Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8447-8450

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14775

Preparation and Application of Hydroxyacetic Acid Esters as Methanol-Gasoline Additives

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(*Received*: 3 November 2012; *Accepted*: 24 August 2013) AJC-13970

In this paper, hydroxyacetic acid esters (glycolic esters) were synthesized and used as phase stabilizer and saturation vapour pressure depressor of methanol-gasoline. The results show that the stabilities of the blends depend on the length of the glycolic esters' alkoxy group. Among these glycolic esters, hexyl glycolic ester and octyl glycolic ester were found to be the most effective in various gasoline-methanol blends. Besides, the glycolic esters display high capacity to depress the saturation vapour pressure of methanol-gasoline and decyl glycolic ester is the most effective one. According to the results, it can be concluded that the glycolic esters have the great potential to be used as bifunctional gasoline-methanol additives.

Key Words: Methanol-gasoline, Glycolic esters, Phase stability, Evaporation.

INTRODUCTION

With the rapid rising consumption of oil and the strict emission controlling of the vehicle, the development of clean and alternative fuels increasingly draws worldwide attentions[1]. In a large number of alternative fuels, methanol not only has fine combustion properties similar to gasoline, but also has advantages such as high octane number, low emissions, anti-knock, rich resource, mature technology, *etc*., so it can be used as alternative fuel for gasoline[2]. In recent years, extensive research of the low percentage methanol-gasoline has been carried out and it has been gradually applied in Shanxi, Sichuan, Zhejiang, Inner Mongolia, Shaanxi, Xinjiang and other places of China[3]. However, there are several problems needing to resolve in methanol-gasoline and the phase stability is the most important one. One of the popular solutions is to add phase stabilizer to reduce alcohol-oil interfacial tension[4,5], such as ethers, ketones, esters, fatty alcohols, aliphatic hydrocarbons, fatty acids, non-ionic surfactants, acetal/ketones, biodiesels and amidines[6-11]. Secondly, the low boiling point of methanol leads to increase the possibility of vapour lock by increasing the vapour pressure of methanol-gasoline[12-14]. Vapour lock happens in internal combustion engines as the methanol-gasoline vapourizes easier than that of gasoline under the same conditions. Vapourized fuel, which has lost its liquefied state, can no longer flow into the intake system and atomize with air to produce combustion ignition. The current solution for vapour lock is to add a pressure reducer, including aliphatic ketones, fatty aldehydes, fatty ethers, acetals/ketals, *etc*.[15-24]. At present, few researches have carried out to develop bifunctional additives with the abilities of both phase stability and vapour pressure depressing for methanol-gasoline. In this work, a series of hydroxyacetic acid esters (glycolic esters) was synthesized and screened in the methanol-gasoline as a bifunctional additive.

EXPERIMENTAL

All the solvents were AR grade and purchased from Xi'an Chemical Agent Co and the 93# gasoline is commercially available. The phase stabilizing and pressure reducing were tested on DFY-cryostat instrument (Xi'an Yuhui Instrument Co. Ltd.) and DSL-080 vapour pressure detector (Dalian the Ceon Electronic Equipment Co. Ltd.).

Synthesis of glycolic esters

Method A: Glycolic acid (12 g), methanol (25 mL) and *p*-toluenesulfonic acid (TsOH) (0.6 g) was added to the flask. After 10 h of refluxing, the reaction mixture was cooled to room temperature. Methanol and methyl glycolic ester were distillated, respectively. The synthesis of ethyl glycolic ester and propyl glycolic ester is same to method above[25].

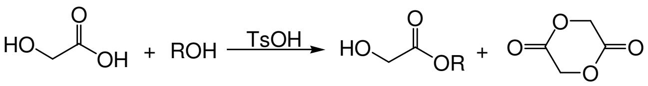
Method B: Glycolic acid (0.1 mol), *n*-butanol (0.25 mol), cyclohexane (30 mL), *p*-toluenesulfonic acid (0.5 g) were refluxed for 5 h and the produced water was separated by a water separator. After cooled to room temperature, cyclohexane, *n*-butanol and *n*-butyl glycolic ester were separated by vacuum distillation. The synthesis of amyl glycolic ester, hexyl glycolic ester, hepyl glycolic ester, octyl glycolic ester and decyl glycolic ester is same to method above[26,27].

Phase stability test: The fuel blends were prepared by blending 15, 30, 50 and 65 vol. % of methanol with base gasoline and the fuel blends were designed as M15, M30, M50 and M65. The phase stabilizing tests were carried out according to Chinese standards of GB 8017-87, GB/T 23799-2009, DB61/T 352-2004 and DB51/T 448-2004. First the test tube full of methanol-gasoline with different ratios was placed in a cryostat and then the temperature was adjusted from 40 ºC to -25 ºC. At each degree, the tube was taken out and was shaken for two to three seconds and the phase separation temperature was determined as the solution becomes cloudy[28-30].

Vapour pressure test: The effect of glycolic esters on vapour pressure of methanol-gasoline was investigated according to Chinese standards of GB 8017-87. The methanol-gasoline was poured into the vapour pressure detector and put into the water bath of 37.8 ºC. The methanol-gasoline was intensive mixed by taking the detector from the water bath every 5 min and reversing violently. The operation was repeated until the pressure becomes steady.

RESULTS AND DISCUSSION

Synthesis of glycolic esters: The reaction of glycolic acid and alcohol are shown in **Scheme-I** and both the reaction conditions and the yield are summarized in Table-1. In this reaction, there may be two kinds of ester production, one is the main product of alcoholic glycolic ester and the other is the byproduct, glycolide (1,4-dioxane-2,5-dione). To reduce the byproduct, high quantities of alcohol was used. For the synthesis of the first three esters, the alcohols were employed with higher ratio over 1:30. For the rest esters, the glycolic acid and alcohol ratio is as high as 1: 5. The yields were obtained in the range from 81.3 to 87.2 % as shown in Table-1.



Scheme-I: Reaction of glycolic acid and alcohol

TABLE-1
RESULTS OF THE SYNTHESIS OF GLYCOLIC ESTERS

Esters	Glycolic acid:alcohol	Method	Yield (%)
Methyl glycolic ester	1: 30	A	87.2
Ethyl glycolic ester	1: 30	A	82.8
Propyl glycolic ester	1: 30	A	84.9
Butyl glycolic ester	1: 50	B	85.1
Amyl glycolic ester	1: 50	B	80.8
Hexyl glycolic ester	1: 50	B	85.9
Hepyl glycolic ester	1: 50	B	83.0
Octyl glycolic ester	1: 50	B	84.0
Decyl glycolic ester	1: 50	B	81.3

Effect of glycolic ester on the phase stability of methanol-gasoline: The phase stabilities of glycolic esters for the methanol-gasoline blends of M15, M30, M50 and M65 at different temperatures from -25 ºC to 40 ºC were investigated and summarized in Figs. 1-4. The experimental data indicate that the length of carbon chain of glycolic ester effects on the phase stability of

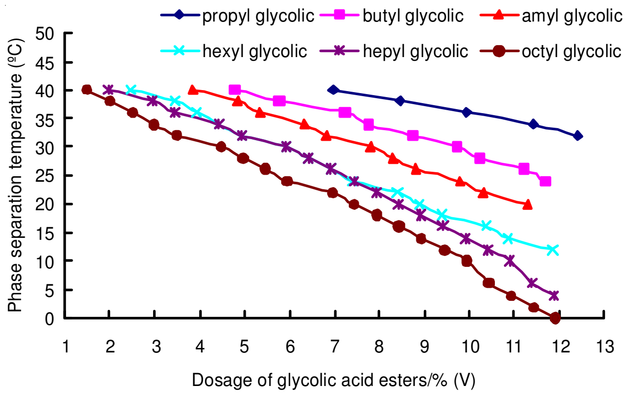


Fig. 1. Effect of the glycolic ester dosage on the phase stability of M15

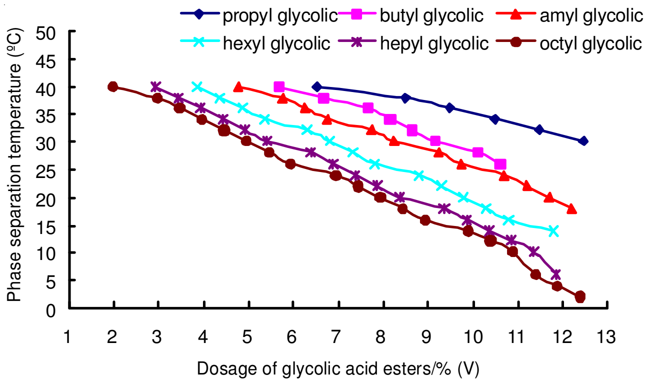


Fig. 2. Effect of the glycolic ester dosage on the phase stability of M30

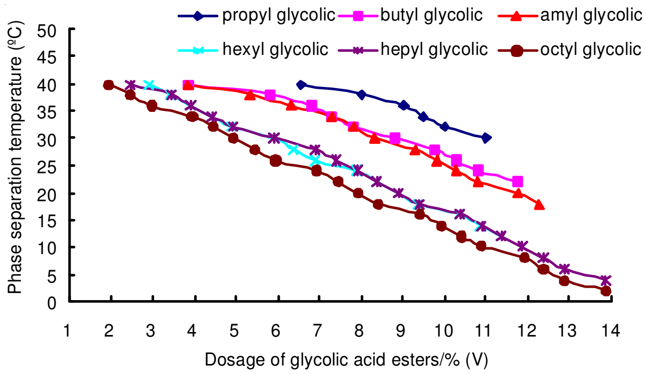


Fig. 3. Effect of the glycolic ester dosage on the phase stability of M50

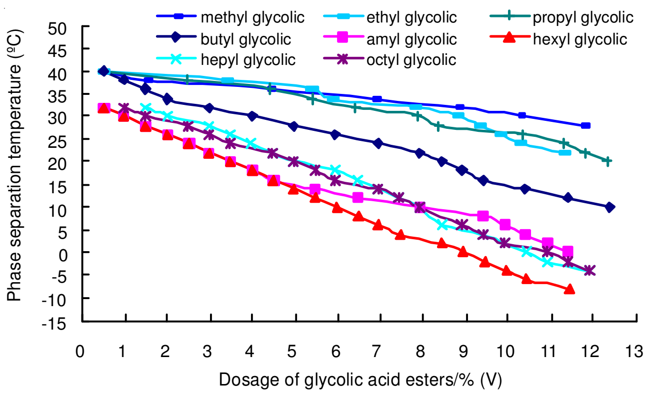


Fig. 4. Effect of the glycolic ester dosage on the phase stability of M65

methanol-gasoline significantly. For the esters with very short or long chains, such as methyl glycolic ester, ethyl glycolic ester and decyl glycolic ester, the phase stability to methanol-gasoline are ineffective, even as the dosage over 10 %, methanol and gasoline homogenized blends can not obtained in M15, M30, M50 and M65 at 40 ºC. The reason may be due to the strong hydrophilic property but weak lipophilic property of short-carbon-chained glycolic ester, leading them not to dissolve in gasoline. With the increase of the carbon chain of glycolic esters, lipophilic property of the ester is markedly enhanced and the dissolution in gasoline is intensified, resulting in higher solubilization in the various blends. With too long carbon chain, decyl glycolic is hardly soluble in methanol, resulting to the poor phase stability even under high temperature. According to the results, it can be found that only glycolic esters with moderate carbon atoms are with the effective phase stability to methanol-gasoline. The esters with alkoxy groups of 5-8 carbon atoms are more effective than others. The phase separation temperatures of the four methanol-gasoline blends with the ester dosage of 10 % was estimated and shown in Fig. 5. It can be found that the phase separation temperature declines along with the length of the alkoxy group. For M15, M30 and M50 and the phase separation temperature comes to the lowest as the carbon atom number of alkoxy group comes to 8, while it rises sharply as the carbon atom number lengthens to 10. For M65, the lowest phase separation temperature was obtained as the carbon atom number of alkoxy group comes to 6.

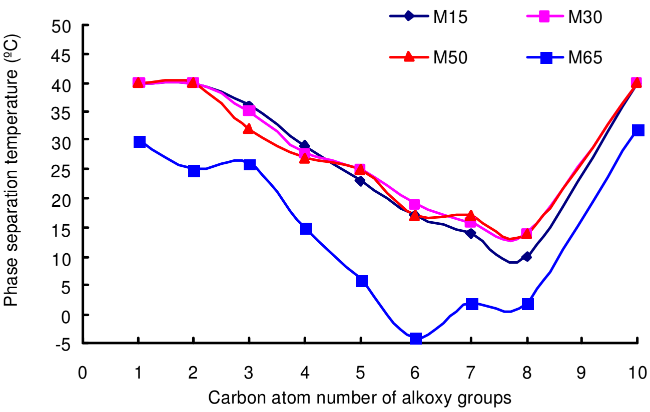


Fig. 5. Relationship of the alkoxy groups and the phase separation temperature

Effect of glycolic ester on the evaporation of methanol-gasoline: The saturation vapour pressure will rise over that of gasoline as it blends with low percentage methanol such as M15 and M30, which will lead to vapour block as it used under relative high temperature. Some chemicals with lower saturation vapour pressure can be added to depress the high pressure of gasoline. In this work, the effect of glycolic ester on the saturation vapour pressure of M15 methanol-gasoline was investigated referred to GB 8017-87 "petroleum products the vapour pressure determination method (Reid Method)" and the results are shown in Fig. 6. The original saturation vapour pressure of M15 is 63.5 kPa, which is 5.7 kPa higher than that of gasoline. As little amount of esters were added in, the saturation vapour pressure was depressed obviously. With the esters' dosage of 0.1 %, ethyl glycolic ester, propyl glycolic ester, butyl glycolic ester, amyl glycolic ester, hexyl glycolic ester and decyl glycolic ester can depress the saturation vapour

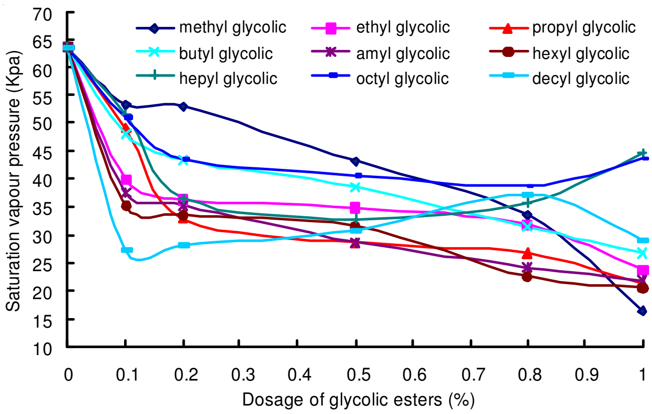


Fig. 6. Effect of glycolic esters on the evaporation of methanol-gasoline M15 system

pressure lower than that of gasoline, among which decyl glycolic ester is the most effective one. Further increase of the dosage depresses the saturation vapour pressure ineffectively. The main reason is contribute to the distribution of glycolic esters on the surface of methanol-gasoline, which prevent the formation of an azeotrope with low boiling point.

Conclusion

Glycolic esters were synthesized and screened for their performances of phase stabilizing in M15, M30, M50 and M65 and pressure reducing in M15. The results show that the length of alkoxy group of glycolic esters effects on the phase stability of methanol-gasoline significantly. Methyl glycolic ester, ethyl glycolic ester and decyl glycolic ester, are ineffective on the phase stability of methanol-gasoline, even as the dosage over 10 %, while hexyl glycolic ester and decyl glycolic ester are the most effective for M15, M30, M50 and M65, respectively. All of the synthesized esters are potent to depress the saturation vapour pressure of methanol-gasoline. With the dosage of 0.1 %, ethyl glycolic ester, propyl glycolic ester, butyl glycolic ester, amyl glycolic ester, hexyl glycolic ester and decyl glycolic ester can depress the saturation vapour pressure lower than that of gasoline and decyl glycolic ester is the most effective one.

ACKNOWLEDGEMENTS

This work was financially supported by the grants from Scientific Research Program Funded by Shaanxi Provincial Education Department (11JK0898, 2013JK0646) and National Science Foundation of China (No. 21306149).

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