Investigation of the castor oil and its methylester in methanol-gasoline as dual-functional additives

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Abstract: In this work, the castor oil and its methyl, as additives, have been studied under the conditions of the phase separation temperature of M15, M30, M50, M65 and M85 methanol gasoline at the temperature range from -25.0°C to 40.0°C, respectively. The influence of the additives on the phase stability and saturation vapor pressure of methanol gasoline was discussed. It turns out that, castor oil and its methyl derivatives, especially methyl castor oil, have good phase stability when be used for different ratio methanol gasoline blends. Introducing that more methyl castor oil will be needed to get homogeneous in water-methanol gasoline blends system. In addition, the castor oil and its methyl derivates can decrease the saturation vapour pressure of methanol gasoline effectively as well.

Keywords: Castor oil, additive, methanol gasoline, phase stability, vapour pressure.

1. Introduction

Nowadays, the sustainability of traditional energy is getting more and more attention, and this problem is considered to be a most critical social challenges. The development of clean fuels or the substitutes of traditional fuels is one of such important challenging question. As the rapid increasing demand of oil and the more stringent emission standards of the vehicle, the study of clean fuels and the substitutes of conventional fuels have attracted the attention of scholars gradually. In plenty of alternative fuels, methanol has similar combustion performance to gasoline, and has other good properties and advantages such as high octane number, low emissions, high antiknock and low cost. So, methanol has been selected for the alternative fuel for gasoline because of above features. But because methanol can not be dissolved in gasoline in any proportion, the miscibility question is one focus of this research area. A lot of surfactant as additives was reported to improve the solubility between methanol and gasoline. So far, the reports about the application of castor oil and its methyl...
esters as methanol-gasoline additives is really rare because of the poor solubility and stability in methanol and gasoline. Castor oil, oil of Palma Christi, is a fixed oil obtained from the seeds of Ricinus communis Linn. A triglyceride, in which the main fatty acids are ricinoleic acid (>90%), oleic acid, linoleic acid, palmitic acid, and stearic acid. It is widely used as lubricants, cutting fluids, methanol-gasoline additives resistance to rancidness [1-4]. The percentage of castor oil content which have about 90% ricinoleic acid (9-alkenyl-12-hydroxyoctadecanoic acid) is about 30%-60%. Castor oil is a kind of transparent, colourless or light yellow viscous liquid, which has a good solubility in alcohol. Compared castor oil to the other vegetable oils, it is the only hydroxyl acid-based grease and has the properties of higher hydroxyl value and acyl value[5-12]. In the other side, methanol and gasoline have a certain degree of solubility in castor oil, which illustrating "a multi-effect" methanol gasoline additive structural characters. So castor oil can be used as the ideal methanol gasoline phase Stabilizing agent [13-16]. In this study, the effects about the phase stability and saturated vapour pressure of methanol gasoline was researched under the condition that castor oil and its methyl derivates or biodiesel were used as cosolvents. The objective of this research is to explore a novel technical route for good performance in the system of biodiesel-methanol-gasoline, and get a product with alternative clean energy sources[17-19].

2. Experiment

2.1. Materials and instruments
In this research, Gasoline was supplied by Changqing Chemicals. And the other chemical reagents are chemically purity and were purchased directly from market. The analytical instruments used in the work are DFY-cryostat, DSL-080 petroleum products vapor pressure detector.

2.2. Preparation for Natural Oil Derivatives
Castor oil (150 mL), methanol (150 mL), concentrated sulfuric acid (7.5 mL) were placed into a 500 mL round bottom flask, then reaction begains under reflux conditions. The reaction mixture was cooled to room temperature, and then excess sodium carbonate solution was added until no gas produced. After washing with saturated brine solution for 3 times, the water exists in oil phase was removed by anhydrous sodium sulfate, then a pale yellow liquid was obtained after a distillation at 65℃ [20-21].

2.3. Test of Phase Stability
Adding different amount of methanol to the base gasoline, according to the contents of methanol, the fuel mixtures were obtained. Methanol volume content 15, 30, 50 and 65 vol.%, we named the fuel mixture as M15, M30, M50, M65 and M85. The implementation standards of the phase stabilizing tests were in accordance with the National standards [24].

2.4. Vapor Pressure Test
In our study, the effect of additive on vapor pressure of methanol-gasoline system was investigated in accordance with standards of GB/T 23799-2009. The methanol-gasoline sample was infused into the vapor pressure detector and then placed into the water bath under 37.8℃, the analysis device was taken out of the water bath firstly, and constant shock it intensely. then put the device into the water
bath secondly. Repeating the above operation every interval 5 min until the pressure of system is steady [25].

3. Results and Discussion

3.1. The phase stability in methanol-gasoline blends

The phase stabilities of castor oil and its methyl esters for the methanol gasoline system of M15, M30, M50, M65 and M85 at different temperatures from -25°C to 40°C were investigated and the results were depicted in Fig. 2 to Fig. 5. The experimental date indicates that molar ratio of methanol to gasoline have great effect on the phase stability in presence of castor oil and its methyl esters as additives. In the course of the research, the experimental phenomenon illustrates that a significant hierarchical will show up as the grows of dosage of castor oil and its methyl ester from 1% to 26%, the phase separation temperature has a significantly decreased from 40°C to -25°C. Furthermore, it was discovered that the stability of castor oil methyl ester used for the methanol gasoline blend is better than castor oil.

**Fig. 2** Effect of castor oil and its methyl ester on the phase stability of absolute M15

Within our explore system temperature range, it was found that the M15, methanol-gasoline mixtures began to be mutual dissolved at the 2.3% and 3.7% dosage of castor oil methyl ester and castor oil. As shown in Fig.1, as the amount of ester increases, the phase separation temperature will dropping gradually, and get the determined phase separation temperature to lowest value of -21°C, which indicated that the better solubilization role of methyl castor oil compared with castor oil at low methanol ratio in methanol-gasoline blends.
When the phase separation temperature was settled at 10℃, the dosage of methyl castor oil and castor oil increased to 9% and 15% respectively in M30, more cosolvent, 12% and 18% dosage of castor oil methyl ester and castor oil, should be introduced when phase separation temperature decreased to 0℃. The experimental data (Fig.3) shows that when the dosages of methyl castor oil was increased to 16%, the phase separation temperature can be arrived the lowest value at -21℃.

From above results it was found that when the amount of the additive, castor oil and methyl castor oil is increased, the methanol-gasoline blends system temperature for phase separation will decrease, which can be further confirmed from the following experiments by increasing the volume ratio of methanol. From Fig. 4, it can be seen that only 11.1% dosage of castor oil can make the homogenization of methanol and gasoline at 0℃, which is much lower than the amount used in M30 as shown in Fig. 3.
In Fig. 5, the methanol volume ratio was increased to 65%. From the results, the same tendency of cosolvent to the homogenization temperature of methanol-gasoline blends was also observed. It was found that phase stability of castor oil and its methyl ester to methanol gasoline at methanol volume ratio of 65% was significantly superior compared to low methanol volume as shown in Fig. 4. Furthermore (The dosages of additive are 10%). It can be found that methyl castor oil still kept more effective phase stability than the castor oil.

![Graph showing phase stability comparison between castor oil and methyl ester with varied methanol volume ratios.](image)

**Fig. 5** Effect of castor oil and its methyl ester on the phase stability of absolute M65

In order to compare the phase stability of castor oil and its methyl ester, the phase separation temperatures of various methanol-gasoline mixture system containing 10% dosage of additive were listed in Table 1. From the table, it can be revealed that the phase separation temperature of M15 reaches 0 °C under the optimized condition, while for M30 and M50 the phase separation temperature reaches 8 °C and 10 °C respectively in the presence of castor oil methyl ester. If the amount of methanol increases to a high level the solubility of gasoline with methanol can be greatly improved after adding castor oil methyl ester as shown in M65 with -5 °C phase separation temperature in presence of castor oil methyl ester.

### Table 1. The relationship of the additives and the phase separation temperatures

| methanol volume ratio | phase separation temperatures/°C |
|-----------------------|----------------------------------|
|                       | castor oil                      | castor oil methyl ester          |
| M15                   | 13                              | 0                                |
| M30                   | 30                              | 8                                |
| M50                   | 29                              | 10                               |
| M65                   | 10                              | -5                               |

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### 3.2. The phase stability in water contained methanol-gasoline blends

As we now know, that methanol has a strong polarity and can be infinitely miscible with water. The presence of water will increase the critical miscibility temperature of methanol and gasoline, and even in some cases, the moisture in commercial methanol and air will has a considerable impact on the stability of methanol-gasoline system and lead to methanol gasoline re-division. The phase stabilities of the castor oil and its methyl esters for the methanol gasoline blends of M15, M30, M50, M65 and
M85 containing 0.15% water were researched at various temperatures in the range of -25°C to 40°C, and depicted in figures from Fig.9 to 10.

Fig. 6 Effect of castor oil and its methyl ester on the phase stability of M15

Within the experimental temperature range, as to the sample of M15, 8% castor oil and 11% castor oil methyl ester cause the mutual solubility of methanol-gasoline blends in presence of 0.15% water. As the raising content of additive, the phase separation temperature steadily decreases indicating the good solubility of castor oil methyl ester in water contained system. In line with above observation, the temperature was lowered to 0 °C, and little further improvement was obtained.

Fig. 7 Effect of castor oil and its methyl ester on the phase stability of M30

The well role of castor oil and castor oil methyl ester to the mutual solubility of methanol and gasoline can be still maintained even contained 0.15% water and the phase separation temperature of methanol-gasoline blends reduces to -18°C for castor oil and -25°C for castor oil methyl ester, as illustrated in Fig.7. Furthermore, it can be found that with the increasing amount of castor oil and
castor oil methyl ester the phase separation temperature of methanol-gasoline was significantly reduced, especially for castor oil methyl ester, which indicates that castor oil methyl ester is more effective to the phase stability of methanol and gasoline. As the addition amount of castor oil methyl ester is 24.2%, the methanol-gasoline blends can be homogenized stable at low temperature at -25°C in methanol volume ratio of 30.

![Fig. 8 Effect of castor oil and its methyl ester on the phase stability of M50](image)

As the methanol volume ratio was raised to 50, the solution of M50 still remains homogeneous and clear in the experimental temperature range and water content of 0.15%. As displayed in Fig.8, it was indicated that the phase separation temperature reaches to 10°C when the dosage of castor oil methyl ester and castor oil were 13% and 16% respectively. If the colder phase separation temperature, 0°C, was settled, the dosage of castor oil methyl ester and castor oil should be increased to 16.5% and 18%.

![Fig.9 Effect of castor oil and its methyl ester on the phase stability of M65](image)

3.3. The vapour pressure of M15 and M30
As we now know, when small percentage methanol was added into the methanol-gasoline blend, the saturation vapor pressure will further improve and exceed the gasoline itself due to the high vapor pressure of methanol additive. As a result the vapor block became difficult to avoid especially at comparative high temperature. In factor, chemicals, which have lower saturation vapor pressure, can
usually be used to weaken the high pressure of the mixture system [26]. In this research, the influence about the castor oil methyl ester on the saturation vapor pressure of M15 and M30 was investigated, which consulted the vapor pressure determination method (GB 8017-87) of petroleum products, and the research conclusion are depicted in Fig. 10.

![Fig. 10](image_url)

**Fig. 10** Effect of castor oil methyl ester dosage on saturated vapour pressure of M15 and M30

We can draw such conclusion that the subjects’ saturated vapour pressure will descend with the growth dosage of the castor oil methyl ester and the decrease tendency will be significant when methanol ratio was increase. The main reason should be contributed to the amphiphilicity of castor oil methyl ester which improving the molecules adsorbed on the phase interface between methanol, gasoline. By the way, the amphiphilicity of castor oil methyl ester can prevent to form the methanol-alkane low-boiling azeotropes in the fuel-mixtures. The quantity of castor oil should be settled at the range from 0.1% to 0.2% to meet the saturated vapour pressure requirement of M15, M30 blends in market.

### 4. Conclusion

Castor oil and its methyl ester have used as the phase stabilizer of methanol-gasoline blends. Both of them exhibited well phase stability performance to the system of methanol-gasoline system, and castor oil methyl ester showed much better solubilization effect than castor oil. With the continuous raising content of methanol in the blends, the amount of additives to keep low homogenaztion temperature can be reduce. In addition, water exists in the blends system has a obviously influence on the phase stability of blends. Similar tendency of additive amount and its phase separation temperature can be found in the hydrous condition. Important role of castor oil methyl ester to the saturated vapor pressure of methanol gasoline blends has been found, and at least 0.1-0.2% of castor oil methyl ester should be used to keep the saturated vapor pressure in a low level, when the methanol ratio is relatively low in the blends.

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