PROPERTIES OF JET FUELS AT LOW TEMPERATURE AND THE EFFECT OF ADDITIVES

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Introduction

Long-duration, high altitude aircraft flights expose jet fuel to extremely low ambient temperatures (<-70°C). The relatively large normal alkanes (n-C_{16} to n-C_{18}) present begin to crystallize at these low temperatures, ultimately resulting in fuel gelation that can prevent the fuel from being available for combustion in the engine. In addition, as the viscosity increases with decreasing temperature, the ability of fuel to flow at sufficient rate through tight tolerance valves and filters can be inhibited. The US Air Force JP-8+100LT program is exploring the use of additives to improve the low temperature properties of conventional jet fuels (1).

In this work, we report on studies of changes in jet fuel properties at low temperatures using the scanning Brookfield viscometer; pour, cloud, and freeze point measurements; and differential scanning calorimetry (DSC). We will show how changes in viscosity correlate with other property measurements, such as cloud point. Another goal of this work is to enable use of these measurements in predicting the operability of fuel tanks and systems at low temperature. In addition, we will show how these measured properties change upon addition of additives that interfere with crystallization of the large normal alkanes present.

Experimental

DSC data were acquired using a TA Instruments DSC 2920 equipped with a Liquid Nitrogen Cooling Accessory (LNCA). The LNCA directs a mixture of gaseous and liquid nitrogen to the sample chamber that permits thermal analysis data to be acquired at sub-ambient temperatures. Typically, 20 mL of liquid fuel is sampled using a chromatographic syringe, injected into an open aluminum sample pan, and subsequently weighed. An empty aluminum pan is used for the reference. Most data were acquired at a cooling rate of 1°C/min over the temperate range -45 to -65 °C.

Cloud point, pour point, and freeze point data were acquired using a Phase Technology PSA-70V Petroleum Analyzer, via ASTM D5773, D5949, and D5972, respectively. The pour point analyses were conducted at 1°C intervals. The freeze and cloud point analyses have uncertainties of ±1°C, while the pour point analyses have uncertainties of ±3°C.

Viscosity measurements were performed using a Tannas Scanning Brookfield Plus Two Viscometer. As the fuel sample (30 mL) is cooled from -40 to -65°C at 1°C/hour, the viscosity is measured continuously by the increasing torque generated by a spindle rotating in the fluid at constant speed (12 rpm). The viscosity at -40°C is calibrated by measurements obtained using ASTM D445, which measures the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer.

The jet fuels were obtained from the Fuels Branch of the Turbine Engine Division of the Propulsion Directorate of the Air Force Research Laboratory (AFRL/PRTG) at Wright-Patterson AFB, Ohio. The candidate cold flow additives are proprietary polymers acquired from Lubrizol and Betz Dearborn.

Results and Discussion

JPTS is a relatively expensive specialty fuel used by the U.S. Air Force for aircraft that subject fuel to temperature extremes (high temperatures in the engine, and low temperatures in the wing tank). The goal of the US Air Force JP-8+100LT program is to develop an additive package which will supply the commonly used JP-8 fuel with the ability to perform at both the high and low temperatures for which JPTS is designed. It is expected that the high temperature thermal stability goals can be met by the addition of the JP-8+100 additive package (2,3). The development of additives that increase the flowability of JP-8 at low temperatures (<-47°C) is the current concern.

Currently, the only low temperature properties in the specifications for these fuels are freeze point (-47°C maximum for JP-8, and -53°C maximum for JPTS) and viscosity (8.0 centistokes maximum at –20 °C for JP-8, and 12.0 centistokes maximum at –40°C for JPTS). The freeze point specification is a conservative measure and is of limited use because it is actually a melting point measurement obtained while heating solidified fuel and does not evaluate fuel flowability. The specification viscosity measurements are at a single temperature and do not evaluate flowability near temperatures of fuel solidification. In this study, we explore the effect of reduced temperatures on fuel properties and operability via measurements of viscosity over a range of temperatures; freeze, cloud, and pour points measurements; and differential calorimetry.

Table 1. Properties of the Fuels Studied

Fuel	Freeze point (°C)	Cloud point (°C)	Pour point (°C)
2799 (JPTS)	-57.6	-63.1	-67.5
2976 (JPTS)	-58.5	-62.9	-67.0
3657 (JPTS)	-53.0	-57.2	-59.6
3775 (JPTS)	-53.6	-57.3	-59.7
4036 (JPTS)	-55.7	-59.3	-60.5
3804 (JP-8)	-47.6	-51.4	-56.0
3219 (Jet A)	-46.4	-50.7	-56.5

Table 1 shows the measured freeze, cloud, and pour points for five JPTS fuels. Figure 1 shows plots of viscosity vs. temperature using the scanning Brookfield technique on these same JPTS fuels. The scanning Brookfield technique measures dynamic viscosity (η) that can be related to the kinematic viscosity (υ) via the density (ρ) by, $\eta = \upsilon\rho$. The figure shows that the fuels display a gradual rise in viscosity as the fuel is cooled below –40°C. Upon further cooling, the fuels display a relatively sudden rapid increase in viscosity. Also plotted in the figure are the measured cloud points for each of the fuels. It is apparent that the sudden rapid rise in viscosity occurs very close to the measured cloud point. Thus, the increase in viscosity is due to the occurrence of solid formation in the fuel, as the cloud point is the temperature at which visible solids are first observed upon cooling. It is interesting to note that two pairs of fuels display very similar viscosity curves as well as freeze, cloud, and pour points. These data indicate that these fuel pairs, 2799/2976 and 3657/3775, appear to be the same fuels. As JPTS specialty fuel is only produced intermittently at a small number of refineries, this observation is not surprising.

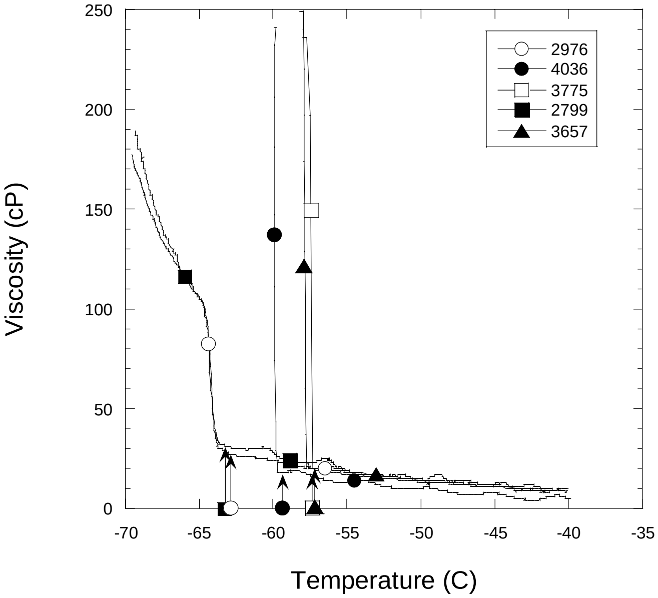

Figure 1. Plots of viscosity vs. temperature for five JPTS fuels. Also shown are the measured cloud points.

The measured cloud points for these fuels occur over the viscosity range 20 to 40 cP, indicating the highest single phase liquid viscosities measured. The measured pour points (Table 1) for fuels 2976/2799 occur at viscosities near 120 cP, indicating an approximate viscosity level which can completely prevent fuel flow. The change in viscosity below the cloud point varies for these five fuels. Three fuels, 4036, 3657, and 3775 display very rapid increases in the viscosity. The other two fuels, 2799 and 2976, show much more gradual increases, with a characteristic slowing of the viscosity increase within one degree of the cloud point. These differences in viscosity behavior vs. temperature may be due to differences in concentrations of the n-alkanes present in these fuel samples. It is well-known that the breadth of the n-alkane distributions can strongly affect fuel low temperature properties. Another complication is that the meaning of the viscosity measurement below the cloud point, where two phases are present, is not well understood.

Figure 2 shows plots of viscosity vs. temperature for a JP-8 fuel with and without candidate cold flow improving additives. The plot shows that the neat JP-8 fuel has low viscosity until -52°C, where the viscosity increases dramatically. As in the JPTS samples, the viscosity rise occurs near the measured cloud point (see Table 1). The cloud point and viscosity increase occur at temperatures approximately 5°C higher than the highest freezing JPTS sample. Thus one goal in making a JP-8 fuel behave like a JTPS would be to decrease the temperature of this rapid viscosity increase by at least 5°C.

Also shown in Fig. 2 are viscosity plots for JP-8 fuel 3804 with three proprietary cold flow improving additives. Each of the additives lowers the temperature at which the viscosity begins to increase. The best performing additive (4120) lowers the temperature at which the viscosity increases by 4°C. This change is quite close to that required to approximate the behavior of the highest freezing JPTS sample. The additives also modify how the viscosity changes below the cloud point. Additives 3977 and 3990 keep the viscosity low down to a temperature of -60°C, relative to the neat fuel.

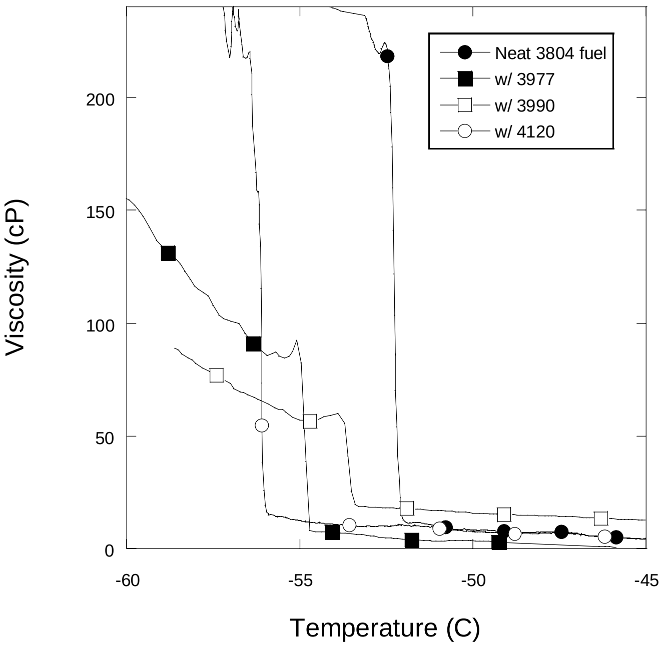

Figure 2. Plots of viscosity vs. temperature for a JP-8 fuel (3804) neat and with three cold flow improving additives.

Most cold flow improving additives are thought to improve the flowability of low temperature fuel by interfering with the crystallization of the large n-alkanes present. The additives attach to the rapidly growing crystal faces, resulting in a marked slowing of the crystal surface growth. This greatly alters the crystal habit, resulting in smaller crystals which form porous cakes and are thus less likely to clog fuel filters and narrow passageways (4,5). The changes in the viscosity vs. temperature profiles observed in Fig. 2 can be due to such changes in crystal habit or other interactions of the additive with the fuel mixture.

To further explore the mechanism by which these additives perform, we performed DSC measurements on neat and additized fuel as shown in Fig. 3. In previous work, we showed that the DSC exotherm which occurs during jet fuel cooling is primarily due to the crystallization of the large n-alkanes present (6). The figure shows that the JP-8 exothermic peak occurs near -54°C and that candidate additive 3977 lowers the temperature of the exotherm peak by 2 to 3°C over a concentration range of 500 to 8000 mg/L. This lowering of the temperature of the exotherm indicates that the additive is changing more than just the crystal habit. The additive is changing the temperature at which the exothermic response occurs, which implies that the temperature at which crystallization begins is actually being reduced. Interestingly, at the highest concentration, 8000 mg/L, a second exothermic peak occurs near -59°C. The cause of the second low temperature peak is not known, but it is reminiscent of the low temperature eutectic peak observed in mixtures of model fuel compounds (6). This separation into two exothermic peaks is indicative of the separation of a mixture into lower and higher freezing fractions. The identity of these fractions is not know at this time.

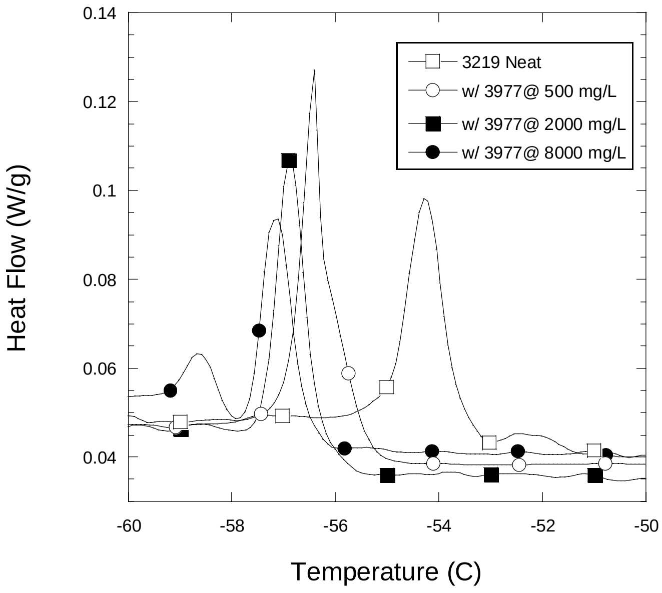

Figure 3. DSC plots of heat flow vs. temperature for fuel 3219 with various amounts of cold flow additive 3977.

We have also performed freeze, cloud, and pour point measurements of fuel 3219 with two concentrations of additive 3977. The results are shown in Table 2. The table shows that upon addition of the additive the freeze point is slightly increased, although this change is within our experimental uncertainty at 4000 mg/L. The cloud point is reduced by 1.2°C at 4000 mg/L, and 1.8°C at 8000 mg/L. The pour point change is <2°C, which is lower than the experimental uncertainty, and is thus likely not significant. Interestingly, the cloud point changes due to the addition of the additive measured by the Phase Technology instrument are smaller than both the changes observed in the viscosity profiles and the DSC profiles. Unfortunately, these changes are small enough that it is difficult to employ the cloud point test to select additives and/or use the results to gain an understanding of the additive mechanism.

Table 2. Freeze, Cloud, and Pour Points of Fuel/Additive Mixtures

Fuel/Additive	**Freeze point (°C)**	**Cloud point (°C)**	**Pour point (°C)**
Neat Fuel 3219 (Jet A)	-46.4	-50.7	-56.5
Additive 3977 @ 4000 mg/L	-45.4	-51.9	-57.7
Additive 3977 @ 8000 mg/L	-45.2	-52.5	-57.0

The viscometer, cloud point, and DSC measurements show that the temperature at which crystallization begins upon cooling is being changed by these candidate additives. Such changes upon the addition of additives are poorly understood. One study (7) of an α-olefin/stearylacrylate/N-alkylmaleimide terpolymer additive employed in diesel fuels finds evidence that additive effectiveness is due to the formation of a colloidal phase which selectively separates large normal alkanes from the fuel. Further study is required to determine the working mechanism of the additives studied here.

Conclusions

We have reported on results of viscometry; freeze, cloud, and pour point measurements; and DSC measurements on jet fuels and fuels with cold flow improving additive candidates. The results indicate that large increases in viscosity occur upon reaching the measured cloud point, where a solid phase begins to form upon cooling of the fuel. The cold flow additive candidate polymers studied here decrease the temperature of rapid viscosity rise in the viscometer. Changes in freeze, cloud, and pour points are quite small. These additives also decrease the temperature at which the DSC exotherm occurs, implying that the crystallization of n-alkanes is being inhibited.

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