# Investigation of Bifunctional Ester Additives for Methanol-Gasoline System

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**Summary**: To explore new and multifunctional additives for methanol-gasoline, tartaric ester were synthesized and screened as phase stabilizer and saturation vapor pressure depressor for methanol-gasoline. The effect of the esters' structure on the efficiency was discussed. The results show that the stabilities of the blends depend on the length of the glycolic esters' alkoxy group. In addition, the tartaric esters also can depress the saturation vapor pressure of methanol-gasoline effectively in M15. Effect of the structure on the efficiency was also discussed.

Key Words: Methanol-gasoline; tartaric esters; phase stability; evaporation.

## Introduction

With the rapid rising consumption of oil and strict emission controlling of the vehicle, the development of clean and/or alternative fuels increasingly have drown worldwide attentions [1]. Among large number of alternative fuels, methanol has both fine combustion properties similar to gasoline and advantages such as high octane number, low emissions, high antiknock and low cost, so it has been used as an alternative fuel for gasoline [2]. On the other hand, the capacity of methanol is rising rapidly in recent years, it reached to 50,000,000 t/y, and production is more than 30,000,000 t in 2012. Now the methanol-gasoline has been commercially used in Shanxi, Sichuan, Zhejiang, Inner Mongolia, Shaanxi, Xinjiang and other provinces of China [3].

But there are still several problems needing to resolve in methanol-gasoline application, among which the phase poor stability under low temperature and high vapor pressure under high temperature are the two most important ones. Using phase stabilizer is the effective solution to reduce alcohol-oil interfacial tension [4, 5], including ethers, ketones, esters, fatty alcohols, aliphatic hydrocarbons, fatty acids, non-ionic surfactants, acetal/ketones, biodiesels and amidines [6-8]. The high vapor pressure of methanol-gasoline will lead to increase the risk of vapor lock [9-11] and such chemicals as aliphatic ketones, lynn classes, fatty aldehydes, fatty ethers, acetals/ketals have been employed to depress the vapor pressure. At present, few researches have pay attention to multifunctional additives for methanol-gasoline application. In this work, a series of tartaric esters was synthesized and screened in the methanol-gasoline as a bifunctional additive for phase stabilizing and pressure depressing.

## Experimental

### *Materials and Methods*

All 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 test were performed on DFY-cryostat instrument (Xi'an Yuhui Instrument Co.Ltd.) and DSL-080 vapor pressure detector (Dalian the Ceon Electronic Equipment Co.Ltd.).

### *Synthesis of glycolic esters*

Method A: Tartaric acid (12g), methanol (25mL), and p-toluenesulfonic acid (TsOH) (0.6g) were added into a flask. After refluxed for 10 h, the mixture was cooled to room temperature. Methanol and methyl tartaric were distillated out respectively. The synthesis of ethyl tartaric and propyl tartaric is same to method above [12-13].

Method B: Tartaric acid (0.1mol), n-butanol (0.25mol), cyclohexane (30mL), *p*-toluenesulfonic acid (0.6g) were added into a flask equipped with a water separator. After refluxed for 5h, the mixture was cooled to room temperature. Then cyclohexane, *n*-butanol and *n*-butyl tartaric were distillated out respectively. The synthesis of amyl tartaric, hexyl tartaric, hepyl tartaric, octyl tartaric, decyl tartaric is same to method above [14, 15]. The reaction of tartaric acid and alcohol are shown in Scheme-1.

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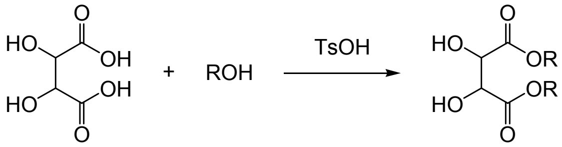


Scheme-1: The reaction of tartaric acid and alcohol.

*Test of Glycolic Ester in Methanol-Gasoline*

The phase stabilizing tests were carried out according to Chinese National Standards of GB8017-87, GB/T23799-2009, DB61/T352-2004 and DB51/T448-2004. The test tube full of methanol-gasoline with different ratios was placed in a cryostat, the temperature was reduced from 40°C to -25°C. At each degree, the tube was taken out and shaken for two to three seconds, until the solution becomes cloudy, the temperature was determined as the phase separation temperature [16].

The effect of tartaric esters on vapor pressure of methanol-gasoline was investigated according to Chinese National Standards of GB8017-87. The methanol-gasoline solution was poured into the vapor pressure detector and put into the water bath of 37.8°C, the measure device was taken out of the water bath, reversed violently and then put into the water bath. Repeat the operation every 5min, until the pressure became steady.

## Results and Discussion

*The Effect of Tartaric Ester on the Phase Stability of Methanol-Gasoline*

The effect of the esters on the stability of M15, M30, M50, M65 and M85 methanol-gasoline was screened. With the optimal dosage, 2.0% for M15, 10.0% for M30, 10.0% for M50, 10.0% for M65 and 1.0% for M85, the effect of esters on the phase stability was investigated and summarized in Table-1.

Table-1: The effect of tartaric acid ester on the phase stability of methanol-gasoline system.

| Esters | Phase Separation Temperature(℃) | | | | |
|---|---|---|---|---|---|
| | M15 | M30 | M50 | M65 | M85 |
| blank | >60.0 | >60.0 | 49.1 | 34.8 | -21.3 |
| methyl tartaric | >60.0 | >60.0 | >60.0 | >60.0 | -17.5 |
| ethyl tartaric | >60.0 | >60.0 | >60.0 | >60.0 | -18.4 |
| propyl tartaric | >60.0 | >60.0 | >60.0 | >60.0 | -16.2 |
| butyl tartaric | 59.0 | 19.0 | 21.6 | 7.4 | -21.8 |
| amyl tartaric | 50.0 | 5.8 | 2.5 | -8.7 | -25.5 |
| hexyl tartaric | 55.0 | -13.6 | -0.9 | -9.8 | -24.8 |
| hepyl tartaric | 55.5 | -22.3 | -3.4 | -19.5 | -17.4 |
| octyl tartaric | 26.8 | -12.0 | -1.4 | -8.5 | -11.8 |
| decyl tartaric | 31.5 | -21.7 | -11.5 | -19.0 | -27.8 |

It was found from Table-1, the length of alkoxyl group of glycolic ester play an important role in the phase stability of methanol-gasoline. The methyl, ethyl and propyl esters are ineffective in all methanol-gasoline systems, and they can even increase the separation temperature in M85. The reason is due to the strong hydrophilic but weak lipophilic property of short-carbon-chained glycolic ester. With the increase of the carbon chain of glycolic esters, the lipophilic property of the ester is markedly enhanced, and they can stabilize various methanol-gasoline systems. As the carbon atoms of the alkoxy group increase over 4, the esters can stabilize the methanol-gasoline at low temperature. The efficiency of the esters are quite difference in various methanol-gasoline systems. It is less effective in M15 and M85 than that of M30, M50 and M65. The esters can reduce the separation temperature in the three systems. For different systems, the most effective additive is quite different, and octyl ester, hepyl ester, octyl ester, octyl ester and decyl ester are the most effective ones for M15, M30, M50, M65 and M85 respectively. Especially, hepyl ester an reduce the separation temperature of M30 from more than 60.0°C to -22.3°C.

*Effect of Tartaric Ester on the Evaporation of Methanol-Gasoline*

The saturation vapor pressure will rise over that of gasoline as it blends with low percentage methanol such as M15 and M30, which will lead to the risk of vapor block as it used under relative high temperature. Vapor lock happens in internal combustion engines as the methanol-gasoline vaporizes easier than that of gasoline under the same conditions. Vaporized fuel can no longer flow into the intake system, which can lead to flameout or hard to ignition.

Some chemicals with lower saturation vapor pressure can depress the pressure of methanol-gasoline. In this work, effect of tartaric esters on the saturation vapor pressure evaporation of methanol-gasoline was screened referred to GB8017-87 “petroleum products the vapor pressure determination method (Reid Method)”. The relationship between the dosage of tartaric esters and saturation vapor pressure of M15 was summarized in Fig. 1.

The saturation vapor pressure of M15 is 63.5 kPa, which is 5.7 kPa higher than that of gasoline. With esters added in, the saturation vapor pressure decreases obviously. With the dosage of 0.1%, ethyl tartaric, propyl tartaric, butyl tartaric, amyl tartaric, hexyl tartaric and decyl tartaric can depress the saturation vapor pressure lower than that of gasoline, among which decyl tartaric is the most effective one with the dosage of 0.5%.

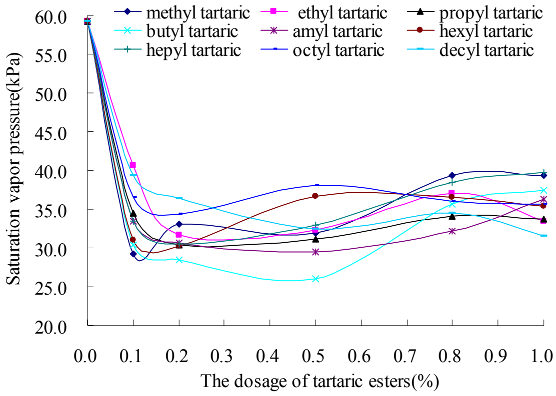


Fig. 1: The effect of tartaric esters on the evaporation of M15.

Then the effect of 0.1% tartaric esters on the evaporation of different methanol-gasoline systems was investigated in the following work, and it was summarized in Fig. 2. The fig shows that tartaric esters can depress vapor pressure of different methanol-gasoline systems, in which their behavior is quite different. In M15, methyl tartaric is the most effective additive to depress vapor pressure, the following is decyl tartaric, and other esters are less effective. But in other methanol-gasoline systems, methyl tartaric is the almost the last effective one, and the other esters, with longer alkoxyl groups, are effective additives. It is also found in Fig. 2, the efficiency increases along with the increases of alkoxyl groups, which may be due to the increased vapor pressure of the esters. The main reason is the ester molecules disperse on the surface methanol-gasoline and combined into a film to prevent the evaporation of methanol-gasoline, which results in the decline of the vapor pressure.

## Conclusions

Tartaric esters were synthesized and screened for phase stabilizing in M15, M30, M50 and M65 and pressure reducing in M15. The results show that the length of alkoxy group effects on the phase stability of methanol-gasoline significantly octyl ester, hepyl ester, octyl ester, octyl ester and decyl ester are the most effective ones for M15, M30, M50, M65 and M85 respectively. With the dosage of 0.1%, methyl tartaric is the most effective additive in M15, while, in other methanol-gasoline systems, the other esters are effective additives, and the efficiency increases along with the increases of alkoxyl groups. In one word, the tartaric esters have the potential to be bifunctional additives for methanol-gasoline.

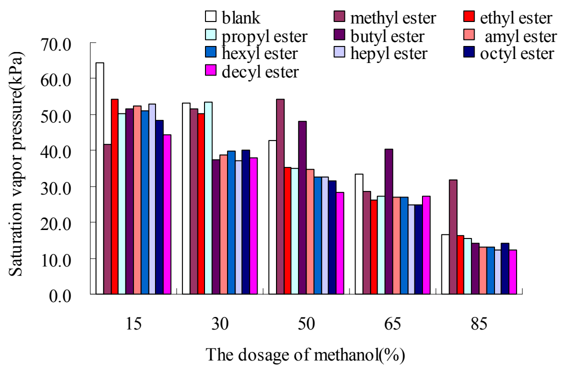


Fig. 2: The effect of tartaric esters on the evaporation of methanol-gasoline systems.

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