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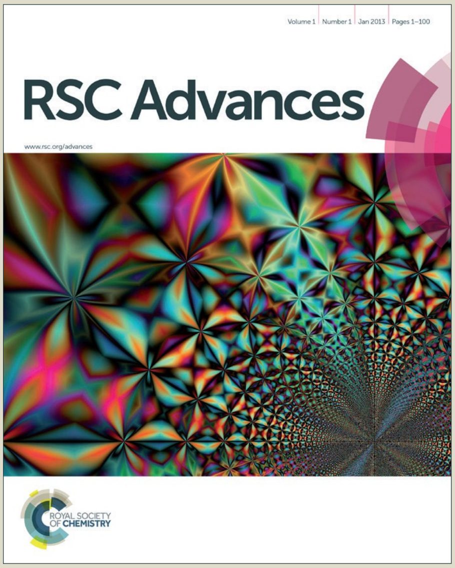

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Synthesis of levulinic acid-based polyol ester and its influence on tribological behavior as potential lubricant

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Abstract

Levulinic acid (LA) has been identified by the US Department of Energy as a top platform chemical and regarded as one of the twelve most promising molecules derived from biomass. In this study, it was used to prepare lubricant base stocks by esterification with three different polyols including neopentyl glycol (NPG), trimethylolpropane (TMP), and pentaerythritol (PE) in the presence of sulfuric acid. The crude product was distilled to obtain target product with a purity above 95%. These products of polyol ester were characterized using ^{1}H NMR and mass spectral techniques. The lubricant properties, such as kinematic viscosity, viscosity index, pour and flash points, were evaluated using standard ASTM methods. Among the base stocks prepared, TMP-tri-LA ester exhibited superior lubricant properties like good kinematic viscosity at 40°C (87.28) and at 100°C (8.42), viscosity index (48), low pour point (-25 °C), high flash point (238 °C), cloud point (-4 °C) , copper strip corrosion (1a) and Volatility at 120°C (0.41%). Wear prevention characteristics of this ester was tested and performed low coefficient of friction and small wear scar diameters. It was found that this kind of polyol ester was suitable for lubricant base stocks.

Keywords: Levulinic acid, Polyol esters, Biolubricant, Lubricant properties

1. Introduction

Biodegradable polyol esters, which served as biolubricant components, have aroused more interest because of their excellent lubricity, biodegradability, viscosity-temperature characteristics, and low volatility.[1] However, natural triglycerides are thermally sensitive at high temperature. The main reason of this phenomenon is the presence of hydrogen atoms on the β position of the glycerol molecule backbone, [2] since this structural feature is prone to the partial fragmentation of the molecule and the formation of unsaturated compounds. The formed compounds under polymerization led to the increase of the liquid's viscosity and resulted in the formation of precipitate particles.[3] Thus, natural triglycerides are generally not appropriate for the applications of lubricant that require heat resistance. This problem could be easily solved by replacing glycerol with another special polyhydric alcohol which does not contain β-hydrogen atoms. [4, 5] In previous literatures, researchers used neopentyl polyols such as neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) for this purpose.[6-8] So far, the investigation of polyol esters biolubricant preparation has been conducted using polyols with various fatty acids by transesterification or esterification. Most of fatty acids reported in literature are generally obtained from animal oils such as beef tallow, lard, mutton tallow as well as vegetable oils, such as soybean oil, sunflower oil, rapeseed oil, castor oil, olive oil, palm kernel oil and waste cooking oil.[9-15] These high monounsaturated oils have optimal performance as raw materials to generate environment friendly lubricants with high performance. However, part of these oils are edible, and their use for the production of lubricants will indirectly influence the food demand. Hence, more attention is paid for the preparation of non-edible oil-based polyol esters containing any unusual fatty acids.

Levulinic acid (LA), having five carbon atoms with carboxyl group and ketone functional groups, can be easily produced from glucose, fructose, starch and lignocellulosic residues.[16] It has been identified by the US Department of Energy as a top platform chemical and regarded as one of the twelve most promising molecules derived from biomass, because it can be transformed into a variety of other important compounds in the chemical industry.[17-18] In the 1990s, there were some patents about the conversion of LA production from lignocellulose by acid degradation at an elevated temperature and the theoretical yield of LA could reach 55% (molar yield based on hexose polymer content of wood feed) under the optimal condition.[19-20] Recent research demonstrated that LA could be obtained from cellulose in the presence of catalyst such as functionalized ionic liquids,[21] dilute acid,[22] alkaline-treated zeolite,[23] and Fe/HY catalyst.[24] LA produced from cellulose has attracted considerable attention and become one of the key steps for the biomass refining.[21] Meanwhile, the esterification of levulinic acid with polyols could easily implemented and the polyol esters based on levulinic acid are expected to have similar properties of lubricant compared to other polyol esters. Therefore, there might be broader application prospects for it to produce biolubricant compared to other vegetable oils.

Hence, this study was aimed at employing levulinic acid and polyols such as NPG (dihydric), TMP (trihydric) and PE (tetrahydric) for the synthesis of polyol esters. The potential of the synthesized esters as base stocks for biodegradable lubricants was also evaluated.

2. Materials and methods

2.1. Chemicals

NPG, TMP and PE were obtained from Fuchen Chemical Co. Ltd. (Tianjin, China); levulinic acid (LA) with the purity of 99% was purchased from Adamas Reagent Co., Ltd.; the sulfuric acid with purity of 98% was procured from Beijing Chemical Factory. The other solvents of analytical grade were obtained from Beijing Chemical Factory; mineral oil with similar viscosity of LA-based TMP ester was provided kindly by SINOPEC in Beijing.

2.2. Analysis

^{1}H NMR spectra were obtained using a Bruker AR X 400 Spectrometer (400, 200 MHz). Mass spectra were recorded on a VG Auto Spec-M (Manchester, UK) and the compounds including LA, mono-, di- and trisubstituted esters in the reaction mixture were quantified using a GC-2010 gas chromatography (Shimadzu, Japan) equipping with a DB-1ht capillary column (30m × 0.25mm × 0.1μm; J&W Scientific, USA) and a flame ionizing detector (FID). The column temperature was held at 110°C, then heated to 132°C at 12°C/min, and to 180°C at 30°C/min and finally to 300 °C at 20 °C/min and then maintained for 5min. The temperatures of the injector and detector were both set at 300 °C.

2.3. Viscosity

Viscosity measurements were conducted at 40°C and 100°C using Cannon Fenske viscometer tubes in a Cannon Constant Temperature Viscosity Bath (Hunan Petrochemical Instrument CO., LTD.). Viscosity and the viscosity index were calculated using ASTM methods D445 and D2270, respectively. All viscosity measurements were carried out in triplicate, and the average value was reported.

2.4 Pour point

Pour points were determined by ASTM method D97 with an accuracy of ±3°C an using Automatic Pour Point Tester, manufactured by Hunan Petrochemical Instrument CO., LTD.. All runs were carried out in duplicate. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring.

2.5 Flash point

Flash point of the products was determined using a Flash Point Tester (Hunan Petrochemical Instrument CO., LTD.) according to ASTM D93 method. The lowest temperature for application of the test flame, which caused the vapor above the surface of the liquid to ignite, was taken as the flash point of the product at ambient barometric pressure.

2.6 Cloud point

Cloud points were determined by standard ASTM D2500 using Cloud Point Apparatus (Beijing Timepower Measure and Control equipment CO., LTD.).

2.7 Copper strip corrosion

Copper strip corrosion was determined using Copper Strip Corrosion Tester (Beijing Timepower Measure and Control equipment CO., LTD.). The appearance of the Cu strip was assessed by comparison with Copper Strip Corrosion Standards (ASTM D130).

2.8 The volatility determination

The volatility was determined in agreement with ASTM method D6184 in an electrical stove using glass pans of 4 cm in diameter.

2.9Themogravimetric analysis (TGA)

Themogravimetric analysis (TGA) is a measure to evaluate the thermal stability of materials. A higher TGA onset temperature represents a higher thermal stability of a material. Thermal behavior of the LA-based polyol esters were studied using a PerkinElmer thermo gravimetric differential thermal analyzer (TG/DTA) under a flow of nitrogen (flow rate of 40 ml/min) at a constant heating rate of $10^{o}C$ /min.

2.10HFRR (High frequency reciprocating rig) configuration

The HFRR wear test was used to investigate the effect of ester under fluid film lubrication as shown in Figure 1. The HFRR test (ASTM D6079) used in this study involves a weighted cast iron pin cylinder (6 mm length) and a stationary cast iron plat (15 mm*15 mm), which is completely submerged in a 10 ml of sample. The ball and disk is tested at room temperature and brought into contact with each other and the entire apparatus is vibrated at 50 Hz for 75 min with the load 200g. The sliding stroke is maintained at 2 mm. Several blends of LA-based TMP ester including 1%, 3%, 7%, 10%, 20% and 100%, are tested and analyzed. Each test was carried out three times repeatedly to observe any errors need to be analyzed.

2.11 Synthesis methods

2. 11.1 Preparation of NPG diester of LA (NPG-di-LA)

Synthesis of NPG-di-LA was according to Figure 2 (A), and the catalyst was sulfuric acid. The reaction was performed in a temperature controlled reactor with mechanical stirring. The reaction mixture contained 500.00g (4.30mol) LA and 149.15g (1.43mol) NPG. It was incubated for 2h at $95^{o}C$ in presence of 6.49g sulfuric acid (1% of total mixture). The process of the reaction was monitored by GC, and after completion of the reaction, the crude product was distilled by Rotary Film Molecular Distillation (VTA GMBH & Co. KG, Germany) at 140°C and 1mbar to remove sulfuric acid and excess LA. After that, the obtained product from the first distillation was distilled once again at 170°C and 0.3mbar to get the final NPG-di-LA product with purity of 96.21%. The structure of the target product was characterized by ^{1}HNMR and mass studies.

^{1}H NMR ($CDCl_3$, δ ppm): 0.97 [s, 6H, 2×(–CH_3)], 2.21 [s, 6H, 2×(–CO–CH_3)], 2.59-2.62 [m, 4H, 2×(–CO–CH_2–)], 2.76-2.79 [s, 4H, 2×(–CH_2–CO-)], 3.90 [s, 4H, 2×(–CO–CH_2–)]; ESI MS: m/z 323.15 $[M+Na]^+$.

2. 11.2. Preparation of TMP triester of LA (TMP-tri-LA)

Synthesis of TMP-tri-LA was according to Figure 2 (B), and the catalyst was sulfuric acid. The reaction was performed in a temperature controlled reactor with mechanical stirring. The reaction mixture including 500.00g (4.30mol) LA and 144.43g (1.08mol) TMP. It was incubated for 2h at 95°C in presence of 6.44g sulfuric acid (1% of total mixture). The process of the reaction was monitored by GC, and after completion of the reaction, the crude product was distilled by Rotary Film Molecular Distillation (VTA GMBH & Co. KG, Germany) at 140°C and 1mbar to remove sulfuric acid and excess

LA. Thereafter, the obtained product from the first distillation was distilled once again at 230°C and 0.009mbar to get the final TMP-tri-LA with purity of 95.82%. The structure of the target product was characterized by ^{1}HNMR and mass studies.

^{1}H NMR ($CDCl_3$, δ ppm): 0.89-0.92 [s, 3H, (–CH_3)], 1.48-1.50 [s, 2H, (–CH_2–CH_3)], 2.20 [s, 9H, 3×(–CO–CH_3)], 2.58-2.60 [s, 6H, 3×(–CO–CH_2–)], 2.76-2.79 [s, 6H, 3×(–CH_2–CO-)], 4.03 [s, 6H, 3×(–CO–CH_2–)]; ESI MS: m/z 451.20 $[M+Na]^+$.

2. 11.3 Preparation of PE tetraester of LA (PE-tetra-LA)

Synthesis of PE-tetra-LA was according to Figure 2 (C), and the catalyst was sulfuric acid. The reaction was performed in a temperature controlled reactor with mechanical stirring. The reaction mixture contained 500.00g (4.30mol) LA and 117.24g (0.86mol) TMP. It was incubated for 12h at 115°C in presence of 6.17g sulfuric acid (1% of total mixture). The process of the reaction was monitored by GC, and after completion of the reaction, the crude product was distilled by Rotary Film Molecular Distillation (VTA GMBH & Co. KG, Germany) at 140 °C and 1mbar to remove sulfuric acid and excess LA. Afterward, the obtained product from the first distillation was distilled once again at 290 °C and 0.0085mbar to get the final TMP-tri-LA product with purity of 95.01%. The structure of the target product was characterized by ^{1}HNMR and mass studies.

^{1}H NMR ($CDCl_3$, δ ppm): 2.19 [s, 12H, 4×($–CO–CH_3$)], 2.57-2.60 [s, 8H, 4×($–CO–CH_2–$)], 2.75-2.78 [s, 8H, 4×($–CH_2–CO-$)], 4.12 [s, 8H, 4×($–CO–CH_2–$)]; ESI MS: m/z 551.21 $[M+Na]^+$.

3. Results and discussion

3.1 Characterization and physico-chemical properties of esters

Polyol esters, derived from esterification or transesterification using plant oils and animal oils with neopentyl polyols without hydrogen atoms on the β carbon, have been widely used for lubricants. Due to their superior physico-chemical properties and performances compared with mineral oils, its applications have expanded largely. The present study was focused on the use of non-edible levulinic acid, a promising platform chemical derived from biomass, combined with dihydric, trihydric and tetrahydric alcohols named NPG, TMP and PE respectively to produce LA-based polyol esters. The polyol esters based on levulinic acid were expected to have similar properties of lubricant compared with other polyol esters.

The purity of the levulinic acid-based polyol esters was determined by GC analysis and found to exceed 95%. The structures of polyol esters were confirmed using ^{1}H NMR (Figure 4) and ESI-MS (Figure 3) spectral studies. The molecular ions 323.15 $[M+Na]^+$, 451.20 $[M+Na]^+$, 551.21 $[M+Na]^+$ correspond to compounds NPG-di-LA; (B) TMP-tri-LA; (C) PE-tetra-LA, respectively. All the products were characterized for their physico-chemical properties, such as viscosity at 40°C and 100°C, viscosity index (VI), pour point, flash point, cloud point and copper strip corrosion (Table 1).

Kinematic viscosity is an important characteristic to exhibit the relationship between viscosity and temperature. The property of the viscosity–temperature directly represents lubricant's performance and determines its application. Table 1 showed the kinematic viscosities of different ester products. The NPG-di-LA, TMP-tri-LA and PE-tetra-LA exhibited their kinematic viscosity at 40 °C in the range of ISO VG10, reaching 17.29, 87.28 and 417.45, respectively. At 100°C their kinematic viscosities were 3.35, 8.42 and 19.14 cSt. Viscosity of the polyol ester base fluids generally increases with the increase of the number of present acyl functionalities.[25] In this study, the LA based esters prepared with NPG, TMP and PE exhibited similar trend with the result of Gryglewicz's and Padmaja's in term of the relationship between pour point and the number of branches in molecule. [25-26]

The viscosity index (VI) is an another parameter generally used for evaluating the performance of a potential lubricant. By detecting the value of viscosity index, variation of the kinematic viscosity with temperature can be known. Generally, the higher its value, the lower variation of viscosity with the temperature, and so the better performance of the lubricant. Table 2 also showed the property of NPG-di-LA, TMP-tri-LA, PE-tetra-LA with viscosity index 30, 48 and 15, respectively. As a high viscosity index means there was little change over a wide temperature range. The performance of the three synthesized esters need futher improvement to become lubricant with high viscosity index which was a desirable property for a lubricant by adding additives in formulated lubricants. The low viscosity index can also be overcome by increasing the molecular weight of the products and altering the structure of their molecules, especially the introduction of double bond in their composition.[27,28] The reaction between LA and furfural, which is also a platform chemical from lignocellulosic residues, can be easily implemented in aq. NaOH.[29] The product, 6-furfurylidene levulinic acid, can be used to prepare biolubricant base stocks by esterification with polyols. This kind of polyol esters contains the double bond and the molecular weight is higher than levulinic acid-based polyol esters. So the viscosity index could be improved obviously.

Pour point is an another key parameter to assess the performance and application of a potential lubricant. It is the temperature that a lubricant can't flow when a jar is tilted during cooling environment. Lubricants with a low pour point is conducive to the operation of the engine in cold temperature climates. The pour point of ester products in this study was measured by ASTM D97. Generally, pour points of polyol esters prepared from unsaturated fatty acids were very low, and a similar trend was observed in term of the pour points of NPG-di-LA (-34 ^{o}C), TMP-tri-LA(-25 ^{o}C) and PE-tetra-LA (-8 ^{o}C). It was found that the pour point of NPG-di-LA with less number of acyl chains was lower compared to other polyols, which could be due to more effective disruption of molecules packing compared to PE and TMP esters. However, the pour point of PE-tetra-LA was high. It suggested that the molecular configuration of NPG and TMP esters was more effective at disrupting molecule packing compared to PE ester. Such low pour points were useful for applications in machine tool and hydraulic systems.[30] Compared with recent researches which reported the pour points of other fat acid-based polyol esters, the NPG-di-La and TMP-tri-LA ester exhibited competitive characteristic of lower temperature, it's pour points lower than product (pour point -27 ^{o}C) from castor oil and TMP [12] and that of the polyol ester (pour point -18 °C) from rapeseed oil and TMP, [32] and polyol ester (pour point -6 °C) from rubber seed oil and TMP. [33]

The flash point is defined as the minimum temperature at which the liquid produces a sufficient concentration of vapor above it that it forms an ignitable mixture with air. The lower flash point is, the greater fire hazard. The TMP-tri-LA ester possessed excellent thermal stability with flash points at 228°C followed by PE-tetra-LA ester at 210°C and NPG-di-LA at 185°C. The TMP-tri-LA ester had higher thermal stability followed by NPG-di-LA and PE-tetra-LA esters. This trend was different from other synthetic esters.[31] Flash points of all the polyol esters were found to be very high within the range of 185–228 °C, and the esters with flash point ≥ 165°C lie well within the range of hydraulic oils.[34]

Cloud point was the temperature at which liquid becomes cloudy in appearance. A high cloud point could lead to filter plugging and poor pumpability in cold weather applications. Among the new three kinds of esters in this paper, NPG-di-LA had the lowest cloud point, which reached -11 oC and even lower. The cloud point of TMP-tri-LA was -4 °C followed by 7 °C of PE-tetra-LA.

Copper corrosion test was also conducted in order to measure the tendency to cause metal deterioration. The result indicated that three kinds of the levulinic acid-based polyol esters were class 1a (slight tarnish). The term "class" represents the property of copper corrosion, and it is judged according to the color of the copper strip. The lower the copper corrosion property the lower the "class" of the oil. 1a was the lowest class in Copper Strip Corrosion Standards (ASTM D130). Thus, all the esters in this study had low corrosion on metal materials.

The volatility relates to the potential loss of lubricant and to the environmental impact of the volatile components of the fluid. Both European and U.S. OEM and industry organizations include volatility in their specifications.[35] In this study, NPG-di-LA, TMP-tri-LA and PE-tetra-LA exhibited very low volatility with only 0.57%, 0.41% and 0.33% of weight loss at 120 ^{o}C, respectively. The loss of three kinds of the levulinic acid-based polyol esters due to high-temperature volatility was found to decrease steadily with an increase in carbon numbers. Therefore, in levulinic acid-based polyol esters formulations, volatility is not a problem, which is due to higher molecular weight associated with the structure of glycerol analogues.

TGA is a measure to evaluate the thermal stability of materials. Generally, the higher T_{onset} of a material, the higher is its thermal stability. In previous literatures, some researchers have used this method to measure the thermo-oxidative stability of oils.[36-37] According to the TGA analytical results as shown in Figure 5, TGA curves of all samples had similar behavior. The accurate analysis of TGA curves was summarized in Table 2. It was also found that the three prepared levulinic acid-based polyol esters possessed good thermal stability. NPG-di-LA, TMP-tri-LA, and PE-tetra-LA were thermally stable with less than 4% mass weight loss below the temperature of 189^{o}C, 255^{o}C and 222^{o}C, respectively. Besides, about 9-10% of weight loss was observed for each sample within the temperature range of 203–205^{o}C, 281–286^{o}C and 252–259^{o}C, respectively. The weight loss of the NPG-di-LA, TMP-tri-LA, and PE-tetra-LA reached 97% when each of the temperature achieved 579, 487 and 684°C, respectively. Then, there was no further loss of weight with any increasing temperature. It is known that levulinic acid-based polyol esters are not susceptible to undergo autoxidation reactions. While these TGA measurements provided a preliminary estimate of the stability of a lubricant, further chemical studies would be necessary to check for the stability and functions in these lubricants.

Among the three levulinic acid-based polyol esters, TMP ester exhibited superior properties such as pour point, viscosity index and oxidation stability which were similar to that of TMP trioleate.[38] Due to its high viscosity index, high thermal stability and low pour point, TMP-tri-LA ester could be considered as a potential biodegradable lubricant base stock.

3.2 Tribological properties of TMP-tri-LA

3.2.1 Coefficient of friction (COF)

Figure 6. showed the friction coefficient plotted against the sliding time for various percentages of TMP-tri-LA biolubricants. The results of the figure depict that the value of friction coefficient ranged from 0.007 to 0.17. For ordinary mineral oil (0% ester), it can be seen that the coefficient of friction which is 0.15 on average is the highest within the operation time. For samples of 3%, 7%, 10%, 20% TMP-tri-LA in mineral oil, the coefficient of friction was higher at the beginning and then it fell down rapidly. The 100% TMP-tri-LA kept constantly low coefficient of friction which was 0.09 on average within the operation time. A considerable improvement of friction coefficient was observed with addition of TMP-tri-LA ester in ordinary mineral oil. This phenomena was consistent with Madankara's work which claimed that friction coefficient was reduced significantly by adding hydroxy ester product to diesel fuel.[39] The TMP-tri-LA component of biolubricants formed multi and mono

layer on the surface of the rubbing zone and make stable film to prevent the contact between the surfaces.

3.2.2 Wear scar diameter (WSD)

The frictional wear results by the addition of different percentages of TMP-tri-LA ester to mineral oil were studied using HFRR apparatus. Microscope images of wear scar generated on the surface of a test sample were showed in Figure 7 when different percentages of TMP-tri-LA in ordinary mineral oil were used as lubricant contact fluids. It is evident in Figure 8, the highest wear scar diameter of 300µm was generated when 1% ester in ordinary mineral oil. The ordinary mineral oil (0% ester) has generated a wear scar diameter of 291µm. There was a significant reduction in wear scar diameter with a higher percentages of TMP-tri-LA in ordinary mineral oil. The significance improvement in wear scar diameter of 132µm was found for the 100% TMP-tri-LA product. It was reported in previous researches that TMP esters of palm and palm kernel (*E.gue-neensis*) oil had resulted in wear scar diameters of 200–350µm and200–400µm, respectively.[40] Comparatively, the TMP-tri-LA ester exhibited superior lubricity performance comparing with other biolubricants.

The possible mechanism by which the friction was reduced was that the uniform molecule structure of TMP-tri-LA ester formed a monolayer film in the contact area with the addition of different percentages of ester to mineral oil.of lubrication is the good monolayer film formed by the uniform molecule structure of TMP-tri-LA ester in the contact area with the addition of different percentages of ester to mineral oil. Basically, poyol esters are well known that they can provide good lubricity because of its uniform molecule structure.[41,42] Fatty acids used to synthesize poyol esters have longer branched chains than ordinary mineral oil. This kind of molecule structure offers formation of good monolayer film on sliding surface. The second possible mechanism of lubrication is the polarity of molecule of TMP-tri-LA ester that contributes to better lubricity characteristic. The property of the molecular structure of the polyol ester is a polar at one end and non-polarity at the other end. The reason that friction was reduced as percentages of ester to mineral oil increased is that molecular adsorption on the surface of metal was enhanced. The friction was reduced as percentages of ester added to mineral oil increased was resulted from the enhancement of molecular adsorption on the surface of metal. One end of the molecular was attracted strongly to metal surface due to the polarity and the other one end was extended out. This distribution of moleculars in the mixture samples produced a strong barrier to avoid direct friction between two surfaces. [43,44,45] So, there is a significant reduction in wear scar diameter with addition of TMP-tri-LA ester in ordinary mineral oil. This phenomena was consistent with other researchers' results that wear scar diameter got smaller and friction was reduced obviously when carboxylate group in ester and the polarity increased in the ordinary mineral oil. [46,47]

4. Conclusions

LA was a promising derivative derived from biomass. In this study, a new kind of levulinic acid-based polyol esters was prepared by esterification of levulinic acid with three different kinds of polyol. The crude product was distilled to obtain target product with purity of above 95%. Among the three polyol esters obtained in this study, TMP-tri-LA ester exhibited superior properties of lubricant like good viscosity index, low pour point, high flash point, low cloud point and copper strip corrosion, low volatility. The biolubricity of TMP-tri-LA ester was tested on a High Frequency Reciprocating Rig (HFRR) apparatus. The result exhibited that this kind of biolubricant performed low coefficient of friction and wear scar diameters. It suggested that this kind of polyol ester could be regarded as potential base stocks for production of lubricant with high performance.

Acknowledgements

The authors wish to express thanks for the supports from the National High Technology Research and Development 863 Program of China (grant no. 2013AA050702, 2012AA022304), the Fundamental Research Funds for the Central Universities (YS1407) and the Second Generation Biofuel Feedstock System of China Petroleum Funding, this project also supported by the State Key Laboratory of Motor Vehicle Biofuel Technology (KFKT2014004).

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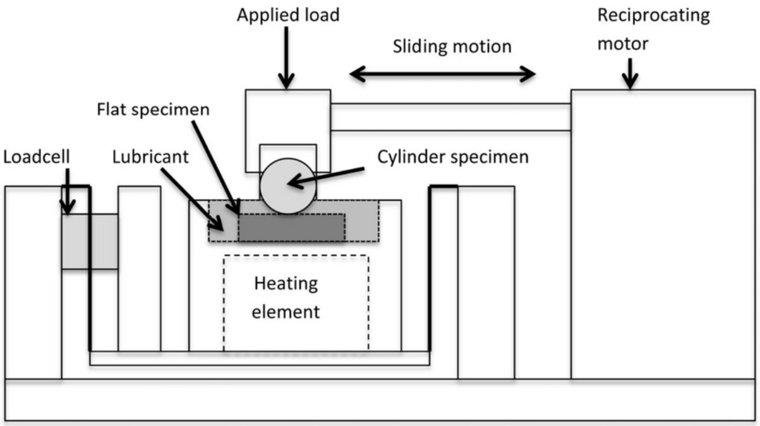

Fig. 1. The schematic diagram of HFRR wear test.

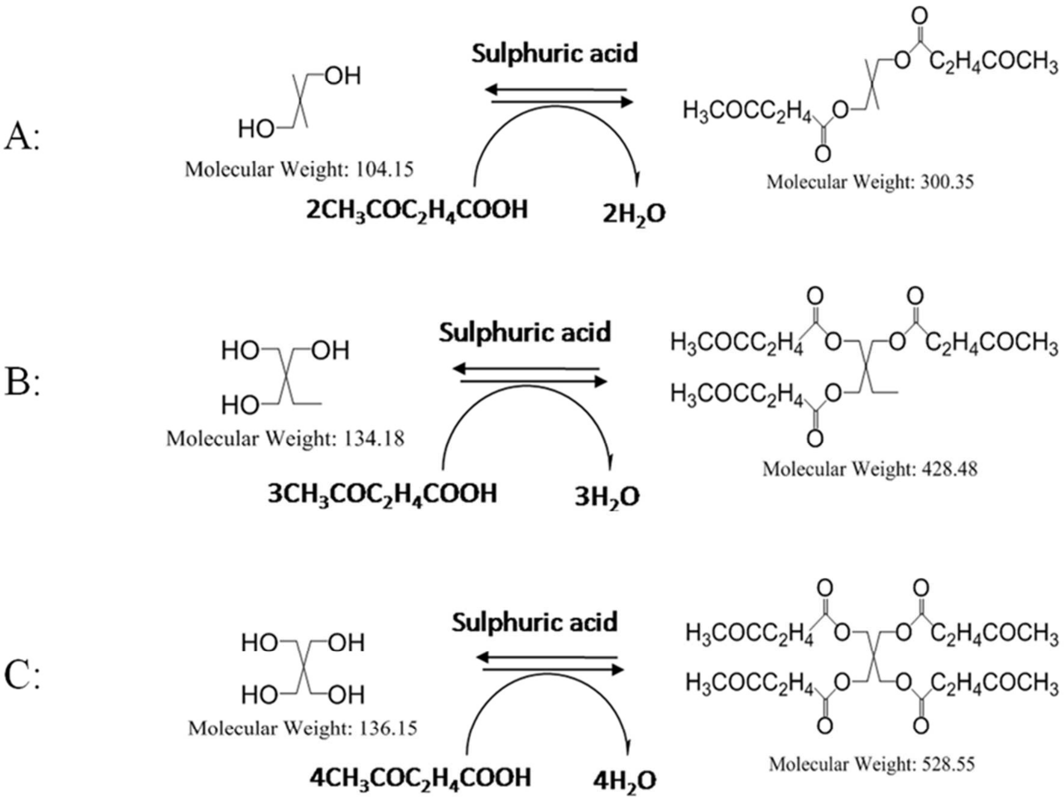

Fig. 2. Schematic representation of esterification reaction between LA and NPG, TMP, PE, respectively.

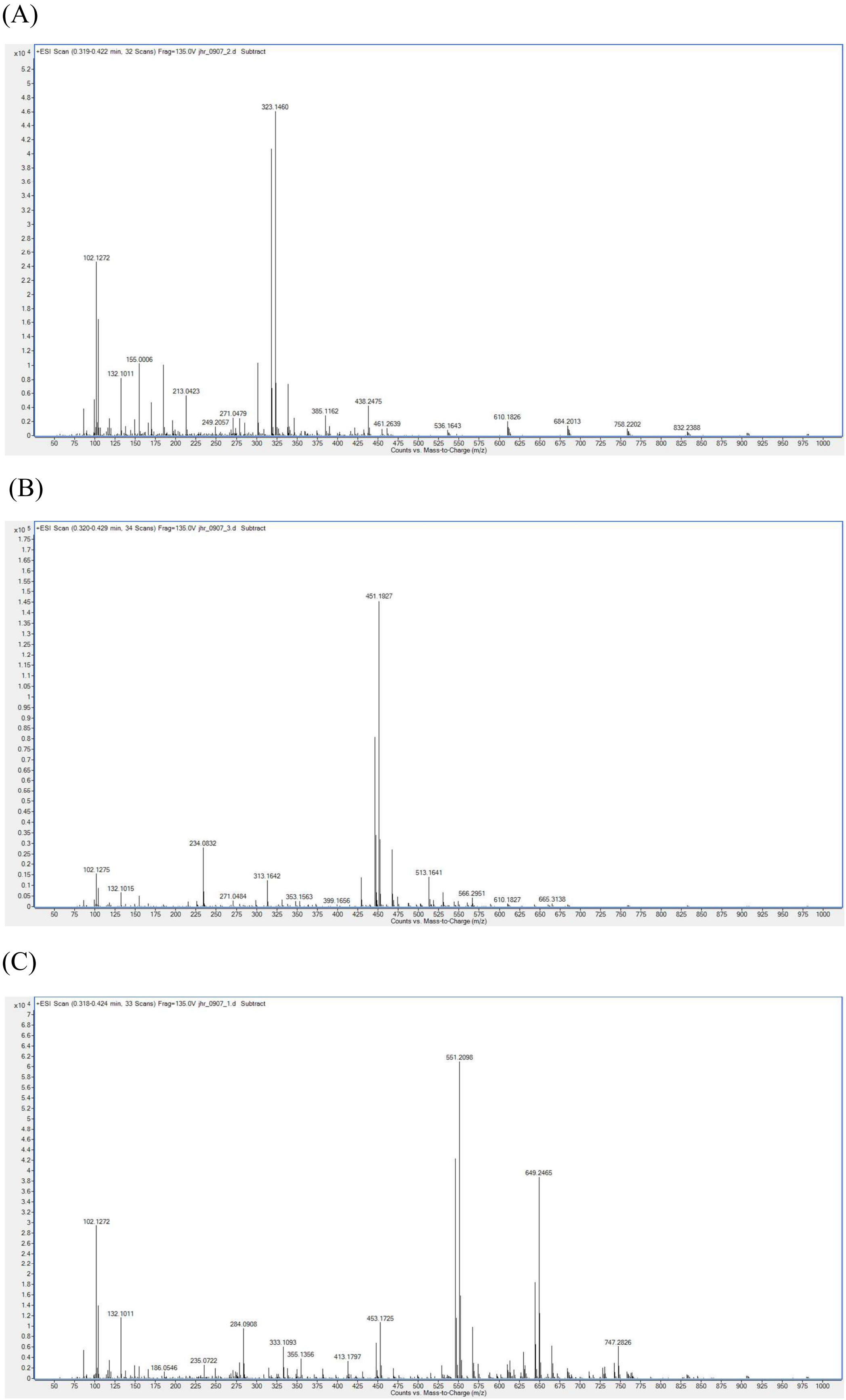

Fig. 3. Mass spectra of levulinic acid-based polyol esters：(A) NPG-di-LA; (B) TMP-tri-LA; (C) PE-tetra-LA.

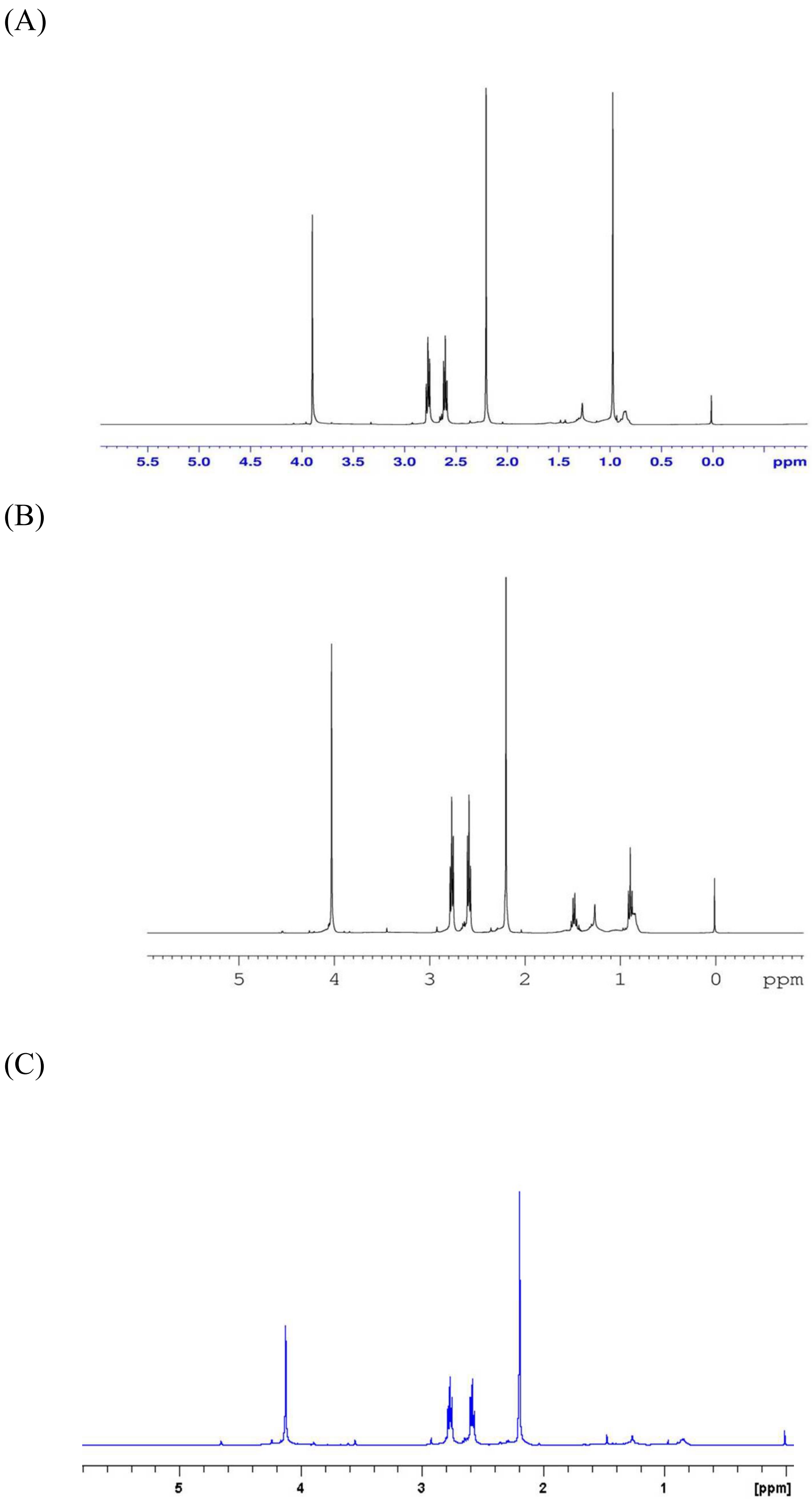

Fig. 4. ^{1}H NMR spectra of levulinic acid-based polyol esters：(A) NPG-di-LA; (B) TMP-tri-LA; (C) PE-tetra-LA.

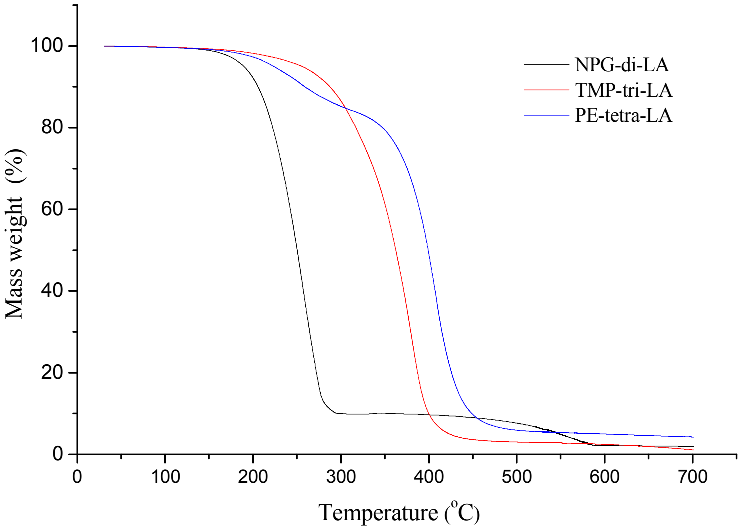

Fig. 5. The TGA curves of of LA-based polyol esters.

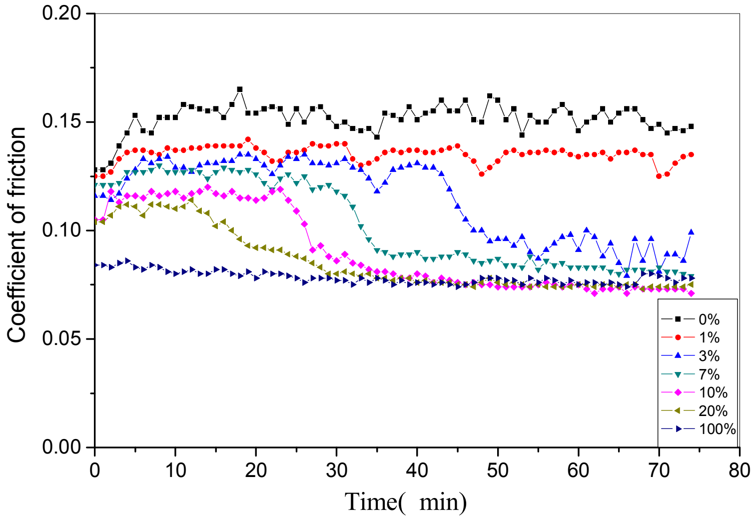

Fig. 6. Variation in coefficient of friction different percentages of TMP-tri-LA in ordinary mineral oil.

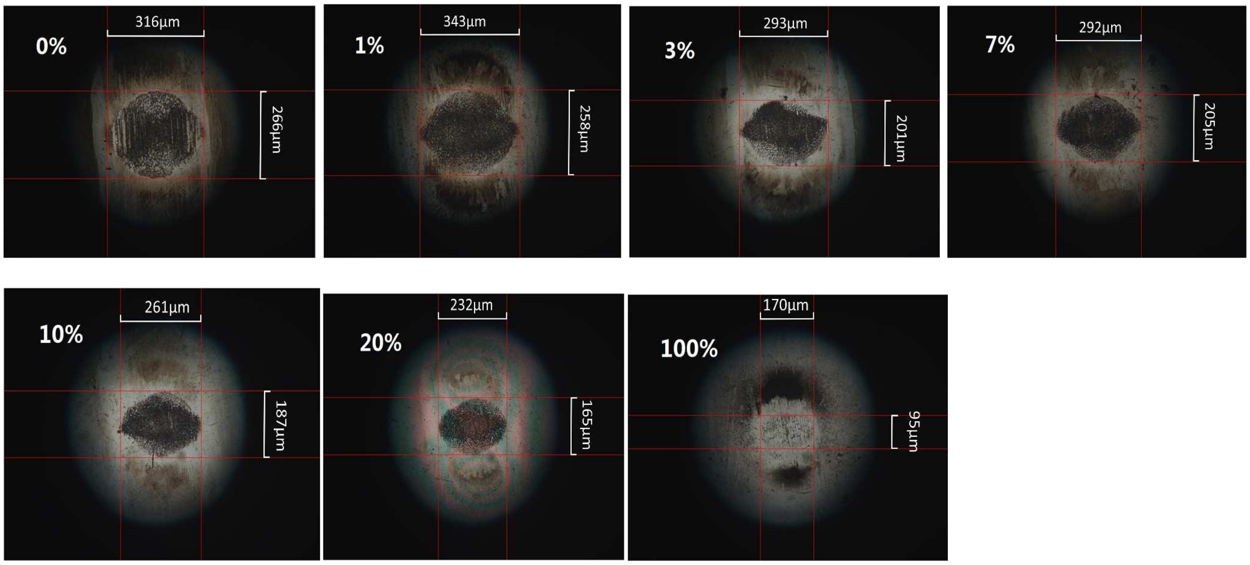

Fig. 7. Microscope of wear scar with different percentages of TMP-tri-LA in ordinary mineral oil.

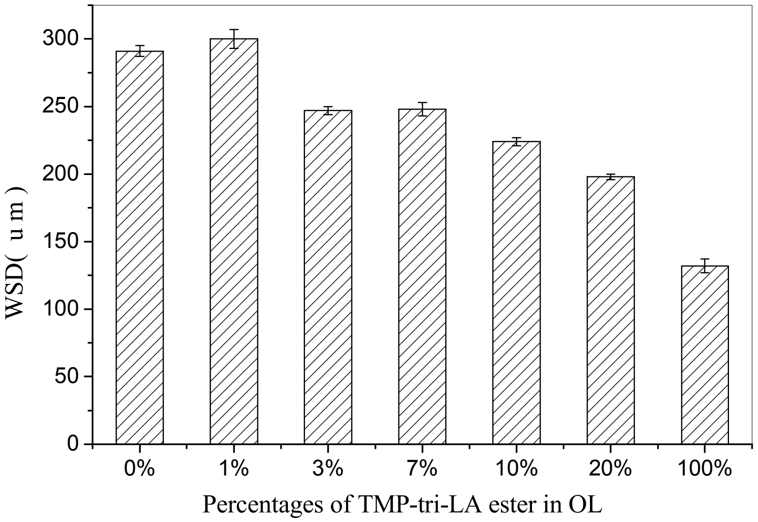

Fig. 8. Wear scar diameter of different percentages of TMP-tri-LA in ordinary mineral oil.

Table 1 Physico-chemical properties of LA-based polyol esters.

Property	NPG-di-LA	TMP-tri-LA	PE-tetra-LA
Viscosity at 40 °C ,（mm^2/s）	17.29	87.28	417.45
Viscosity at 100 °C,（mm^2/s）	3.35	8.42	19.14
Viscosity index	30	48	15
Pour point (°C)	-34	-25	-8
Flash point (°C)	185	228	210
Cloud point (°C)	-11	-4	7
Copper strip corrosion	1a	1a	1a
Volatility at 120 °C (%)	0.57	0.41	0.33

Table 2 Thermal stability data of the ester products.

Product	T_{onset} (◦C)	9–10% wt loss (◦C)	97% wt loss (◦C)
NPG-di-LA	189	203-205	579
TMP-tri-LA	255	281-286	487
PE-tetra-LA	222	252-259	684