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Investigation on the dependence of flash point of diesel on the reduced pressure at high altitudes

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HIGHLIGHTS

- Field flash point determinations are performed at six different altitudes.
- Flash point decreases nonlinearly with the reduced pressure at high altitudes.
- Two methods are proposed to estimate the flash point under reduced pressure.
- The predictive accuracy of the two methods is better than the linear relation.
- The Clapeyron relation can expound the dependence of flash point on pressure.

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ABSTRACT

The high altitudes of the plateau areas lead to a decreasing flash point temperature of liquid fuels due to the reduced ambient pressure. It indicates that liquid fuels suffer greater fire and explosion hazards at high altitudes. To reveal the dependence of flash point on reduced pressure at high altitudes, a series of field flash point determinations are performed at six different altitudes on the Qinghai–Tibet Plateau. The results show that flash point decreases nonlinearly with the reduced pressure, which is inconsistent with the current standards of flash point determination, where adopt a linear correction for the pressure effect on flash point. Taking diesel as an example, two methods, the Clausius–Clapeyron relation method and the LCR method, are proposed to predict the flash point of diesel under different pressures. The results show that the predictive accuracy of the two methods is similar, and both of the two methods give more accurate predictive flash point than the linear relationship. The Clausius–Clapeyron relation is validated to be able to expound the dependence of flash point of liquid fuels on reduced pressure. These two methods can complement each other. The Clausius–Clapeyron relation method is recommended when the accurate the phase-transition enthalpy is known, the LCR model is an available method when the phase-transition enthalpy is unknown or uncertain, especially for the complicated fuel mixtures.

1. Introduction

The plateau areas are characterized by the environment with low ambient pressure and low oxygen mass concentration due to their high altitudes. The unique environment leads to different ignition and burning properties for liquid fuels used in these areas compared with those used in plain areas. Flash point is one of these properties which is significantly influenced by reduced pressure at high altitudes.

Flash point is defined as the lowest temperature at which the liquid fuel can vaporize to form a flammable mixture in air when an ignition source (hot surface, spark, or flame) is applied. It is an important property to distinguish flammable liquids from combustible liquids, and is usually used to assess the overall flammability hazard of a material. The lower the flash point, the greater the fire and explosion risk.

Flash point values of most pure compounds have been obtained through experimental determinations and can be searched from online databases such as Merck Index, DIPPR and NIOSH. For

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miscible fuels and more complex multi-component oil fuels (e.g. gasoline, aviation kerosene and diesel), the flash point values can also be obtained through experimental determination or the production manual. However, these flash point values are generally specified to standard atmospheric pressure (101.3 kPa). Previous studies [1–4] have shown that the reduced pressure at high altitudes will significantly decrease the flash point of liquid fuels, which will definitely increase the fire hazards of fuels. Therefore, if the flash point values corresponding to a pressure of 101.3 kPa are directly used in the safety evaluation of liquid fuels at high altitudes, the flammability hazard of liquid fuels may be underestimated. Therefore, understanding the dependence of flash point on the reduced pressure at high altitudes is of great significance for the safety of the storage, processing, transportation and practical use of liquid fuels in plateau areas.

In the current standards of flash point determination, for example ASTM D93 [5], ISO 2719 [6] and GB/T261-2008 [7], a linear correction is utilized to counteract the pressure effect on flash point:

$$T_{cf} = T_{of} + 0.25(101.3 - P) \quad (1)$$

where T_{cf} is the corrected flash point value, which is the flash point corresponding to 101.3 kPa; T_{of} is the observed flash point value, which is the real flash point under a certain pressure; P is the ambient pressure of measure condition.

According to Eq. (1), when the pressure differs from 101.3 kPa, the observed flash point value is corrected to 101.3 kPa using this equation. It is apparent that the dependence of flash point on ambient pressure is simplified as a linear relationship in the current standards. However, the fact is a nonlinear relationship has been proved to be existed between flash point and ambient pressure.

The effect of reduced pressure at high altitudes on flash point of liquid fuels has been of great interest to researchers for a long time. In 1996, the flight TWA800 exploded at an altitude of 14,000 feet, the reason was suspected to be the unknown ignition in the fuel tank. More attentions were paid to the pressure and altitudes effect on the flash point of aviation kerosene (Jet A) due to this accident. Woodrow [8–10] measured the vapor pressure of single n-alkane hydrocarbons and complex hydrocarbon mixtures at various temperatures using headspace gas chromatography. On the foundation of Woodrow's studies, Shepherd et al. [2] examined the relationship between chemical composition and flash point through eight samples of aviation kerosene with flash point between 29 °C and 74 °C. Two flash point prediction methods were proposed to describe and examine the relationship between chemical composition and flash point. With these methods, they predicted that the flash point of aviation kerosene when TWA800 explored is between 38 and 40 °C. Kong et al. [11] developed a new "equilibrium closed bomb" instead of the standard closed testers to measure the flash point in the oxygen-rich environment. They found that increased oxygen concentration had little effect on the flash points of the tested flammable liquid (dichloromethane). Tang et al. [1] measured the vapor pressure of four fuels under different temperatures, it certified that it is feasible to apply the Clausius–Clapeyron relationship to multi-component fuels like Jet A. Tang also determined the flash points of Jet A in the hypobaric chamber, where the environment pressure is controlled from 55 to 101.3 kPa. The measurements revealed that flash point decreased nonlinearly with reduced pressure. Same conclusions were got in the works of Shepherd et al. [2] and Nestor [12]. Ding et al. [4] conducted field flash point determinations of flammable liquids at five altitudes between 3650 m and 4750 m. Combining with theoretical analysis, they found that the nonlinear relationship between flash point and altitude can be expressed as a linear relationship between the reciprocal of flash point and the logarithmic of altitude, which was especially appropriate for relatively low altitudes but preformed a little badly for high altitudes.

In conclusion, although numerous works have been done, studies on pressure dependence of flash point of liquid fuels at high altitudes are still insufficient. The relationship between flash point and pressure or altitude is not expounded clearly, the reliability of the linear correction for pressure effect on flash point used in the current standards is also questionable. An accurate and reliable method for estimating the flash point of liquid fuels at high altitudes is still an urgent need. In this work, taking diesel as an example, field flash point determinations are performed at six altitudes rising from 0 m to 4775 m to reveal the variation of flash point with the reduced pressure at increasing altitudes. Two prediction methods are proposed to expound the dependence of flash point on pressure and altitudes and give a more accurate flash point estimation for multi-component fuels used at high altitudes. It is of benefit to the safety evaluation and fire prevention of liquid fuels used at high altitudes.

2. The determination of flash point

There are two basic methods for the determination of flash point of a liquid fuel: closed cup and open cup. Each method has its corresponding measurement standards, for example, ASTM D93, ISO 2719 and GB/T261-2008 for Pensky–Martens closed cup method; ASTM D92, ISO 2592 and GB/T3536-2008 for Cleveland open cup method. The method and the corresponding experimental apparatus are described in detail in these standards. In both of the two methods, liquid fuel samples are heated with a specified rate in a copper cup and an ignition source with specified strength is equipped 10–14 mm above the sample surface to ignite the vapor–air mixture. The temperature at which flashover occurs and propagates through the vapor–air mixture to the liquid surface is taken as the flash point of this sample. The flash point temperature determined by the two methods may be different. Generally, the close cup method gives lower values (typically 5–10 °C) than open cup method. The difference is mainly due to the difference in experimental apparatus. For close cup method, there is a cover on the copper cup, and there is a shutter on the cover. The shutter is closed when the sample is heated, and the fuel vapors accumulates in the cup until the shutter opens for ignition, so the fuel vapor in the cup is easier to reach its lower flammability limit than open cup method. This is why the flash point temperature determined by close cup method is lower than open cup. Besides, the cover and the shutter in the close cup method minimize the interference from environmental factors like wind, so the close cup method gives more repeatable and reliable flash point values. In addition, the closed cup method is recommended for light oil with relatively low flash point, such as gasoline and diesel, while the open cup method is recommended for heavy compounds, such as lubricating oil. The standard followed in this work is ASTM D93 [5] for close cup method. According to the standard, the methane flame used as ignition source in this work is adjusted to a diameter of 3.2–4.8 mm in order to maintain the strength of ignition source, so the effect of the strength of ignition source on flash point is not taken into consideration in this work.

In this study, a series of field flash point measurements are performed at five altitudes (0 m, 2070 m, 2830 m, 3640 m and 4290 m) in Qinghai–Tibet Plateau aiming to reveal the dependence of flash point on the reduced pressure at high altitudes. The experimental fuel is -35# diesel, which is a power fuel widely used in plateau areas. The altitude and pressure are obtained by field measurements, and the corresponding relationship between them is presented in Table 1. It is apparent that the ambient pressure is reduced with the increasing altitudes in plateau areas. It should