Development of the Adipates as Bifunctional Additive in Methanol-Gasoline

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Summary: In this paper, a series of adipates were synthesized and used as phase stabilizer and saturation vapor pressure depressor of methanol-gasoline. The results show that the stability of the methanol-gasoline depends on the length of alkoxy group over adipates. Several adipates were found to be effective in various gasoline-methanol blends, and the adipates display high capacity to depress the saturation vapor pressure of methanol-gasoline. According to the results, it can be concluded that the adipates containing long carbon chain have the great potential to be bifunctional gasoline-methanol additives.

Keywords: Methanol-gasoline; Adipates; Phase stability; Evaporation.

Introduction

Facing on the rising huge consumption of oil, development of clean and alternative fuels increasingly draws worldwide attentions [1]. In a large number of alternative fuels, methanol displays fine combustion properties similar to gasoline and has such advantages as high octane number, low emissions, antiknock, 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 applied in Shanxi, Sichuan, Zhejiang, Inner Mongolia, Shaanxi, Xinjiang and other places of China gradually [3]. However, there are several problems needing to resolve in methanol-gasoline research, in which 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 boil point of methanol leads to high possibility of vapor lock by raising the vapor pressure of methanol-gasoline [12-17]. The current solution for vapor lock is to add pressure depressor, such as aliphatic ketones, fatty aldehydes, fatty ethers, acetals/ketals, etc. [18-27]. At present, few researches have carried out to develop bifunctional additives with the abilities of both phase stability and vapor pressure depressor for methanol-gasoline. In this work, a series of the adipates was synthesized and screened in the methanol-gasoline as a bifunctional additive for the phase stability and vapor pressure depressor.

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 were tested 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 the Adipates

Method A: Ratio of the number of moles of adipic acid and methanol was 1:5. P-toluenesulfonic acid and the zeolite was added to the flask. After four or five hours of the refluxing, the mixture was cooled to room temperature and was dried by anhydrous sodium sulfate. Methanol was distillated, and a pale yellow oily liquid was left, then the dimethyl adipate was obtained by vacuum distillation. The synthesis of diethyl adipate and dipropyl adipate was the same method above.

Method B: Adipic acid, *n*-butanol with a mole ratio of 1:5 and 5% *p*-toluenesulfonic acid were refluxed in a flask equipped with a water separator. The reaction was stopped as no water was separated. After cooled to room temperature, the product was

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washed with saturated sodium carbonate solution and saturated brine solution each 2 or 3 times until it was neutral. The product was dried by anhydrous sodium sulfate. The cyclohexane of water-carrying agent was removed by atmospheric distillation. The *n*-butanol was separated and dibutyl adipate was obtained by vacuum distillation. Diamyl adipate, dihexyl adipate, dihepyl adipate, dioctyl adipate, didecyl adipate were synthesized by the same method above [28].

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 assigned as M15, M30, M50 and M65. The phase stabilizing tests were carried out according to Chinese National 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 to -25ºC. 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 [29-31].

Vapor Pressure Test

The effect of the adipates on vapor pressure of methanol-gasoline was investigated according to Chinese standards of GB 8017-87. The methanol-gasoline was poured into the vapor pressure detector and put into the water bath of 37.8ºC. 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.

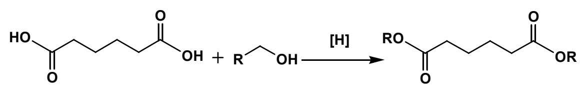
Table-1: The results of the synthesis of the adipates.

Adipates	Adipic acid : alcohol	Method	Yield (%)
dimethyl adipate	1:5	A	75.67
diethyl adipate	1:5	A	68.40
dipropyl adipate	1:5	A	76.94
dibutyl adipate	1:5	B	94.05
diamyl adipate	1:5	B	94.53
dihexyl adipate	1:5	B	97.39
dihepyl adipate	1:5	B	86.03
dioctyl adipate	1:5	B	89.14
didecyl adipate	1:5	B	92.54

Results and Discussion

Synthesis of the Adipates

The reaction between adipic acid and alcohols are shown in Scheme-1, and both the reaction conditions and the yield are summarized in Table-1. In this reaction, for the short chain alcohol, to reduce the byproduct, high quantities of alcohol were used. For the long chain alcohol, adipic acid and alcohol ratio is as high as 1:5, due to the insoluble of long chain alcohol in water so as to separate the produced water during the reaction. The yields were obtained in the range from 68.40% to 97.39%.



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

Effect of the Adipates on the Phase Stability of Methanol-Gasoline

The phase stabilities of the adipates for the methanol-gasoline blends of M15, M30, M50, M65 and M85 at different temperatures from -25 ºC to 40 ºC were investigated and summarized in Fig. 1 to Fig. 4. The experimental data indicates that the length of carbon chain of the alkyl oxygen group effects on the phase stability of methanol-gasoline significantly. For the adipates containing short chain, such as dipropyl adipate, dibutyl adipate, diamyl adipate, the phase stability to methanol-gasoline is ineffective, even over 11.1% dosage was used methanol and gasoline cannot homogenize in M15, M30, M50 and M65 at 40ºC. The reason may be due to the strong hydrophilic property but weak lipophilic property of short-carbon-chained the adipates, leading them not to dissolve in gasoline. During the experiment, the phenomenon shows that it was the obvious hierarchical that with the increase of the carbon chain of the adipates, lipophilic property of the adipates is markedly enhanced, which resulted in higher solubilization in the various blends.

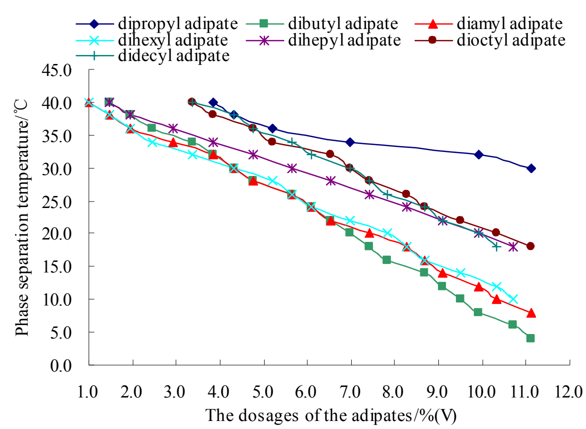


Fig. 1: The effect of the adipates dosage on the phase stability of M15.
(The dosages of dimethyl adipate and diethyl adipate are beyond 11.1% at 40ºC)

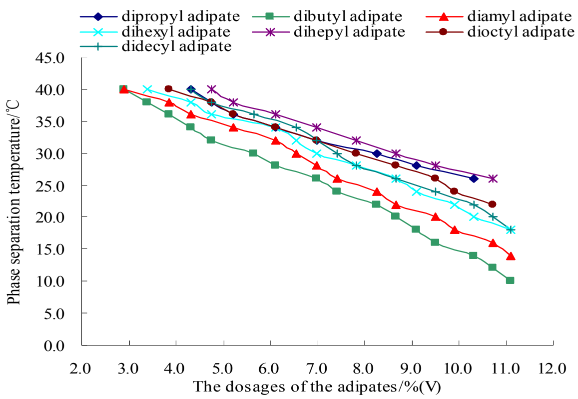


Fig. 2: The effect of the adipates dosage on the phase stability of M30.

（The dosages of dimethyl adipate and diethyl adipate are beyond 11.1% at 40 ºC）

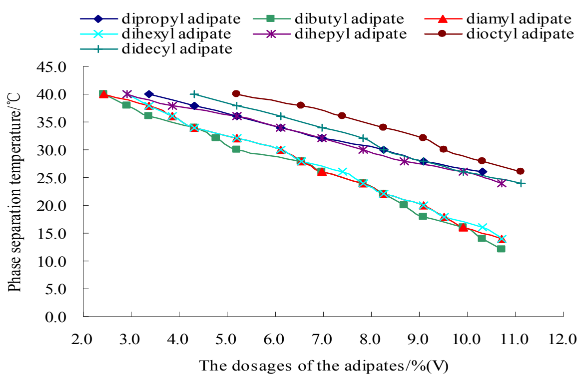


Fig. 3: The effect of the adipates on the phase stability of M50.

（The dosages of dimethyl adipate and diethyl adipate are beyond 11.1% at 40 ºC）

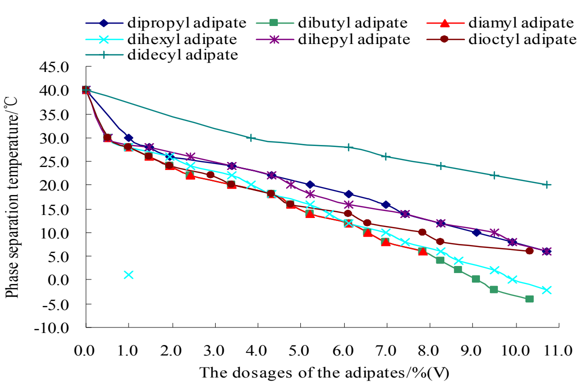


Fig. 4: The effect of the adipates dosage on the phase stability of M65.

（The dosages of dimethyl adipate and diethyl adipate are beyond 11.1% at 40 ºC）

When carbon atom number of the carbon chain increases to 10, didecyl adipate as a phase stabilizer, the lipophilic property is stronger than its hydrophilic property. During the experiment, didecyl adipate has good solubility in gasoline while the solubility in methanol is poor by showing obvious layer in the mixture of didecyl adipate and methanol. The adipates as bifunctional additive was investigated in methanol-gasoline by detecting the phase separation temperature and its performance of vapor press. The phase separation temperatures of four methanol-gasoline blends with the adipates dosage of 10% was used as the basis temperature under same standards. The phase separation temperature of M15 reaches 8 ºC after adding the additive of dibutyl adipate. The phase separation temperature of M30 and M50 reaches 15 ºC and 16 ºC respectively in the presence of dibutyl adipate. If the amount of methanol increases to a high level the solubility of gasoline with methanol can be greatly improved after adding dibutyl adipate. The phase separation temperature of M65 system decreased to -3 ºC with the additive of dibutyl adipate. When the temperature drops to -25 ºC, M85 system of the solution was still the homogeneous and clear state.

According to the results, it can be found that the long-carbon-chained adipates have the effective phase stability to methanol-gasoline. The phase separation temperatures of the four methanol-gasoline blends with the adipates dosage of 10% was estimated and shown in Fig. 5. It can be found that the phase separation temperature of M15, M30 and M50 declines at first, then increases, finally tends to stabilize with the length of the alkoxy group. The phase separation temperature of M65 declines at first and then increases along with the length of the alkoxy group. For all the blends, the phase separation temperature comes to the lowest as the carbon atom number of alkoxy group comes to 4. From the results, t can be concluded that dibutyl adipate containing long carbon chains is the best cosolvent for the methanol-gasoline blends.

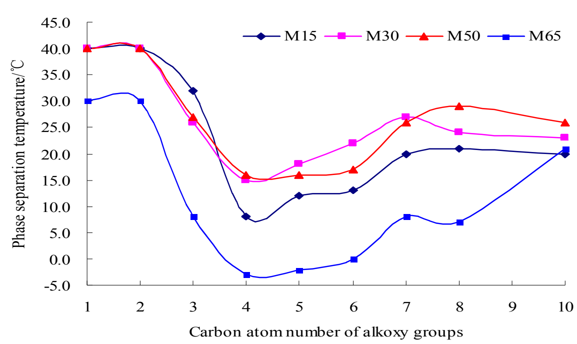


Fig. 5: The relationship of the alkoxy groups and the phase separation temperature.

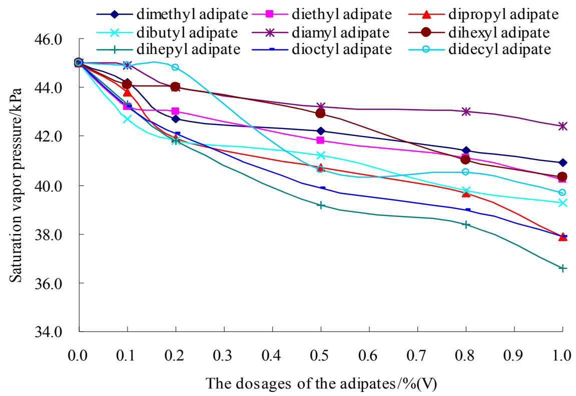


Fig. 6: The effect of the adipates on the evaporation of methanol-gasoline M15 system.

The Effect of the Adipates 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 vapor block as it used under relative high temperature. Some chemicals with lower saturation vapor pressure can be added to depress the high pressure of the blend. In this work, the effect of the adipates on the saturation vapor pressure of M15 methanol-gasoline was investigated referred to GB 8017-87 "petroleum products the vapor pressure determination method (Reid Method)", and the results are shown in Fig. 6. The original saturation vapor pressure of M15, 50kPa, is 5.7kPa higher than that of gasoline. As the adipates added, the saturated vapor pressure of methanol-gasoline system reduces with the increasing the length of carbon chain over adipates. As shown in Fig.6, the saturation vapor pressure of methanol-gasoline is depressed obviously after little amount of the adipates added. When the chain length of alkoxy group of the adipates increases, diethyl adipate, dimethyl adipate and dipropyl adipate can depress the saturation vapor pressure lower than that of gasoline, among which dipropyl adipate is the most effective one. When 1.0% amount of dihepyl adipate was used, the saturated vapor pressure of M15 can reduce to 8.4kPa. The main reason to the good performance to decrease the vapor depress of adipate derives should be contribute to the distribution of the adipates on the surface of methanol-gasoline, which prevents the formation of an azeotrope with low boiling point. When the chain length of alkoxy group of the adipates continues to increase, such as dihexyl adipate, didecyl adipate and dioctyl adipate, can depress the saturation vapor pressure lower than that of gasoline, among which dihepyl adipate is the most effective one. The lipophilic property of the adipates is more effective than its hydrophilic property. In the phase interface, the adipate has slightly stronger binding capacity with gasoline which causing the decrease of the gasoline evaporate by bonding with the methanol molecules to form the low-boiling azeotrope.

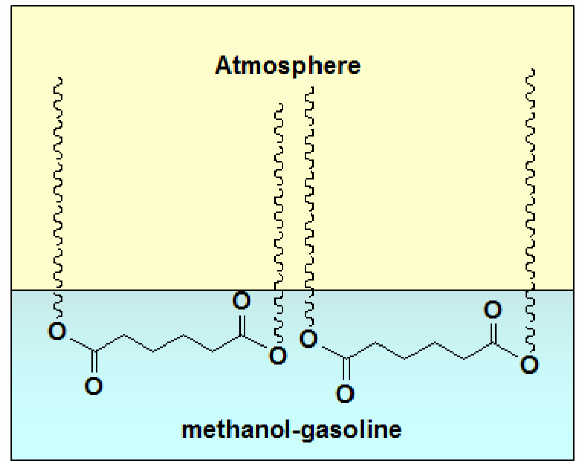


Fig. 7: Distribution of the molecules of the adipates on the interface of methanol-gasoline and atmosphere.

Conclusions

The adipates and its derives were synthesized and screened for their performances of phase stabilizing in gasoline-methanol mixture (M15, M30, M50, M65, M85) and pressure reducing in M15. The results show that the length of alkoxy group of the adipates effects on the phase stability of methanol-gasoline significantly. The phase stability of the adipates with long length of hydroxy group is more effective than that with short length. All of the synthesized adipates have great performance to depress the saturation vapor pressure of methanol-gasoline. 1.0% of the dihepyl adipate is the most effective bifunctional additive to gasoline-methanol mixture with good performance to the phase stability and depresses saturation vapor pressure.

Acknowledgment

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