INTRODUCTION

After more than a century of development, the internal combustion engine has become the most widely used power unit with its advantages of high thermal efficiency and good reliability. According to the OPEC report, global car ownership will double by 2040 compared to 2016 and nearly 80% of cars will still be powered by conventional internal combustion engines. Therefore, the internal combustion engine will still occupy a dominant position in the future. However, the rapid development of the internal combustion engine industry presents us with new challenges, including energy consumption and environmental pollution.

Petroleum is the most important energy source in the world, accounting for one-third of total energy consumption. Therefore, it is necessary to carry out research on energy conservation to alleviate the dependence on petroleum resources. The internal combustion engine consumes about two-thirds of the petroleum resources each year. New energy vehicles such as electric vehicles and hybrid vehicles are developing...
rapidly, which can alleviate excessive dependence on petroleum resources to a certain extent. However, their holdings are very small, which is still not enough to slow down the consumption of petroleum resources. Therefore, it is necessary to reduce the dependence of internal combustion engines on petroleum resources to realize sustainable development. Another major challenge for internal combustion engines is environmental pollution which is directly threatening the human health. For example, car ownership reached 217 million in 2017, and the total amount of four regulated emissions including nitrogen oxides ($\text{NO}_x$), particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) has reached an astonishing 38.44 million tons in China.\textsuperscript{3} It should be noted that diesel vehicles only account for 9.4% of the total number of vehicles, but the main types of this kind of diesel vehicles were large buses and trucks with the higher displacement volume. Thus, $\text{NO}_x$ emissions of diesel vehicles are close to 70% of total vehicle emissions, and PM emissions are even more than 90%. To summarize, exhaust emissions from diesel vehicles have become one of the main sources of air pollution. In order to effectively solve the current shortage of petroleum resources and serious environmental pollution, it is necessary to develop a renewable and sustainable fuel with excellent engine performance and emission characteristics so as to achieve partial or complete substitution for fossil fuels.\textsuperscript{3}

Biofuel has a promising prospect for the development and utilization of renewable energy resources. It generally refers to solid, liquid, or gas fuels consisting of or extracted from biomass,\textsuperscript{5} which is all plant and plant-derived. Moreover, according to the Kyoto protocol, the $\text{CO}_2$ emission for biofuel combustion is balanced due to the plants for biofuel can absorb the $\text{CO}_2$ emission for biofuel combustion and thus can achieve carbon neutral. Therefore, the use of biofuels can reduce the greenhouse emissions more significantly compared to that of fossil fuels and alleviate the increasingly serious global warming problem.

As a renewable energy source, ethanol is mainly made from biological raw sugary, starchy, and lignocellulosic materials. Because of its abundant material sources such as corn, sugarcane, and biomass waste, ethanol has become the most widely used biofuel in the world.\textsuperscript{6,8} Statistical data showed that, in China, over 61.6 million liters of ethanol was used as fuel in 2015.\textsuperscript{6} The International Energy Agency also indicated that the ethanol supply would climb from 1 million barrels of oil equivalent per day (mboe/d) in 2010 to 3.4 mboe/d in 2035.\textsuperscript{9} Therefore, ethanol receives considerable attention and is the most studied alcohol for blending with conventional mineral fuels.\textsuperscript{10-16} If ethanol is used to replace part of diesel oil in the mixed fuel system, the consumption of petroleum-based fuel can be reduced to a certain extent. Moreover, ethanol has good volatility to solve the problem that diesel fuel cannot be well mixed with air, thereby reducing soot emissions. In addition, the oxygenation of ethanol can further reduce soot emissions.\textsuperscript{17} At the same time, ethanol has a large latent heat of vaporization, which can effectively reduce the temperature of the engine cylinder, thereby reducing NO\textsubscript{x} emissions.\textsuperscript{18} However, ethanol has limited solubility in diesel fuel because of their difference in chemical structures and characteristics. Phase separation and water tolerance in ethanol-diesel blend fuel are crucial problem, especially at low temperatures.\textsuperscript{19-24} Therefore, the study of the miscibility of ethanol and diesel is the basic work to solve the practical application of diesel/ethanol-blended fuel.

Fernando et al\textsuperscript{25} investigated that most ethanol/diesel mixtures were rapidly separated into two distinct phases at room temperature. Therefore, in order to ensure the phase stability of the entire mixture system, it is necessary to use some additives.\textsuperscript{8,14,15,19,20} Higher alcohols own hydrogen donor groups (AOH) in association with molecular functional groups that accept hydrogen, which interacts more strongly with the polar materials. Besides, through van der Waals forces, the nonpolarity or low polarity carbon chains of higher alcohols possess good affinity with the hydrocarbons of diesel. For this reason, the additives of higher alcohols present a much better soluble performance in theory. In reality, higher carbon number alcohols, especially n-butanol as a relatively short straight-chain alcohol, have been applied as a surfactant additive in ethanol/diesel blends.\textsuperscript{13,26,27} Liu et al\textsuperscript{28} and Jin et al\textsuperscript{29} systematically studied the effect of high-carbon alcohols on the solubility of hydrous ethanol and diesel mixtures at various temperatures of 5, 15, and 30°C. The influence of alcohol chain length on solubility was investigated, and the effect of straight and branched chain on solubility was studied via comparing with four isomers of butanol (n-butanol, 2-butanol, iso-butanol, and tert-butanol). Additionally, effects of various functional groups including both hydroxy and ketone groups were studied. Results showed that alcohols with higher carbon numbers provided a better insolubility, but a higher carbon number alcohol such as n-dodecanol correlated with a lower pour point which led to the gelling for the blends. Based on the performance of 6-carbon alcohols on phase stability, it was clear that the straight-chain structure and hydroxy group showed a better hydrotropism than cyclic structure and ketone group, respectively. For butanol isomers, straight-chain butanols had better solubility performance than that of branched structures.

Cetane number is used as an important property to represent the compression ignition characteristic of fuel. Because the cetane number of ethanol is very low (less than 10), the cetane number of the ethanol/diesel mixed fuel is lower. As the blending ratio of ethanol increases, the overall cetane number decreases, which causes high pressure rise rate at low loads. In addition, too low cetane number will increase emissions of CO, HC, and NO\textsubscript{x}.\textsuperscript{30} The main reason is that the lower cetane number leads to unstable diesel engine operation owing to cyclic cylinder pressure variability or irregularity.\textsuperscript{31} Therefore, the surfactant additive not only can
effectively dissolve mixtures of ethanol and diesel, but also should have a high cetane number to ensure the ignition of ethanol/diesel fuel. Although high-carbon alcohol can effectively solve the delamination problem in hydrous ethanol/diesel mixed fuels, the cetane number of high-carbon alcohol is moderate, which does not increase the cetane number of the blended fuels of ethanol/diesel.

Polyoxymethylene dimethyl ethers is a mixture that composed of many short oligomers. The general chemical formula is CH₃O-(CH₂O)n-CH₃ with n ranging from 1 to 8; moreover, the chain length can be more than 10. It can be derived from natural gas, coal, and waste biomass. The research on the production of PODE has made a breakthrough recently. The addition of PODE was shown to improve some properties of the blend. Surfactant is a substance that can change the interfacial state of solution system by adding a small amount of surfactant. It has both hydrophilic and lipophilic groups, which can be aligned on the surface of the solution, with the hydrophobic group of –O– and the lipophilic groups of –CH₂– and –CH₃. PODE can be used as surfactant. In the previous study, PODE has been considered as a good surfactant to improve the miscibility of anhydrous ethanol/soybean oil. However, there is little report on the solubility of PODE for ethanol/diesel blends to author’s knowledge. Furthermore, PODE has a higher cetane number than diesel, which can increase the cetane number of ethanol/diesel blends when PODE is used as a surfactant additive.

Therefore, in order to evaluate the solubilizing ability of PODE on the mixture of ethanol and diesel, the phase behavior of the ternary system (PODE, anhydrous ethanol, and diesel) was investigated at different ambient temperatures in the current study. Additionally, once ethanol is added to diesel fuel, the blend can easily absorb water from ambient humidity. The excessive water content in the blend tends to cause phase separation. It is necessary to investigate the effect of water addition on the phase behavior of the system. Then, the phase behavior of hydrous ethanol with different purity, PODE, and diesel system was also studied in the current study works. This study provides the possibility of the application of new alternative fuels of ethanol/PODE/diesel in engines.

### 2 | EXPERIMENTAL SETUP AND METHODS

The test diesel used in the experiment was commercially available. The ash content of tested diesel is lower than 0.1 wt.%, and the water content was lower than 0.02 vol.%, which has little influence on the solubility performance. Meanwhile, in order to avoid the effect of different diesel component such as aromatic content on phase behavior, the same diesel fuel was used for all experimental tests. The detailed physicochemical characteristics of the tested diesel fuel are shown in Table 1. The analytical (AR) grade pure ethanol was used. The purity of ethanol exceeded 99.5% by volume. Additionally, hydrous ethanol with different purities, including 98% and 95% ethanol, was obtained by mixing ultrapure water at a corresponding proportion. The mass distributions

| TABLE 1 Physicochemical characteristic of the tested diesel fuela | Physicochemical characteristic | Tested diesel | Tested diesel |
|---|---|---|---|
| Flash point (°C) | 67.0 | Tricyclic alkanes (wt.%) | 3.1 |
| Cetane value | 52.6 | Total cyclic alkanes (wt.%) | 29.3 |
| Cetane index | 52.9 | Total saturated hydrocarbon (wt.%) | 76.8 |
| T10/T50/T90/T95 (°C) | 209.1/274/342/355.5 | Alkylbenzene (wt.%) | 6.2 |
| Ash content (wt.%) | 0.0182 | Tetrahydronaphthalene or indan (wt.%) | 10.1 |
| Carbon residue (wt.%) | 0.0182 | Indene (wt.%) | 3.3 |
| Density (g/mL) at 20°C | 0.833 | Total monocyclic aromatic hydrocarbons (wt.%) | 19.6 |
| Lower heating value (MJ/kg) | 42.6 | Naphthalene (wt.%) | 0.6 |
| Corrected wear scar diameter (60°C)/μm | 359 | Naphthalenes (wt.%) | 1.3 |
| Colloid (mg/100 mL) | 119.6 | Acenaphthene (wt.%) | 1.2 |
| Heat stability (mg/100 mL) | 5.0 | Acenaphthenes (wt.%) | 0.4 |
| Sulfur content (mg/kg) | 6.0 | Total bicyclic aromatic hydrocarbons (wt.%) | 3.5 |
| Alkanes (wt.%) | 47.5 | Tricyclic aromatic hydrocarbons (wt.%) | 0.1 |
| Monocyclic alkanes (wt.%) | 16.1 | Polycyclic aromatic hydrocarbons (wt.%) | 3.6 |
| Dicyclic alkanes (wt.%) | 10.1 | Total aromatics (wt.%) | 23.2 |

*aThe fuel characteristics of the tested diesel are experimental results."
and the molecular structure of PODE used in this experiment are shown in Table 2. It can be seen that each carbon atom is connected to an oxygen atom and there is no C-C bond in PODE, which is a superior molecular structure to suppress soot formation.\textsuperscript{54} The properties of the tested fuels are given in Table 3. It should be noted that both ethanol and PODE can be made from biomass and are renewable energy sources. Therefore, if nonrenewable petrochemical diesel is replaced by these two fuels, it is of great significance on reducing the greenhouse emissions.

In this study, phase boundary was determined using the addition method,\textsuperscript{55} which can analyze the sample quantitatively and accurately. The changes of clear one liquid phase and clear two liquid phases were judged as the end point of addition in this experiment. First, the ambient temperature of phase separation for PODE/diesel, PODE/anhydrous ethanol, and anhydrous ethanol/diesel was investigated. These mixtures were placed into a digital constant temperature incubator with 0.1°C precision. Then, the setting temperature was gradually increased until the clear one liquid phase was visually observed. Second, the solubility effects of PODE on the mixtures of diesel and ethanol (100%, 98%, 95% purity) were systematically studied at different ambient temperatures. Ethanol/diesel mixtures were blended at different ratios that varied from 0 to 100 vol.% in 10 vol.% increments. The initial volume of these blends was set to 3 mL and placed into the centrifuge tube. Then, PODE (surfactant) was gradually added into the blends by a high-precision pipette (0.1 μL accuracy) until the stratification of the mixture was completely eliminated and the clear one liquid phase was visually observed. At this moment, the volume of PODE was recorded. During the intersolubility reaction, in order to obtain a homogeneous blending rapidly, a vortex mixer with a rotating capacity of about 210 g was used. Finally, in order to explore the main reason for the instability of the ternary system with the addition of water, the water absorption of diesel, anhydrous ethanol, PODE, and the blend of PODE/diesel were investigated separately. The tested fuels were separately placed in a centrifuge tube, and then, water was gradually added into the centrifuge tube until the state of the clear one liquid phase was destroyed. At this moment, the water volume was recorded.

### RESULTS AND DISCUSSION

#### 3.1 | Phase behavior of PODE, anhydrous ethanol, and diesel system

#### 3.1.1 | Phase behavior of anhydrous ethanol/diesel system

To use ethanol in diesel engine, the solubility between anhydrous ethanol and diesel fuel has to be known and thus was investigated firstly. The phase behavior of anhydrous ethanol/diesel system is shown in Figure 1. The area above the curve represents that anhydrous ethanol and diesel can be soluble, whereas the area below the curve is the insoluble region. It can be found that anhydrous ethanol and diesel are relatively easy to mix at high temperatures. This is because the thermal motion of the molecules is more violent at high temperature. When the temperature is higher than 48°C, anhydrous ethanol and diesel can be soluble with each other at any proportion. As the properties of diesel fuel change in the binary fuel system, the specific temperature for the solubility between ethanol and diesel can vary a little due to the different properties of diesel fuel, but the trends on solubility are same to previous results.\textsuperscript{56} The solubility decreases sharply with decreasing ambient temperature, resulting in phase separation of anhydrous ethanol and diesel. The phase behavior of the system is also affected by the volume ratio of anhydrous ethanol. When the volume proportion of anhydrous ethanol is close to 40%, the solubility of the system is the worst and the lowest critical solution temperature reaches a peak of 48°C. For room temperature (approximately 20°C), the system of anhydrous ethanol/diesel is completely soluble only when the proportion of anhydrous ethanol is large enough or small enough. It can be concluded that the solubility of anhydrous ethanol/diesel without additives is not satisfactory to be used in diesel engines. Therefore, it is necessary to investigate the suitable additive as a surfactant for anhydrous ethanol/diesel system.

#### 3.1.2 | Phase behavior of PODE/diesel and PODE/anhydrous ethanol system

In order to study the effect of PODE as surfactant in diesel-ethanol binary system, it is necessary to study the solubility of PODE with diesel oil and PODE with ethanol.

| Components  | Mass fraction (wt.%) | Flash point (°C) at closed cup | Cetane number | Molecular structure |
|-------------|----------------------|-------------------------------|--------------|--------------------|
| PODE\textsubscript{3} | 44.80               | 43                            | 78           | ![Molecular structure](image) |
| PODE\textsubscript{4} | 28.24               | 77                            | 90           | ![Molecular structure](image) |
| PODE\textsubscript{5} | 17.09               | 103                           | 100          | ![Molecular structure](image) |
| PODE\textsubscript{6} | 9.87                | –                             | 104          | ![Molecular structure](image) |

\textsuperscript{3}The subscript of PODE refers to the index “n” in the chemical formula.
respectively. Therefore, in this section, the mixing of PODE and diesel with different proportion at different ambient temperatures was investigated firstly. The volume proportion of PODE in the mixture increased from 10% to 90% in 10% increment. The phase behavior of PODE/diesel mixture is shown in Table 4. When the ambient temperature is higher than 10°C, the mixtures of PODE/diesel are completely miscible no matter how many PODE fractions in blends. For the ambient temperature of 10°C, when the volume ratio of PODE is less than 20%, several small vesicles in the mixture can be observed. The appearance of several vesicles is due to the fact that PODE/diesel is only partially miscible. When the volume proportion of PODE exceeds 20%, the mixture presents a single-phase liquid system, and PODE/diesel is completely miscible. However, when the ambient temperature is reduced to 0°C, the PODE/diesel system presents two-phase liquid and turbid liquid. But even at the temperature of 0°C, the PODE/diesel system with a small proportion of PODE is still partially miscible.

As described above, it can be concluded that PODE can be blended with diesel fuel at any proportion without phase separation at room temperature, but the PODE/diesel mixture has a relatively poor solubility at temperatures below 10°C and is partially insoluble at 10°C.

In addition, the phase behavior of PODE/anhydrous ethanol system at different ambient temperatures (0°C, 10°C, 20°C, 30°C, 40°C) was also investigated. It was found that PODE and anhydrous ethanol can be soluble with each other at all tested temperatures.

### 3.1.3 Effects of PODE on solubility of anhydrous ethanol/diesel blends

In this section, the additional experiments of PODE were employed to investigate the effect of PODE on the anhydrous ethanol/diesel blends. According to the experimental results of the above anhydrous ethanol/diesel system, the blend of anhydrous ethanol and diesel cannot be soluble with each other at any proportion when the temperature is lower than 48°C. Meantime, considering the mutual solubility of PODE and diesel oil is poor at 0°C. Four different ambient temperatures of 10°C, 20°C, 30°C, and 40°C were selected in this part of the experiment. The phase behavior of the ternary system is shown in Figure 2. In the ternary phase diagram, each line represents the phase boundary from the single-phase isotropic region to the anisotropic region. Any point above the line is a single phase, and a point below the line is in an anisotropic state. At four different tested temperatures especially at lower temperature, the solubility of anhydrous ethanol/diesel without the addition of PODE is poor. The intermiscibility of anhydrous ethanol and diesel is improved with the addition of PODE. This is because the two-component system of PODE and ethanol has an excellent intermiscibility; meanwhile, both PODE and diesel also have good intermiscibility. According to the hydrophile-lipophile balance value (HLB),53 the HLB value of PODE is 15-18 which belongs

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**Table 3** The properties of diesel, ethanol, and PODE\textsuperscript{a,5,32,39,62-64}

|            | Diesel | Ethanol | PODE |
|------------|--------|---------|------|
| Cetane number | 52.6   | 8       | 87.7 |
| Oxygen content (wt.%) | –      | 34.8    | 48   |
| Stoichiometric air/fuel ratio | 14.3   | 9.02    | 6.82 |
| Density (g/mL) at 20°C | 0.833  | 0.789   | 1.068|
| Lower heating value (MJ/kg) at 40°C | 42.6   | 27      | 20.98|
| Kinematic viscosity (mm²/s) | 3.24   | 1.13    | 1.11 |
| Boiling point (°C) | –      | 78      | 156-280 |

\textsuperscript{a}The fuel characteristics of the tested diesel are experimental results. The fuel characteristics of PODE and ethanol obtained from References.5,32,39,62-64

**Table 4** Phase behavior of PODE/diesel system

| PODE vol% | 0°C | 10°C | 20°C | 30°C | 40°C |
|-----------|-----|------|------|------|------|
| 10%       | b   | b    | a    | a    | a    |
| 20%       | b   | b    | a    | a    | a    |
| 30%       | d   | a    | a    | a    | a    |
| 40%       | d   | a    | a    | a    | a    |
| 50%       | d   | a    | a    | a    | a    |
| 60%       | d   | a    | a    | a    | a    |
| 70%       | c   | a    | a    | a    | a    |
| 80%       | c   | a    | a    | a    | a    |
| 90%       | c   | a    | a    | a    | a    |

Note: “a”: single-phase liquid; “b”: several small vesicles; “c”: turbid liquid; “d”: two-phase liquid.
to solubilizer and ethanol belongs to water-in-oil emulsifier with the HLB value of 7.95. The solubilization of PODE is better than ethanol due to the dissolution principles in the binary fuel blend. Thus, theoretically PODE has the ability to improve the solubility of diesel and ethanol.

As can be seen from Figure 2, the ability of PODE to improve the miscibility of anhydrous ethanol/diesel mixtures is greatly affected by the ambient temperature. For different temperatures, the rules of the phase boundaries are different. For the temperatures of 20°C, 30°C, and 40°C, when the ratio of anhydrous ethanol to diesel is close to 1:1, the ternary system has the worst miscibility and the demand for PODE reaches its peak. When the proportion of hydrous ethanol is further increased or decreased, the demand for PODE is gradually reduced. If the temperature is higher than 20°C, anhydrous ethanol and diesel without the addition of PODE can be completely soluble when the proportion of ethanol is greater than 90%. If the temperature is higher than 30°C, anhydrous ethanol and diesel without the addition of PODE can be completely soluble when the proportion of ethanol is more than 80%. However, for the temperatures of 10°C, the peak demand for PODE additive appears on the lower proportion of anhydrous ethanol. When the proportion of anhydrous ethanol in the mixture increases, the demand for PODE decreases dramatically. Although the miscibility of ethanol and diesel is unaltered, the miscibility of PODE and diesel is changed when the volume fraction of PODE is less than 20% and the ambient temperature is 10°C, as shown in Figure 2. Then, the change of the PODE/diesel system causes the inflection point of the ternary diagrams move to the side with high volume fraction of diesel. In addition, by comparing the ternary diagrams at different ambient temperatures as shown in Figure 2, it can be seen that the shadow area decreases when the temperature increases from 10°C to 40°C. This means that the demand for PODE is decreased with the increase of ambient temperature.

Meantime, to present the needs of PODE in ethanol/diesel blends more intuitively, the percentage of PODE addition in different temperatures in the ternary system of ethanol/diesel/PODE for miscibility is shown in Figure 3. The ordinate of Figure 3 shows the proportion of PODE in the ternary system, which is more intuitively, shows the temperature-dependent difference on the solubility of PODE. It can be seen that PODE does not work well to improve solubility of the ternary system at the lower ambient temperature of 10°C. For example, at the temperature of 10°C, the percentage of PODE to be added can account for more than 50% in the ternary system when the volume proportion of anhydrous ethanol is less than 70%. This phenomenon is caused by a sharp decrease in the mutual solubility of PODE/diesel and ethanol/diesel at a lower ambient temperature. It can also be found that the demand for PODE is drastically reduced when the temperature increases. Taking 50% of the volume ratio of ethanol as an example, when the temperature is raised from 10°C to 20°C, 30°C, 40°C, the proportion of PODE in the ternary system is 44%, 26%, 13%, and 9%, respectively. The experimental results can be concluded that PODE can effectively improve the miscibility of anhydrous ethanol and diesel when the ambient temperature is higher than 10°C. Once the ambient temperature reaches 20°C, the needs on PODE are dramatically reduced to keep the miscibility of anhydrous ethanol and diesel. For example, the ternary system about 10% PODE, 10% ethanol, and 80% diesel can keep stable one phase, which may be a good choice to be used in the current diesel engines and should not need any changes in engines.

FIGURE 2 The phase behavior of anhydrous ethanol/diesel/PODE system at different temperatures (The shadow area: 2-phase liquid; the blank area: 1-phase liquid; Line + symbol: phase boundary)

FIGURE 3 The percentage of PODE addition in different temperatures in the ternary system on ethanol/diesel/PODE for miscibility
Furthermore, PODE can significantly improve the cetane number of the blend of anhydrous ethanol and diesel. Based on the cetane number of pure PODE, according to the calculation formula of cetane number of mixture based on Murphy et al., the cetane number of the mixed system was calculated and recorded in Table 5. As shown in Table 5, the improvements of cetane number by PODE decrease with the increase of the proportion of anhydrous ethanol in the ternary system. For example, when the proportion of PODE is the same, the improvement of cetane number is appropriate when the content of anhydrous ethanol is less than 40%, which is close to diesel. At the same time, when the proportion of anhydrous ethanol is large enough, it can be mutually soluble with diesel without PODE. Due to the lack of PODE to improve the cetane number, the system has the lowest cetane number. In conclusion, PODE can be used as an efficient cetane number improver.

In addition, PODE also plays a positive role in improving the flash point of blends, which can ensure the safety performance of the mixed fuel of ethanol and diesel oil during storage, transportation, and use. The closed flash points of gasoline, diesel, and ethanol are −50 to −20°C, −55°C, and 13°C, respectively. For PODE, although the closed flash point of PODE is 43°C, the closed flash point of PODE can reach 103°C as shown in Table 2. Therefore, the high flash point of PODE with higher n can compensate for the low flash point of ethanol. With the increasing proportion of PODE in the blend fuel system, the improvement of flash point should be more significant.

3.2 Phase behavior of PODE, hydrous ethanol, and diesel system

It is well known that alcohols are more hygroscopic than diesel fuel. Once alcohol is used in the engine and the fuel storage tank is not sufficiently sealed during storage and transportation, the blend of diesel and ethanol will absorb water from the ambient humidity. Then, the excessive water content in the blend tends to cause phase separation. In order to avoid phase separation, it is necessary to investigate the effect of water addition on the phase behavior of the system. Therefore, in this part of the experiment, the phase behavior of hydrous ethanol with different purity, PODE, and diesel system is studied. The hydrous ethanol with the purity of 98% and 95% was selected.

Previous experimental results show that the miscibility of PODE, ethanol, and diesel system is satisfactory only when the temperature is higher than 10°C. Thus, the ambient temperatures were selected at 20°C, 30°C, and 40°C in the study of hydrous ethanol with the purity of 100%, 98%, and 95%. The phase behavior of the ternary system on diesel, PODE, and ethanol with different purity is shown in Figure 4. The blends of diesel and hydrous ethanol with 98% purity are immiscible except when the proportion of hydrous ethanol is higher than 90% and the ambient temperature is higher than 30°C. With the addition of PODE, the miscibility of the system is gradually improved. When the volume ratio of diesel to hydrous ethanol is 1:1, there is an inflection point on the curve of the phase boundary. This means that when the volume ratio of hydrous ethanol to diesel is 1:1, the miscibility of the system is the worst, and more PODE is needed to ensure the miscibility of the system. It can be seen from Figure 4 that the shadow area decreases with the increase of ambient temperature. That is, the dependence on the PODE decreases at the higher temperature. When the temperature is raised from 20°C to 30°C and 40°C, the maximum volume ratio of PODE in the blend is reduced from 47% to 40% and 15%, respectively, in the blend with 98% purity hydrous ethanol; and 50%, 42%, and 33% in the blend with 95% purity hydrous ethanol, respectively. This shows that, like the system of PODE, anhydrous ethanol, and diesel, the increase in ambient temperature is also an effective measure to improve the miscibility of the PODE, hydrous ethanol, and diesel system, but the ambient temperature has less effects on improving the miscibility of the PODE, 95% ethanol, and diesel system.

By comparing anhydrous ethanol with hydrous ethanol with 98% purity and 95% purity in Figure 4, it can be seen that the shaded area increases significantly at the same temperature when there is water in the system. That is, the miscibility of hydrous ethanol and diesel is worse than that of anhydrous ethanol and diesel, and the demand for PODE increases sharply at the end of the addition. As shown, the demand for the PODE increases sharply when the purity of the ethanol decreases. Taking the 50% volume ratio of hydrous ethanol at ambient temperature of 30°C as an example, when the purity of ethanol is reduced from 100% to 98%, the proportion of PODE is increased 27% compared to ethanol with 100% purity. Moreover, when the purity of ethanol is reduced from 100% to 95%, the proportion of PODE is increased 30% compared to ethanol with 100% purity. Additionally, when the volume proportion of ethanol in the mixture is 90%, anhydrous ethanol and hydrous ethanol with 98% purity can be soluble with diesel without the help of PODE. But ethanol

| TABLE 5 | Cetane number of the ternary fuel systems on anhydrous ethanol, PODE, and diesel with different proportions of components |
|---------|-------------------------------------------------|
| PODE vol% | Ethanol vol% | Diesel vol% | Cetane number |
| 10       | 10           | 80         | 51.7          |
| 10       | 20           | 70         | 47.2          |
| 10       | 40           | 50         | 38.3          |
| 10       | 60           | 30         | 29.4          |
| 0        | 90           | 10         | 12.5          |

The cetane number of the mixed system was calculated according to Murphy et al.
with 95% purity still requires a large amount of PODE to be soluble with diesel. Therefore, it can be concluded that the addition of water greatly destroys the phase stability of the ternary system. A large amount of PODE is needed to achieve an isotropic single-phase state when the water content increases. This means that the addition of water greatly weakens the solubilizing ability of PODE on ethanol and diesel mixtures.

In order to explore the main reason for the instability of the ternary system after the water is added, the water absorption of diesel, anhydrous ethanol, and PODE was investigated separately. It was found that the water absorption of diesel is close to zero, and ethanol can be soluble with water at any ratio. The water absorption of PODE is shown in Figure 5. It can be seen that the proportion of water absorption of PODE is only about 0.12% at ambient temperature of 10°C. The water absorption of PODE is significantly affected by the ambient temperature. The water absorption of PODE increases rapidly with the rise of temperature. When the temperature is increased to 30°C, the proportion of water absorption of PODE is 3.04%, which is nearly 30 times that of the temperature of 10°C. With the further increase of temperature, the water absorption rate of PODE will gradually decrease. When the temperature is raised from 30°C to 50°C and from 50°C to 70°C, the proportion of water absorption of PODE increased only 27.7% and 8.2%, respectively. As the maximum proportion of water absorption of PODE is 4.15% at ambient temperature of 70°C, PODE has poor water absorption. It can be concluded that the order of hydrophilicity for three fuels is ethanol > PODE > diesel. Therefore, the water is separated from the ternary system by diesel and part of PODE, resulting in the instability of the system.

For further verification, the water absorption of the PODE and diesel system without hydrophilic ethanol was investigated at different temperatures. Polyoxymethylene dimethyl ethers and diesel were blended in different ratios from 10% to 90% in 10% increments. The experimental results are shown in Figure 6. It can be seen that the water absorption of the mixture decreases sharply when the volume fraction of diesel increases. This is because diesel is a hydrophobic fuel and its hydrophilicity is worse than that of PODE. It can also be found from Figure
6 that the water absorption shows a rising trend with increase of the temperature. The reason is that PODE with the relatively stronger water absorption at a higher temperature is as shown in Figure 5. Note that once the volume fraction of diesel in the mixture is more than 60%, the water absorption of the mixture is almost reduced to zero. In summary, it is proved that the hydrophobicity of diesel is the main reason for the instability of the PODE/diesel/ethanol system after adding water.

4 | CONCLUSION

Polyoxymethylene dimethyl ethers has a higher cetane number than diesel, and it can improve the cetane number of ethanol/diesel blend fuel. In order to evaluate the solubilizing ability of PODE on the mixture of ethanol and diesel, the phase behavior of the ternary system (PODE, anhydrous ethanol, and diesel) was investigated at different ambient temperatures. Additionally, the phase behavior of hydrous ethanol with different purity, PODE, and diesel system was also studied. The main conclusions are shown as follows.

1. PODE can be blended with diesel fuel at any proportion without phase separation at room temperature, but the mixture of PODE/diesel has a relatively poor solubility at temperatures below 10°C. PODE and anhydrous ethanol can be soluble with each other at all tested temperatures (0-40°C).

2. PODE has the ability to improve the solubility of diesel and ethanol. The demand for PODE is decreased with the increase of ambient temperature. When the ambient temperature is higher than 10°C, PODE can effectively improve the miscibility of anhydrous ethanol and diesel. The ternary fuel with 10% ethanol, 10% PODE, and 80% diesel fuel has good solubility and cetane number, which can be considered as an alternative fuel in diesel engines. At ambient temperature of 10°C, more PODE is needed when the proportion of ethanol in the blend is relatively low. While as the ambient temperature is rising to 20°C, 30°C, or 40°C, the peak of PODE addition appears when the volume ratio of hydrous ethanol to diesel is 1:1.

3. The addition of water greatly destroys the phase stability of the ternary system. A large amount of PODE is needed to achieve a single-phase state when the water content increases. Like the system of anhydrous ethanol, the increase in ambient temperature is also an effective measure to improve the miscibility of the PODE, 98% ethanol and diesel system, but has less effects on improving the miscibility of the PODE, 95% ethanol and diesel system. PODE can be soluble water up to 4% at high ambient temperature; therefore, the hydrophobicity of diesel is the main reason for the instability of the ternary system of PODE/diesel/ethanol after adding water.

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ORCID

Haifeng Liu, https://orcid.org/0000-0003-0861-4966

REFERENCES

1. World Oil Outlook. OPEC; 2018. https://www.opec.org. Accessed August 15, 2018.
2. World Energy Outlook. International Energy Agency; 2018. https://www.iea.org/weo2018/. Accessed November 13, 2018.
3. China vehicle environmental management annual report. Ministry of Environmental Protection of the People’s Republic of China; 2018. http://www.mee.gov.cn/. Accessed June 1, 2018.
4. Rakopoulos DC, Rakopoulos CD, Kyritsis DC. Butanol or DEE blends with either straight vegetable oil or biodiesel excluding fossil fuel: comparative effects on diesel engine combustion attributes, cyclic variability and regulated emissions trade-off. Energy. 2016;115(1):314-325.
5. Jin C, Zhang X, Geng Z, et al. Effects of various co-solvents on the solubility between blends of soybean oil with either methanol or ethanol. Fuel. 2019;244:461-471.
6. Wang Y, Cheng MH, Wright MM. Lifecycle energy consumption and greenhouse gas emissions from corncob ethanol in China. Biofuels Bioprod Biorefin. 2018;12(6):1037-1046.
7. Kremer FG, Fachetti A. Alcohol as Automotive Fuel-Brazilian Experience (No. 2000-01-1965). SAE Technical Paper; 2000.
8. Cheenkachorn K, Fungtammasan B. An investigation of diesel-ethanol-biodiesel blends for diesel engine: Part 1. Emulsion stability and fuel properties. Energy Sources, Part A: Recover Utiliz Environ Effects. 2010;32(7):637-644.
9. Van der Hoeven M. World Energy Outlook 2012. Tokyo, Japan: International Energy Agency; 2013.
10. Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Papagiannakis RG. Evaluating oxygenated fuel’s influence on combustion and emissions in diesel engines using a two-zone combustion model. J Energy Eng. 2018;144(4):04018046.
11. Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Papagiannakis RG, Kyritsis DC. Influence of properties of various common biofuels on the combustion and emission characteristics of high-speed DI (direct injection) diesel engine: vegetable oil, bio-diesel, ethanol, n-butanol, diethyl ether. Energy. 2014;73:354-366.
12. Rakopoulos DC, Rakopoulos CD, Giakoumis EG. Impact of properties of vegetable oil, bio-diesel, ethanol and n-butanol on the combustion and emissions of turbocharged HDDI diesel engine operating under steady and transient conditions. Fuel. 2015;156:1-19.
13. He T, Chen Z, Zhu L, Zhang Q. The influence of alcohol additives and EGR on the combustion and emission characteristics of diesel engine under high-load condition. Appl Therm Eng. 2018;140:363-372.
14. Zhang Q, Hu X, Li Z, Liu B, Chen Z, Liu J. Combustion and emission characteristics of diesel engines using diesel, DMF/diesel, and N-pentanol/diesel fuel blends. J Energy Eng. 2018;144(3):04018030.
15. Lapuerta M, Armas O, García-Contreras R. Effect of ethanol on blending stability and diesel engine emissions. Energy Fuels. 2009;23(9):4343-4354.
16. Lapuerta M, Armas O, Herreros JM. Emissions from a diesel-bioethanol blend in an automotive diesel engine. Fuel. 2008;87(1):25-31.
17. Leach FC, Stone R, Richardson D, et al. The effect of oxygenate fuels on PN emissions from a highly boosted GDI engine. Fuel. 2018;225:277-286.
18. Hansen AC, Gratton MR, Yuan W. Diesel engine performance and NOx emissions from oxygenated biofuels and blends with diesel fuel. Trans ASABE. 2006;49(3):589-595.
19. Gerdes KR, Suppes GJ. Miscibility of ethanol in diesel fuels. Ind Eng Chem Res. 2001;40(3):949-956.
20. Makareviciene V, Sendzikiene E, Janulis P. Solubility of multi-component biodiesel fuel systems. Biores Technol. 2005;96(5):611-616.
21. Torres-Jimenez E, Jerman MS, Gregorc A, Lisek I, Dorado MP, Kegel B. Physical and chemical properties of ethanol–diesel fuel blends. Fuel. 2011;90(2):795-802.
22. De Caro PS, Mouloungui Z, Vaatilingom G, Berge JC. Interest of combining an additive with diesel–ethanol blends for use in diesel engines. Fuel. 2001;80(4):565-574.
23. Hansen AC, Zhang Q, Lyne PW. Ethanol–diesel fuel blends—a review. Biore. Technol. 2005;96(3):277-285.
24. Selvan V, Anand RB, Udayakumar M. Stability of dieselohol using biodiesel as additive and its performance and emission characteristics in a compression ignition engine under various compression ratios. Int J Appl Eng Res. 2009;4(9):1723-1739.
25. Fernando S, Hanna M. Development of a novel biofuel blend using ethanol–biodiesel–diesel microemulsions: EB-diesel. Energy Fuels. 2004;18(6):1695-1703.
26. Reyes Y, Aranda D, Santander L, Cavado A, Belchior C. Action principles of cosolvent additives in ethanol–diesel blends: stability studies. Energy Fuels. 2009;23(5):2731-2735.
27. Lapuerta M, García-Contreras R, Campos-Fernández J, Dorado MP. Stability, lubricity, viscosity, and cold-flow properties of alcohol–diesel blends. Energy Fuels. 2010;24(8):4497-4502.
28. Liu H, Hu B, Jin C. Effects of different alcohols additives on solubility of hydrous ethanol/diesel fuel blends. Fuel. 2016;184:440-448.
29. Jin C, Pang X, Zhang X, et al. Effects of C3–C5 alcohols on solubility of alcohols/diesel blends. Fuel. 2019;236:65-74.
30. Xing-cai L, Jian-Guang Y, Wu-Gao Z, Zhen H. Effect of cetane number improver on heat release rate and emissions of high speed diesel engine fueled with ethanol–diesel blend fuel. Fuel. 2004;83(14-15):2013-2020.
31. Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Komminos NP, Kosmadakis GM, Papagiannakis RG. Comparative evaluation of ethanol, n-butanol, and diethyl ether effects as biofuel supplements on combustion characteristics, cyclic variations, and emissions balance in light-duty diesel engine. J Energy Eng. 2016;143(2):04016044.
32. Wang D, Zhu G, Li Z, Xia C. Polyoxymethylene dimethyl ethers as clean diesel additives: fuel freezing and prediction. Fuel. 2019;237:833-839.
33. Burger J, Siegert M, Ströfer E, Hasse H. Poly (oxymethylene) dimethyl ethers as components of tailored diesel fuel: properties, synthesis and purification concepts. Fuel. 2010;89(11):3315-3319.
34. Marchionna M, Sanfilippo D. High quality components for clean transport fuels. Hydrocarb Eng. 2002;7(7):49-51.
35. Clarisse D, Laurent G, Jean LC, Jean LD, Jean MS. FR. Patent No. 2,906,815. Arkema, France: TOTAL FRANCE SA; 2008.
36. Hagen GP, Spangler MJ. U.S. Patent No. 6,265,528. Washington, DC: U.S. Patent and Trademark Office; 2001.
37. Burger J, Hasse H. Multi-objective optimization using reduced models in conceptual design of a fuel additive production process. Chem Eng Sci. 2013;99:118-126.
38. Wang D, Zhu G, Li Z, Xue M, Xia C. Conceptual design of production of eco-friendly polyoxymethylene dimethyl ethers catalyzed by acid functionalized ionic liquids. Chem Eng Sci. 2019;206:10-21.
39. Wang D, Zhao F, Zhu G, Xia C. Production of eco-friendly poly (oxymethylene) dimethyl ethers catalyzed by acidic ionic liquid: a kinetic investigation. Chem Eng J. 2018;334:2616-2624.
40. Oestreich D, Lautenschütz L, Arnold U, Sauer J. Production of oxymethylene dimethyl ether (OME)-hydrocarbon fuel blends in a one-step synthesis/extraction procedure. Fuel. 2018;214:39-44.
41. Qi Z, Hui W, Qin ZF, et al. Synthesis of polyoxymethylene dimethyl ethers from methanol and trioxymethylene with molecular sieves as catalysts. J Fuel Chem Technol. 2011;39(12):918-923.

42. Liu H, Wang Z, Wang J, et al. Performance, combustion and emission characteristics of a diesel engine fueled with polyoxymethylene dimethyl ethers (PODE3-4)/diesel blends. Energy. 2015;88:793-800.

43. Wang Z, Liu H, Zhang J, Wang J, Shuai S. Performance, combustion and emission characteristics of a diesel engine fueled with polyoxymethylene dimethyl ethers (PODE3-4)/diesel blends. Energy Procedia. 2015;75:2337-2344.

44. Huang H, Teng W, Li Z, Liu Q, Wang Q, Pan M. Improvement of emission characteristics and maximum pressure rise rate of diesel engines fueled with n-butanol/PODE3-4/diesel blends at high injection pressure. Energy Convers Manage. 2017;152:45-56.

45. Hagen GP, Spangler MJ. U.S. Patent No. 6,166,266. Washington, DC: U.S. Patent and Trademark Office; 2000.

46. Huang H, Liu Q, Pan M, Liu C, Teng W. Improvement of combustion performance and emissions in diesel engines by fueling n-butanol/diesel/PODE 3–4 mixtures. Appl Energy. 2017;227:38-48.

47. Pellegrini L, Marchionna M, Patrini R, Beatrice C, Del Giacomo N, Guido C. Combustion Behaviour and Emission Performance of Neat and Blended Polyoxymethylene Dimethyl Ethers in a Light-duty Diesel Engine (No. 2012-01-1053). SAE Technical Paper; 2012.

48. Pellegrini L, Patrini R, Marchionna M. Effect of POMDME Blend on PAH Emissions and Particulate Size Distribution from an In-use Light-duty Diesel Engine (No. 2014-01-1951). SAE Technical Paper; 2014.

49. Lumpp B, Rothe D, Pastötter C, Lämmermann R, Jacob E. Oxyethylene ethers as diesel fuel additives of the future. MTZ worldwide eMagazine. 2011;72(3):34-38.

50. Liu H, Wang Z, Li B, Wang J, He X. Exploiting new combustion regime using multiple premixed compression ignition (MPCI) fueled with gasoline/diesel/PODE (GDP). Fuel. 2016;186:639-647.

51. Liu H, Wang Z, Zhang J, Wang J, Shuai S. Study on combustion and emission characteristics of Polyoxymethylene Dimethyl Ethers/diesel blends in light-duty and heavy-duty diesel engines. Appl Energy. 2017;185:1393-1402.

52. De Guertechin LO. Classification of surfactants. In: Barel AO, Maibach HI, eds. Handbook of Cosmetic Science and Technology. Park Drive, UK: Taylor & Francis;2001:431.

53. Zhou J, Cui Y, Wu Y. Measurement and calculation of hlb value of surfactants II. The calculation of hlb value. Spec Petrochem. 2001;4:38-41.

54. Corseuil HX, Kaipper BL, Fernandes M. Cosolvency effect in sub-surface systems contaminated with petroleum hydrocarbons and ethanol. Water Res. 2004;38(6):1449-1456.

55. Ghannam MT, Selim M. Stability behavior of water-in-diesel fuel emulsion. Pet Sci Technol. 2009;27(4):396-411.

56. Atmanli A, Yüksel B, İleri E. Experimental investigation of the effect of diesel–cotton oil–n-butanol ternary blends on phase stability, engine performance and exhaust emission parameters in a diesel engine. Fuel. 2013;109:503-511.

57. Li B, Li Y, Liu H, Liu F, Wang Z, Wang J. Combustion and emission characteristics of diesel engine fueled with biodiesel/PODE blends. Appl Energy. 2017;206:425-431.

58. Murphy MJ, Taylor JD, McCormick RL. Compendium of Experimental Cetane Number Data. Golden, CO: National Renewable Energy Laboratory; 2004:1-48.

59. Liu H. Wang Z, Li Y, Zheng Y, He T, Wang J. Recent progress in the application in compression ignition engines and the synthesis technologies of polyoxymethylene dimethyl ethers. Appl Energy. 2019;233:599-611.

60. Liu J, Wang H, Li Y, et al. Effects of diesel/PODE (polyoxymethylene dimethyl ethers) blends on combustion and emission characteristics in a heavy duty diesel engine. Fuel. 2016;177:206-216.

61. Li R, Liu Z, Han Y, et al. Target-oriented fuel design for the homogeneous charge autoignition combustion mode: a case study of an-heptane–PODE3–ethanol mixture. 1. A pathway to increase the combustion efficiency and reduce pollutant emissions. Energy Fuels. 2018;33(1):16-30.

62. Tong L, Wang H, Zheng Z, Reitz R, Yao M. Experimental study of RCCI combustion and load extension in a compression ignition engine fueled with gasoline and PODE. Fuel. 2016;181:878-886.

63. Elfasakhany A. Investigations on performance and pollutant emissions of spark-ignition engines fueled with n-butanol–, isobutanol–, ethanol–, methanol–, and acetone–gasoline blends: a comparative study. Renew Sustain Energy Rev. 2017;71:404-413.

64. Wang D, Zhao F, Zhu G, Li Z, Xia C. High-cetane additives for diesel based on polyoxymethylene dimethyl ethers: density behavior and prediction. J Mol Liq. 2017;234:403-407.

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