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Synthesis and Tribological Performance of Phosphate Ester Containing Nitrogen from Methyl Oleate in Rapeseed Oil

[1]Weiquan Yang, [1]Boshui Chen, [2]Peili Zhang, [1]Jianhua Fang, [1]Jiu Wang and [1]Kecheng Gu
[1]Department of Petro-Chemistry, Logistical Engineering University, Chongqing, 401311, People's Republic of China
[2]Department of Military Petroleum Supply Engineering, Logistical Engineering University, Chongqing, 401311, People's Republic of China

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Corresponding Author:
Boshui Chen,
Department of Petro-Chemistry,
Logistical Engineering University,
Chongqing, 401311, China

ABSTRACT
A phosphate ester containing nitrogen from methyl oleate was synthesized via epoxidation-reaction, epoxy-group nucleophilic ring-opening reaction and esterification, through chemical modification in double bond of methyl oleate molecule. The chemical structure of synthetic product was characterized by Infrared-spectroscopy. The tribological performance of synthetic product in rapeseed oil was investigated by four ball friction test machine. Results showed that, after chemical modification, the anti-wear ability and extreme-pressure performance of methyl oleate were improved significantly. The P_B value increased 520-1323 N enhancing 154.42%, while P_D value increased 1236-3089 N enhancing 149.92% and WSD decreased 0.56-0.39 mm dropping 23.53%. Results also indicated that the synthetic product could be used as a good extreme-pressure and anti-wear lubricant additive in the rapeseed oil. Finally, indicate that the phosphate film generated in the friction surface through tribochemical reaction is the main reason for tribological performance improving of the chemical modified methyl oleate.

Key words: Methyl oleate, phosphate ester containing nitrogen, chemical modification, tribological performance, rapeseed oil

INTRODUCTION

With the development of modern society, the reports about harming people's health and the human beings living environment are more and more, that were mainly caused by environment pollution. For these reasons, the environment protecting concept enjoys popular support in recent years, people begin pay more attention to protect our living environment and reduce all kinds of pollution. It is well known that using traditional mineral lubricant will cause pollution for water body and soil, while this kind pollution can last for very long time. In this context, issues relating to the environmental pollution caused by using traditional mineral lubricant draw much attention. Development of environmental friendly lubricant which can be biodegraded gradually becomes the focus of this field and the most important thing is to develop the additives (Wang and Li, 2010; Liu *et al*., 2010; Luo and Li, 2010; Chen *et al*., 2010). Methyl oleate as one of the main components of biodiesel, which was used as an important biomass fuel, has a great potential application prospect in lubricant domain for its less environmental hazards, renewable property and good anti-wear and anti-friction performance caused by the unique chemical structure (Yao and Min, 2010a, b). In fact, the possible application gives a new method for biodiesel's high-quality use. Phosphorus-containing additive is one of the most widely used and with best anti-friction effect currently due to the good anti-friction, extreme pressure performance in the modern industry (Fang *et al*., 2007). A lot of studies reported introducing anti-friction groups to the active site on the ester bond in the methyl oleate (Ren *et al*., 2011; Fang *et al*., 2003, 2004; Li *et al*., 2012; Chai *et al*., 2007), however, these method still reserve the unsaturated bond that causes the poor anti-oxidation and thermal stability (Geng *et al*., 2009), which limits the performance of the modified methyl oleate as lubricate additives. In this study, a new synthesis route has been designed with methyl oleate as the raw material to introduce groups containing phosphorus and nitrogen by chemical modification, which relates to a series of reactions including the double bond epoxidation, introducing trans-double hydroxyl by asymmetric nucleophilic ring-opening reaction, esterification reaction between hydroxyl and phosphoric anhydride, reaction between phosphate ester and triethanolamine. This method solves the problem of poor thermal stability and improves the anti-friction performance by introducing phosphorus and nitride groups, as well as enhancement of biodegradation. Introduction of nitride element has also restrained the chemical corrosion from phosphorus. This method has also opened up a new route to enlarge the application range of methyl oleate (biodiesel).

MATERIALS AND METHODS

Synthesis of phosphate ester containing nitrogen from methyl oleate:

Step 1: With molar ratio of 1:1, the methyl oleate and 8% formic acid were mixed and transferred to a four-necked flask with a reflux device, a thermometer was inserted and the temperature was controlled by a digital constant temperature water tank. Hydrogen peroxide with concentration of 30% was added slowly under stirring in 3-5 h. The temperature was controlled at 30-35 with ice if needed. After the addition of hydrogen peroxide, the temperature increased up to 55-58 and kept reacting for 7 h. When the reaction finished, washed with 70 deionized water until neutral and dewater in vacuum to get the epoxide methyl oleate

Step 2: The epoxide methyl oleate and water were mixed with molar ratio of 6:1, phosphotungstic acid as the catalyst (Yang *et al*., 2010) and the addition of catalyst was 0.5%, under the condition of 120 and mechanical stirring, reacted for 25 min. After the reaction, the product was transferred to a separating funnel to separate the lower aqueous phase, the organic phase was washed by 50-70 deionized water for several times and dried in vacuum for three times to get trans-dihydroxy methyl oleate (Zhou and Xu, 2011) (Light yellow transparent liquid transformed into white wax-like solid while cooling)

Step 3: With molar ratio of 1:1, hydroxyl methyl oleate and phosphorus pentoxide were mixed completely. Transferred mixtures to a three-necked flask, under 80 oil bath, react for about 4 h. Then, added triethanolamine in reaction system (molar ratio: 1:1), heated up to 120 and reacted for another 1 h. After the reaction the solution was cooled and separated the upper organic phase to get the product (brown transparent oily liquid). The reaction formula as follows in Fig. 1

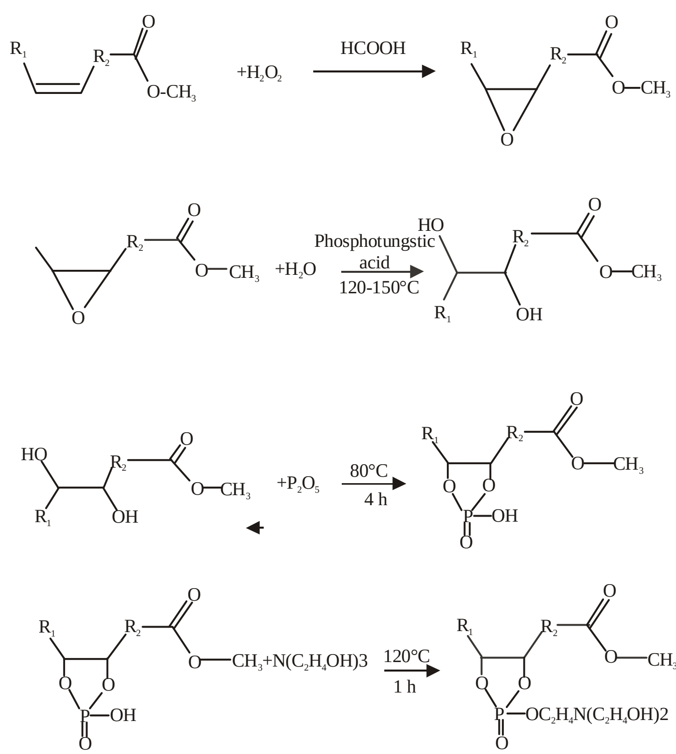

Fig. 1: Synthesis of phosphate ester

Structure characterization of the synthetic product: The chemical structure of the synthetic product was characterized by FTIR.

Tribological performance evaluation: Maximum non-seizure load P_B and weld load P_D was tested according the method of GB/T 3142 by MQ-800 four balls friction tester manufactured by Jinan test factory. Test conditions REV:1450r/min, time: 10s, room temperature, about 25°C. The balls are secondary GCr15 steel balls produced by shanghai steel ball factory with diameter of φ12.7 mm and hardness of 59-61 HRC. The friction coefficient μ was tested according the method of SH/T 0762 with MMW-1 vertical universal friction and wear tester produced by Jinan Shumao Experimental Instrument Co., Ltd. The diameter of lower ball wear scar was read by optical microscope (accuracy 0.01 mm). Test conditions were load 392 N REV 1450 rpm min^{-1} 30 min room temperature about 25°C. The phosphate ester containing nitrogen from methyl oleate as additive was added into the rapeseed oil with the amount of 0.5, 1.0, 1.5, 2 and 2.5%, carrying out the above tests on four ball tester and test the maximum non-seizure load P_B and weld load P_D, the average friction coefficient and average wear scar diameter.

RESULTS AND DISCUSSION

FTIR: Figure 2 is the FTIR spectrum of synthetic product. According to the literature (Shi, 2012) the peak located at 3357.8 cm^{-1} is attributed to hydroxyl, generally speaking, absorbing peak of P = O bond emerges at 1300 1140 cm^{-1}, when there is hydroxyl or amino groups in the molecules, the peaks shifted to lower wave number region due to associating hydrogen bonding, so the peak located at 1176.2 cm^{-1} is attributed to P = O, the peaks at 1079.4 and 1008.7 cm^{-1} is C-O-P, which shows that the synthetic product is phosphate ester. The peak at 1369.8 cm^{-1} is C-N-C, which confirm of the nitrogen element in the additives and the nitrogen-containing group, has been introduced to the molecule. Peaks at 1201.6, 1172.8 and 1079.4 cm^{-1} are the character peak of methyl ester which indicate that the methyl ester was not destroyed.

Tribological performance: In this part, we analyze the tribological performances of phosphate ester containing nitrogen from methyl oleate from four aspects, viz load-carrying capacity, extreme pressure ability, anti-wear ability and friction-reducing ability, discuss the rule of these four tribological index changing with the content of phosphate ester containing nitrogen from methyl oleate in the rapeseed oil.

Load-carrying capacity and extreme pressure ability of phosphate ester containing nitrogen from methyl oleate: Figure 3 indicated the P_B value changed with the content of phosphate ester containing nitrogen from methyl oleate, while Fig. 3 showed the P_D value changed with the content of phosphate ester containing nitrogen from methyl oleate. As shown in Fig. 3, in the rapeseed oil, the corresponding P_B value was greater than that of methyl oleate at the same concentration, which made the maximum P_B value increase to 1323 N. It improved up to 154.42%, which demonstrated that load-carrying capacity of methyl oleate significantly increased after chemical modification. With increased of phosphate ester containing nitrogen from methyl oleate concentration, the corresponding P_B value of system increased at the beginning, then decreased and again increased finally. When the adding amount of phosphate ester containing nitrogen from methyl oleate concentration was 1.5%, P_B value reached the maximum of 1323 N. Figure 4 showed that the P_D value of phosphate ester containing nitrogen from methyl oleate was also higher than that of methyl oleate at the same concentration in the rapeseed oil, which increased 1236-3089 N with improvement of 149.92%. That indicated extreme pressure abilities of methyl oleate improved effectively after chemical modification with introducing phosphorus and nitrogen. In the

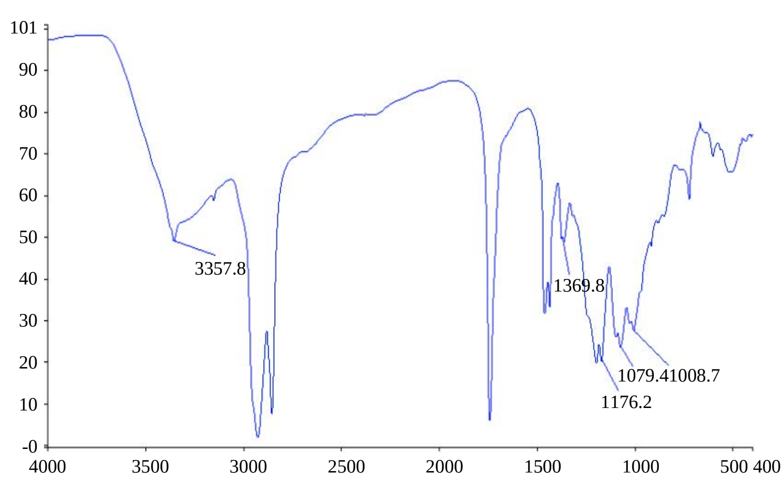

Fig. 2: IR spectrum of phosphate ester containing nitrogen from methyl oleate

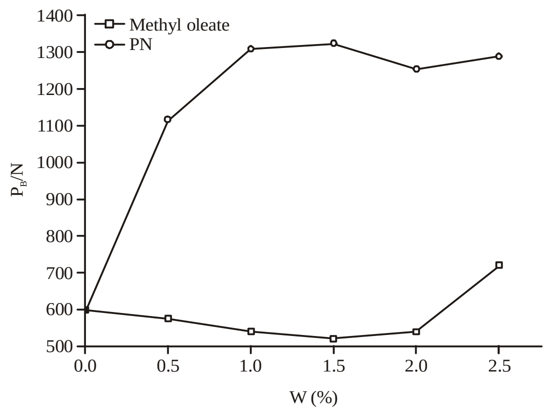

Fig. 3: P_B changes with the content of phosphate ester containing nitrogen from methyl oleate

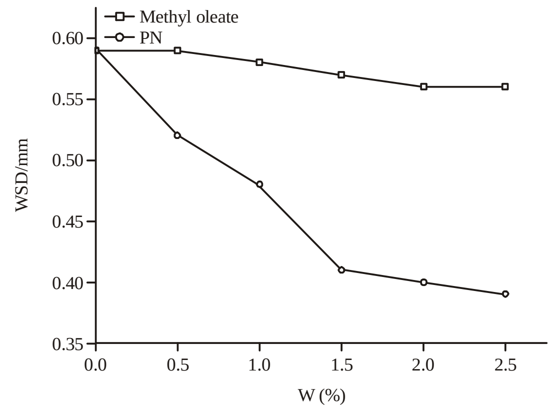

Fig. 5: WSD changes with the content of phosphate ester containing nitrogen from methyl oleate

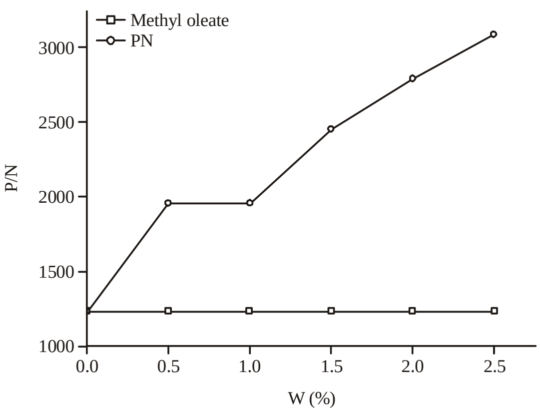

Fig. 4: P_D changes with the content of phosphate ester containing nitrogen from methyl oleate

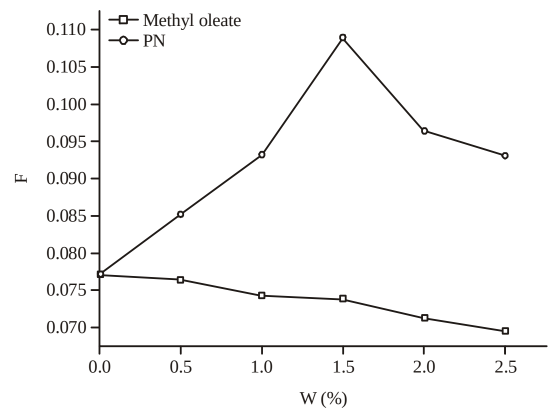

Fig. 6: WSD changes with the content of phosphate ester containing nitrogen from methyl oleate

concentration range of 0.5-1.0%, the P_D value remained the same and then it increased with the increasing of phosphate ester containing nitrogen from methyl oleate concentration and the P_D value of system also increased accordingly. When phosphate ester containing nitrogen from methyl oleate concentration was 2.5%, P_D value reached the maximum of 3089 N.

Anti-wear ability of phosphate ester containing nitrogen from methyl oleate: As shown in Fig. 5, WSD was changed with adding concentration of phosphate ester containing nitrogen from methyl oleate in rapeseed oil. In the rapeseed oil, the corresponding WSD was far smaller than that of methyl oleate at the same content. When the adding concentration of phosphate ester containing nitrogen from methyl oleate was 2.5%, the WSD was only 0.39 mm and decreased 0.17 mm compared with methyl oleate, the reduce rate was up to 30.36%. With increase of phosphate ester containing nitrogen from methyl oleate concentration, the corresponding WSD also decreased, when phosphate ester containing nitrogen from methyl oleate concentration was higher than 1.5%, its reduction tended to be stable. When phosphate ester containing nitrogen from methyl oleate concentration was 2.5%, The WSD reached to the minimum value of 0.39 mm.

Friction-reducing ability of phosphate ester containing nitrogen from methyl oleate: Figure 6 represented friction coefficient change with various additives content in rapeseed oil. Obviously the corresponding friction coefficient of phosphate ester containing nitrogen from methyl oleate was larger than that of methyl oleate at the same content in the rapeseed oil, which demonstrated that Friction-reducing ability of methyl oleate was weaken after chemical modification. With increase of phosphate ester containing nitrogen from methyl oleate concentration, friction coefficient of phosphate ester containing nitrogen from methyl oleate tended to increase firstly and then decrease: Phosphate ester containing nitrogen from methyl oleate concentration was lower than 1.5%, the friction coefficient increased with increase of phosphate ester containing nitrogen from methyl oleate concentration, while phosphate ester containing nitrogen from methyl oleate concentration was higher than 1.5%, the friction coefficient decreased. When the adding concentration of phosphate ester containing nitrogen from methyl oleate was 0.5%, the friction coefficient reached the minimum value of 0.0852. Compared that with the change of WSD following with the content of additive, it should be concluded that there is no consistency between anti-wear ability and friction-reducing ability.

Mechanism of phosphate ester containing nitrogen from methyl oleate: Under various conditions, phosphate ester containing nitrogen from methyl oleate can generate such phosphate reaction film on the friction surface (Godblatt and Appeldoorn, 1970; Gandhi and Sharma, 1979) to avoid direct contact between friction pair surface, therefore load-carrying capacity and extreme pressure ability of methyl oleate significantly improved after chemical modification. After chemical modification, friction-reducing ability of methyl oleate was weakened mainly because the modification methyl oleate viscosity increased. In addition, strong polarity led to increase of surface tension accordingly, which made it easier to form greater strength adsorption film on the friction surface (Sharma *et al*., 2008), thus when relative movement occurs on the friction surface, it required much larger shear force. WSD measurement results indicated that there was no consistency between anti-wear and friction-reducing abilities, as the anti-wear abilities of methyl oleate was improved evidently, but WSD decreased significantly after methyl oleate molecular modified, which mainly due to more easier formation of greater strength adsorption film on friction surface of the modified product, especially in the rapeseed oil. Because of nitrogen containing groups and hydroxyl in modified product, the additive and rapeseed oil can form hydrogen bond to generate synergistic effect (Fang, 2001; Cao and Yu, 2000), which can further strengthen the adsorption film. And the modified products can generate phosphate reaction film on the friction surface, form nitrogen deposition film and enhance the friction surface via nitriding effect. Meanwhile, nitrogen-containing groups can inhibit the chemical corrosion effect of phosphorus, thus effectively reduce the abrasion.

CONCLUSION

According to the experiment results and theoretical analysis, we can draw the conclusions as follows. The phosphate ester containing nitrogen from methyl oleate was synthesized through chemical modification including epoxidation, asymmetric nucleophilic ring-opening reaction, esterification reaction in the double bond of methyl oleate molecular, which successfully introduced the group containing phosphorus and nitrogen. The results of four ball test show that the load-carrying capacity, anti-wear ability and extreme pressure ability of methyl oleate improved significantly after chemical modification with group of containing phosphorus and nitrogen, which indicate that the phosphate ester containing nitrogen from methyl oleate can be used as a good anti-wear and extreme pressure lubricant additive. Tribological mechanism analysis indicates that the phosphate film generated in the friction surface responding for tribological performance improving of chemical modified methyl oleate. It could be an effective method to enlarge the application range of methyl oleate (biodiesel) via introducing anti-wear and fiction-reducing group in the double bond of methyl oleate molecular to improve its tribological performance.

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