^{13}\text{C}$  spectroscopy shows the main signals assignment of D2EHD (Fig. 4). The disappearance of carbon atom of the ester carbonyl group of D2EHD diester clearly appeared at 173.12 ppm. The signals at 10.73 to 39.96 ppm refer to the saturated aliphatic carbons atoms for D2EHD. The other distinctive signals at 67.96 for D2EHD refer to O–C of ester.

### 3.2 Lubricity Properties

Table 1 summarizes the lubricity properties of dodecanedioic acid based ester compound as an effective way to introduce branching on the ester. The branched product has significantly improved low temperature characteristics, viscosity, and higher oxidative stability compared to diesters compounds.<sup>14</sup>

#### 3.2.1 Low temperature fluidity

The results of the pour point properties of this study in Table 1 show that the flow property of ester of dodecanedioic acid with different long-chain alcohol is extremely poor, and this limits its use at low operating temperature, especially as automotive engine oil. However, branching in the alcohol fragments leads to very good low temperature.<sup>6</sup> The branching in the di-2-methyl-1-butyl dodecanedioate (D2MBD), di-2-ethylbutyl dodecanedioate (D2EBD), and di-2-ethylhexanol dodecanedioate (D2EHD) were the most effective in decreasing the pour point (PP) to  $-45\text{ }^\circ\text{C}$ ,  $-50\text{ }^\circ\text{C}$ , and  $-55\text{ }^\circ\text{C}$ , respectively. It can be assumed that the presence of a large branching point on the diester creates a steric barrier around the individual molecules and inhibits crystallization, resulting in lower PP.<sup>15</sup> In practice, the usable liquid range is limited by the pour point (PP) at low temperatures and the flash point at high temperatures.

The pour point of dodecanedioic acid esters depends on the structure and weight of alcohols used, as shown in Table 1; it increases with the long-chain alcohol carbons number.<sup>16</sup> The increase in PP of diester in this study was expected due to the saturation and the high molecular weight of dodecanedioic acid esters. All dodecanedioic acid esters were in liquid state at room temperature except didecyl dodecanedioate (DDD) and didodecyl dodecane-

Table 1 – Lubricity properties of dodecanedioic acid based ester

Diester code	Pour point / $^\circ\text{C}$	Flash point / $^\circ\text{C}$	Viscosity at 40 $^\circ\text{C}$ by CSt	Viscosity at 100 $^\circ\text{C}$ by CSt	Viscosity index	Yield /%	Oxidative stability
DED	$-5\pm 4$	$150\pm 5$	5.26	2.40	221.40	88.71	–
DBD	$5\pm 2$	$162\pm 3$	3.67	3.00	353.89	89.15	–
D2BD	$-5\pm 4$	$140\pm 2$	13.42	4.3	222.93	84.09	178.78
DHD	$10\pm 3$	$195\pm 5$	7.56	4.0	308.33	96.48	–
DOD	$20\pm 2$	$210\pm 4$	14.10	5.7	222.13	94.76	202.83
D2OD	$0\pm 5$	$180\pm 3$	21.70	5.6	176.25	88.71	193.81
DDD	$35\pm 3$	$230\pm 5$	22.23	7.0	189.50	96.47	204.23
DDOD	$50\pm 2$	$240\pm 4$	–	–	–	50.38	195.37
D2MBD	$-45\pm 2$	$175\pm 3$	11.13	3.9	240.95	92.16	–
D2EBD	$-55\pm 5$	$180\pm 5$	14.00	4.6	221.57	77.39	196.00
D2EHD	$-50\pm 5$	$200\pm 6$	19.70	6.2	195.70	82.80	188.51
DC3HED	$-30\pm 4$	$140\pm 5$	14.46	4.6	216.34	95.40	–
DOLD	$10\pm 5$	$280\pm 4$	44.68	12.7	169.13	76.98	173.10

DED: Diethyl dodecanedioate, DBD: Dibutyl dodecanedioate, D2BD: Di-2-butyl dodecanedioate, DHD: Dihexyl dodecanedioate, DOD: Dioctyl dodecanedioate, D2OD: Di-2-octyl dodecanedioate, DDD: Didecyl dodecanedioate, DDOD: Didodecyl dodecanedioate D2MBD: Di-2-methyl-1-butyl dodecanedioate, D2EBD: Di-2-ethylbutyl dodecanedioate D2EHD: Di-2-ethylhexanol dodecanedioate, DC3HD: Di cis-3-hexenyl dodecanedioate, DOLD: Dioleil dodecanedioate

dioate (DDOD) that were in solid state. The solidity of dodecanedioic acid esters started from C10 of alcohol used. These solid diesters have been recently used as novel organic phase change materials for thermal energy storage.<sup>13</sup> Although, the molecular weight and long-chain carbon number of dioleil dodecanedioate (DOLD) was the highest compared to all alcohol used, it showed low PP. This is related to the double bond in DOLD.<sup>16</sup> The unsaturated diester causes decreasing in PP for di *cis*-3-hexenyl dodecanedioate (DC3HD) and DOLD, as shown in Table 1.

Good low-temperature fluidity properties of di-2-butyl dodecanedioate (D2BD) and di-2-octyl dodecanedioate (D2OD) are noted compared to the same carbon number of dibutyl dodecanedioate (DBD) and dioctyl dodecanedioate (DOD) due to the presence of the branching in D2BD and D2OD diester. Flash point is another important factor in determining how well oil will behave as a potential lubricant. There are various international standards for defining each, but most agree that oils with a flash point less than 43 °C are flammable, while those having a flash point above this temperature are combustible.<sup>14</sup> As may be seen in Table 1, the flash point of diester of dodecanedioic acid increases with long-chain alcohol to 240 °C due to the high molecular weight compared to 155 °C of short-chain alcohol. In general, the good volatility of diester of dodecanedioic acid is because of their uniform or close to uniform composition. The flash point is slightly affected by the isomers, e.g., D2EHD, D2OD, and DOD have nearly the same flash points.

These data suggest that all values of the flash points are above 155 °C, mostly approaching the level 155–280 °C. One may notice a slight influence of the molecular mass – the flash point values increasing as the molecular mass increases also. The high flash points of the ester of dodecanedioic acid with long-chain alcohol can be ascribed to their structural homogeneity, that is, they contain well-defined hydrocarbon structures. The flash point of some dodecanedioic acid esters, e.g., dihexyl dodecanedioate (DHD), DOD, D2OD, didecyl dodecanedioate (DDD), and DDOD is high to use in lubricants for high temperature applications. Low volatility in diacid ester is desired to eliminate the need to replenish the lost oil, an increase in viscosity during use, and the negative impact of the evaporated oil on the environment.<sup>17,18</sup> In addition, it lowers the flash and the fire points. While some of the diacid ester are suitable for use in lubricants for broad temperature applications, the DBD, DHD, and DOD are only useful in formulating products for use in high temperature applications. This is because their pour points are somewhat higher. This property among diester is compared in Table 1.

### 3.2.2 Viscosity

Esters of dodecanedioic acid showed viscosities in the range of 7–38 cSt at 40 °C, and 3–6 at 100 °C (Table 1). The viscosities of diesters depend on the alcohol used. The results show that the viscosities of diesters of long-chain alcohols are higher than those of diesters of short-chain alcohols. The branched D2EBD and D2EHD diesters recorded very low pour points of approximately < -50 °C, whereas linear long-chain diesters of DHD and DOD showed high

pour point values at > 5 °C. Such variation of pour points indicates that the branching of alkyl chain of esters plays a significant role in the pour point. The linear chain increases the pour point dramatically. Consequently, esters having branched alkyl chain have lower pour points compared to their linear chain analogous members.<sup>19</sup>

The efficiency of the lubricant in reducing the friction and wear is greatly influenced by its viscosity. The viscosity of diester decreases as temperature increases<sup>14</sup> as shown in Table 1. Generally, the least viscous lubricant, which still forces the two moving surfaces apart, is desired. If the lubricant is too viscous, it will require a large amount of energy to move; if it is too thin, the surfaces will rub and friction will increase. The viscosity index highlights how a lubricant's viscosity changes with variations in temperature. From the Viscosity Indexes (VI) data in Table 1, the results show that viscosity at 40 °C and 100 °C increases with increase in chain length (number of alcohol carbons), such as DOD (14.10 and 5.7 cSt) is higher than other diester as DHD (7.56 and 4.0 cSt) and DBD (3.67 and 3.0 cSt) at 40 °C and 100 °C, respectively. A high VI indicates small viscosity changes with temperature. This was noticed in the case of DBD and DHD, which recorded higher VI among the diesters at 353.89 and 308.33, respectively. Therefore, lubricant oil that has a high VI can be expected to undergo minor change in viscosity with temperature extremes, and is considered to have a stable viscosity-temperature relation.<sup>20,21,22</sup> VI is a measure of the viscosity-temperature (VT) relationship. All liquids lose viscosity with an increase in temperature. It is the rate of loss in the viscosity which is of concern in lubricants; a lower decrease rate is preferred in most applications. VI as a measure of loss of viscosity with increasing temperature is a function of the degree and the type of branching in the molecule. In general, the more linear the structure, the greater is the viscosity. Esters of a good VI can be obtained by proper selection of the starting materials, that is, those that have linear structures.<sup>17</sup> The size of the optimal chain length is around eight carbon atoms. Since branching in the hydrocarbon chain lowers the pour point without significantly affecting the VI, the viscosity was not significantly affected by the branching such as D2EBD and D2EHD compared to the equivalent diesters that have the same weight but linear structures such as DHD and DOD. The synthetic esters for use in low-temperature applications are made by using a mixture of linear and branched starting materials.<sup>17</sup> The presence of the ester functional group has no effect on the viscosity due to the hydrocarbon chain of the synthetic ester molecule. Hence, the synthetic ester viscosity is comparable to that of hydrocarbons of similar molecular weight and branching. One way to explain the similarity of most physical properties between synthetic esters and hydrocarbon oils is by considering the ester functional group an equivalent of a methylene group. Properties that differ between the two as a consequence of the ester functional group include VI, and pour points. The two parameters are lower in esters than in hydrocarbons of the same molecular size. Since synthetic esters contain hydrocarbon chain in the alcohol- and the acid-derived portion, their properties vary depending on the structures of these moieties. As the data shows, an increase in the chain length of the alcohol only increases viscosity but decreases VI. The main advantage

of the good VI is that the base oil does not need a viscosity improver to maintain its viscosity at high temperatures.<sup>23</sup>

### 3.2.3 Oxidative stability

Oxidation stability is of primary concern in the case of synthetic esters. Since the esters contain hydrocarbon chains in both the carboxylic acid and the alcohol portions of their structure, the oxidation stability in esters is important. Esters differ in their rates of oxidation, depending upon the structure and the branching of the hydrocarbon chains.<sup>24,25</sup> Like other hydrocarbon materials, the oxidation rate of esters is higher at higher temperatures. Esters made

from dodecanedioic acid and long-chain alcohol (Table 1) decompose around 178–204 °C, those made from secondary alcohols such as D2BD and D2OD decompose around 178 and 193 °C, respectively. Whereas, esters made from dodecanedioic acid and branched long-chain alcohol such as D2EBD and D2EHD decompose around 196 and 188 °C, respectively. Because of the higher oxidation stability, diesters are favoured over other types of synthetic esters in most high temperature applications. The synthesized diesters of DOD and DDD esters, as shown in Figs. 5 and 6, decomposed at high temperature around 202.83 and 204.23°C, respectively. The oxidative stability increased with increasing chain length of the esterified acid and alcohol.<sup>26,27</sup>

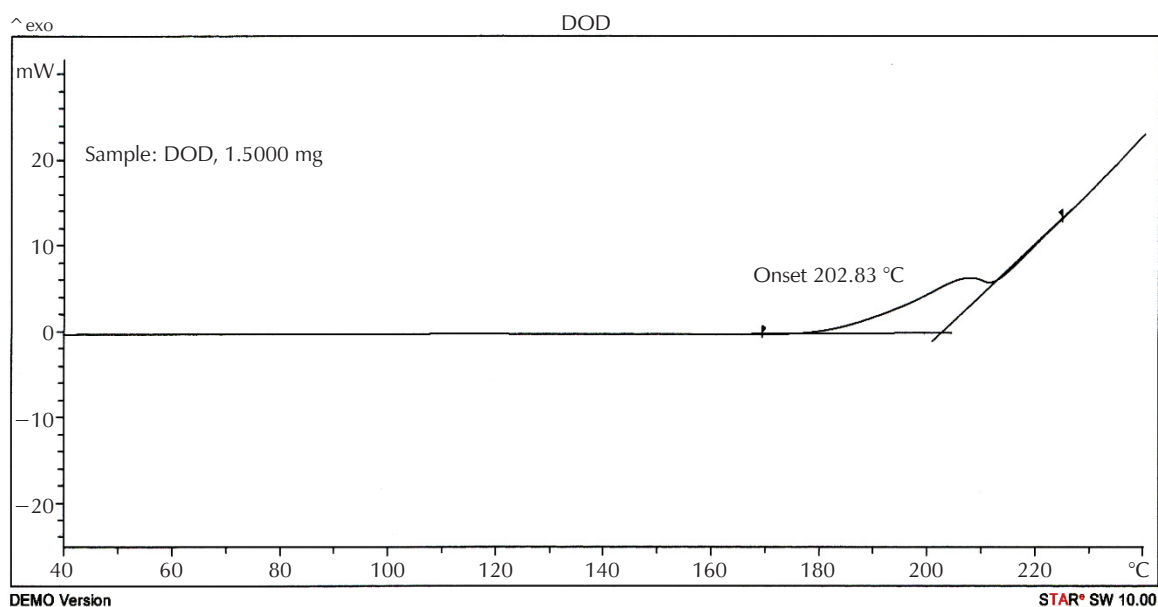


Fig. 5 – Differential scanning calorimetry oxidation stability curve of DOD

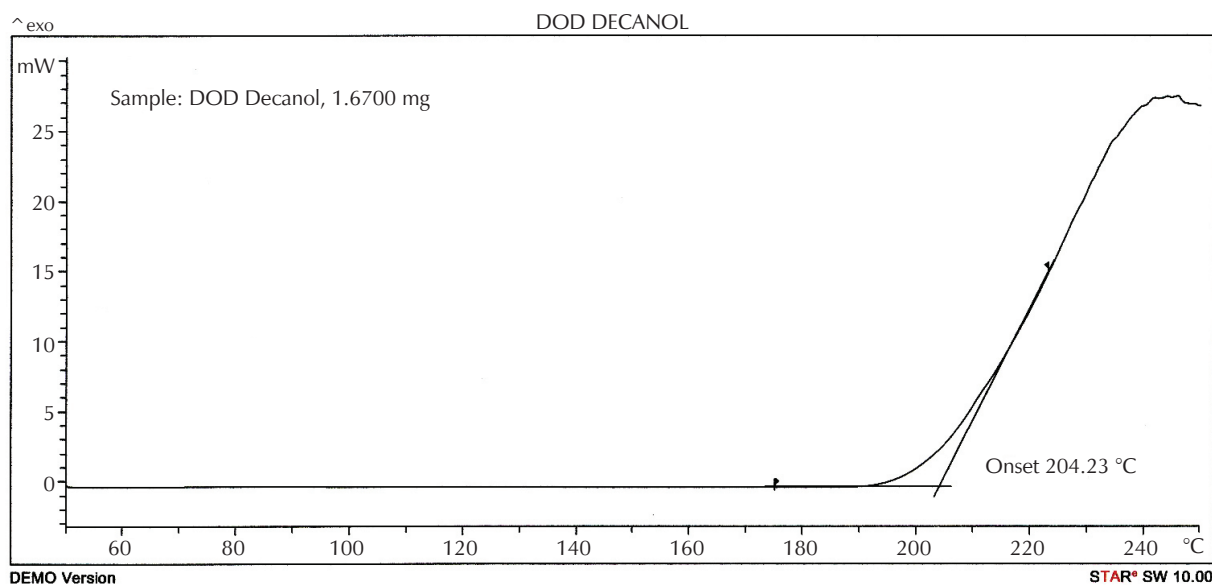


Fig. 6 – Differential scanning calorimetry oxidation stability curve of DDD

The prepared new compound was screened to measure its oxidation stability using PDSC through determination of onset temperature (OT). The OT is the temperature at which a rapid increase in the rate of oxidation is observed at a constant, high pressure (200 psi). A high OT would suggest high oxidation stability of the material. OT was calculated from a plot of heat flow (W/g) vs. temperature that was generated by the sample upon degradation and by definition. Good oxidation and hydrolytic stability properties in lubricants are a pre-requisite to their use in most applications, especially for applications such as engine oils that are exposed to high operating temperatures.<sup>5</sup> Oxidation is initiated by the reaction of oxygen with the hydrocarbon materials to initially form hydroperoxides and peroxides, which thermally decompose or rearrange to form precursors to harmful products.

## 4 Conclusion

Symmetrical diesters based on medium carbon chain acid, dodecanedioic acid, and short- and medium-chain alcohols, such as diethyl dodecanedioate, dibutyl dodecanedioate, dihexyl dodecanedioate, dioctyl dodecanedioate, and selected branched alcohols of di-2-methyl-1-butyl dodecanedioate, di-2-ethylbutyl dodecanedioate, and di-2-ethylhexanol dodecanedioate, have been successfully synthesized. Some new dodecanedioic diesters have high flash points and very good (low temperature) pour points. All values recorded for the viscosity index are above 160. The overall properties can be modified by altering the length of both the alkyl chain provided by the branching. From the present study, it can be concluded that D2MBD, D2EBD, and D2EHD, which have a branched group in their molecular structure, have a low pour point of less than  $-45$  °C and good lubricity qualities. They are especially suitable in formulating lubricants for use in cold climates, without the need of a pour point depressant. Their viscosity indices are well over 200, making them suitable to formulate lubricants for warm climates as well. The major application area for aliphatic diacid esters is in automotive engine oils that require low pour point, low volatility, and good thermo-oxidative stability.

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## List of abbreviations

ASTM	– American Standard Test Method
DA	– dodecanedioic acid
DED	– diethyl dodecanedioate
DBD	– dibutyl dodecanedioate

D2BD	– di-2-butyl dodecanedioate
DHD	– dihexyl dodecanedioate
DOD	– dioctyl dodecanedioate
D2OD	– di-2-octyl dodecanedioate
DDD	– didecyl dodecanedioate
DDOD	– didodecyl dodecanedioate
D2MBD	– di-2-methyl-1-butyl dodecanedioate
D2EBD	– di-2-ethylbutyl dodecanedioate
D2EHD	– di-2-ethylhexanol dodecanedioate
DC3HD	– di cis-3-hexenyl dodecanedioate
DOLD	– dioleyl dodecanedioate
FP	– flash point
IR	– infrared spectroscopy
<sup>1</sup> H NMR	– proton-1 nuclear magnetic resonance spectroscopy
<sup>13</sup> C NMR	– carbon-13 nuclear magnetic resonance spectroscopy
OT	– oxidation onset temperature
PDSC	– differential scanning calorimetry
PP	– pour point
SD	– standard deviation
VI	– viscosity index

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## SAŽETAK

Utjecaj dugolančanog i razgranatog alkohola  
na mazivost estera na bazi dodekandiojske kiseline

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Sintetizirano je trinaest uzoraka estera na bazi dodekandiojske kiseline različitih kemijskih struktura. Među njima su bili di-2-oktil dodekandioat, didecil dodekandioat, di-2-etilheksanol dodekandioat, di-2-etilbutil dodekandioat, dioktil dodekandioat, diheksil dodekandioat i dioleil dodekandioat. Diesteri su sintetizirani esterifikacijom dodekandiojske kiseline s odabranim dugolančanim i razgranatim alkoholima s kiselinskim katalizatorom H<sub>2</sub>SO<sub>4</sub>. Ti su esteri ispitani u smislu njihove prikladnosti za primjenu kao maziva. Rezultati su pokazali da su na svojstva mazivosti, temeljena na njihovoj točki tečenja, točki zapaljenja i oksidacijskoj stabilnosti estera, znatno utjecali upotrijebljeni linearni i razgranati alkoholi. Uočeno je izvrsno svojstvo točke tečenja di-2-etilbutil dodekandioata i di-2-etilheksanol dodekandioata pri –55 °C i –50 °C u usporedbi s njihovim istim ravnopravnim esterima ugljikova broja diheksil dodekandioata pri 10 °C i dioktil dodekandioata pri 20 °C, zbog prisutnosti razgranate skupine u strukturi njihove blizine molekule. Međutim, prisutnost razgranate strukture neznatno je utjecala na točke zapaljenja estera. Odabrani esteri mogli bi se rabiti za biomaziva ili motorno ulje.

**Ključne riječi**

*Ester na bazi dodekandiojske kiseline, točka tečenja, točka zapaljenja, indeks viskoznosti*

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