CHAPTER 3

GTL MATERIAL TESTING

3.1 INTRODUCTION

Transportation of GTL products from the Alaskan North Slope through the Trans Alaska Pipeline System (TAPS) poses several operational problems dependent on the physical and chemical properties of the GTL products and their blends with the Alaskan North Slope Crude oil (ANSC). It may be noted that TAPS was originally designed for carrying a specific type of crude oil. The pipeline being located in an extremely cold region adds to the limitations on moving different fluid types through it.

Two possible modes of transporting GTL through TAPS are being considered. These modes are (i) batch and (ii) commingled with crude oil. In the batch or slug mode, crude oil and GTL are moved as alternating batches or slugs. A second mode is to blend or commingle the GTL products and crude oil into a single liquid phase prior to entering TAPS. In either mode of transportation, the feasibility of moving GTL products through TAPS will depend on the physical properties of the GTL and GTL-crude oil mixtures. For example, fluid properties such as density and viscosity are required to calculate the pressure and horsepower requirements. Since these fluid properties depend significantly on temperature, it is necessary to estimate the properties as functions of temperature as a part of evaluating the feasibility of flowing the fluids through TAPS.

Additional problems in transportation of GTL products through TAPS may be created by components of the transported material being deposited inside the pipe. Buildup of such deposits may impede fluid flow to the extent where the deposits need to be mechanically removed. Furthermore, deposited solids from the pipe walls can re-dissolve into the pure GTL slug in the batch mode of transport, causing serious contamination problems. Finally, one of the most important issues involved in studying the feasibility of moving GTL products through TAPS is cold restart of the pipeline. The material flowing through TAPS must be such that flow through the pipeline can be safely initiated following an extended winter shutdown.

One of the objectives of this project is to select tests and evaluate samples of GTL products and GTL-crude oil blends in order to assess the feasibility of transporting such materials through TAPS. This chapter will discuss some of the tests that can be used to assess the feasibility of transporting GTL products through TAPS and to evaluate the likelihood of cold flow problems. Density and viscosity measurements as functions of temperature are necessary for calculating horsepower requirements. Experimental data on density and viscosity of naturally occurring hydrocarbon mixtures are not well documented. However, measurements on true boiling point (TBP) fractions of various Arab (Amin and Beg 1994) and North Sea Crudes (Dandekar et. al., 1998), Alberta bitumen (Miadoyne et al., 1994) and Saskatchewan oils (Singh et al., 1994) have been reported. Additionally, the predictive capabilities of various viscosity correlations still remain a weak link. Therefore, the need for accurately measured experimental data is indispensable for evaluating the feasibility of transporting GTL products through the TAPS.

Another important GTL testing parameter is the gel strength, which is one of the most important properties necessary to evaluate the feasibility of cold restart of TAPS. The measurement of gel strength gives an indication of the so-called 'cold restart pressure' at which the liquid in the pipeline can yield under the given arctic conditions in Alaska. Thus, bearing in mind the significance of this parameter, gel strengths of various GTL and GTL-ANSC blends need to be determined by the rotating vane technique at different temperatures.

As far as the transport of GTL through TAPS is concerned, there still exists an uncertainty as to exactly which particular type of GTL product will be the potential candidate for flow through TAPS. This chapter describes the types of GTL products that were tested. A number of GTL product matrix possibilities exist, which are dependent on GTL process options such as catalyst used, process employed, operating conditions and type of GTL product upgrading, and other factors such as gas quality, Alaskan North Slope (ANS) logistics etc. In this study, a GTL sample product was obtained from the US Department of Energy and different fractions of the sample material were used to simulate variation of GTL product types. Thus, we were able to represent a wide range of GTL material that could potentially be produced from a North Slope GTL plant. Since GTL can be transported through TAPS as slugs or as commingled fluid, the tests were performed on GTL as well as GTL-crude oil blends.

Experimental studies on measurement of density and viscosity of GTL, crude oil, and GTL-crude oil blends as a function of temperature at atmospheric pressure were carried out. In this chapter, the viscosity and density measurement equipment, procedures, and all other supporting activities are presented in detail. All measurements were performed at the Petroleum Development Laboratory of The University of Alaska Fairbanks (UAF).

The gel strength measurements on the samples were performed at Westport Technology Center International (WTCI) facilities in Houston, Texas. In addition to the gel strength measurements WTCI also carried out Gas Chromatographic (GC) analysis of one of the GTL and TAPS crude oil blends to define the quantitative compositions from C2 to C30+. The work performed by WTCI is summarized in this chapter. The detailed reports written by WTCI on the gel strength measurement work are attached in the Appendices B and C.

The results from these tests are discussed in this chapter. Preliminary considerations as to what type of GTL product will likely have to be produced on the North Slope in order to be transportable over TAPS are also presented.

3.2 QUALITY ASSURANCE PROJECT PLAN

As part of this study, a Quality Assurance Project Plan (QAPjP) was prepared in connection with the potential collaborative project work between UAF and the Alyeska Pipeline Service Company (APSC). The collaborative work includes various aspects of transporting crude oil and/or GTL blends. The QAPjP is presented in Appendix A.

3.3 DESCRIPTION OF THE DENSITY AND VISCOSITY MEASUREMENT APPARATUS

3.3.1 Anton-Parr Densitometer

All density measurements were carried out in the Anton-Paar vibrating tube densitometer. The densitometer (DMA 45) is designed to measure the density of liquids at atmospheric pressures and for temperatures up to 60°C. The sample temperature is controlled by circulating constant temperature mineral oil through the densitometer. The apparatus is shown in Figure 3.1.

The Anton-Paar vibrating tube densitometer contains a U shaped oscillating sample tube. The electronic part of the meter excites the oscillator. A built-in quartz clock measures the period of oscillation; approximately every two seconds and transmits the value to the built-in processor. Then the processor calculates density and displays the value in the digital display. There are two injection ports to the right of density meter on the side. The lower filling inlet is used to inject samples while the upper filling inlet is used to flush the samples and to dry the U-tube. There is an in-built pump, which can be switched on to pass air through the upper filling inlet for drying purposes.

The density meter has a constant buffer where the values of the calibration constants A and B are stored. There is also a display selector, which is used to select the display between A, B, time period of oscillation, T and density values. After every density measurement, the samples are flushed out of the sample tube by giving a proper toluene wash followed by acetone wash and drying the tube using air.

The calibration and density measurement procedure is explained in Section 3.6.1.

3.3.2 Brookfield Rotational Viscometer

In this section a brief description of the Brookfield Rotational viscometer used for the measurement of rheological properties of GTL, crude oil and their blends is provided. The basic unit of the Brookfield Rotational viscometer possesses the capability of using three different kinds of attachments/measuring systems. These are (i) LVDV-II+ Cone Plate Viscometer (ii) LVDV-II+ Viscometer with Small Sample Adapter and (iii) LVDV-II+ Viscometer used with a 500 ml working volume of the sample.

All viscosity measurements reported in this report were carried out using the LVDV-II+ Cone Plate Viscometer. A picture of the apparatus is shown in Figure 3.2. There are three main components of this experimental setup: (i) Cone Plate Viscometer (ii) Refrigerated Bath and (iii) Wingather Data Gathering Software.

The LVDV-II+ cone plate viscometer has a cone and plate arrangement for viscosity measurement. The electronic cone spindle CPE-40 is used to measure viscosity values as low as 0.2cp. Besides, the sample volume needed to measure viscosity is only 0.5cc. This feature is useful when the sample volume availability is limited. The measurement range of LVDV-II+

cone plate viscometer with a CPE-40 spindle is 0.2cp to 3070cp. This fits in well with the GTL and crude oil viscosity measurement span.

The refrigerated bath is connected to the viscometer sample cup by a rubber tubing. The bath fluid temperature can be precisely controlled using a temperature-adjusting knob. The temperature of the sample is controlled by circulating the bath fluid from the bath to the sample cup jacket.

The viscosity data is gathered using a software called "Wingather" manufactured by Brookfield. Wingather can be used to record, save, edit, plot and analyze the testing data. The cone plate viscometer also has an electronic gap-setting feature, which has to be used to set the right gap between the cone and plate (Figure 3.2). It is desirable to set the gap every time the spindle is replaced. The viscometer can be controlled using the touch screen functions available on the face of the viscometer.

The calibration and viscosity measurement procedure is explained in Section 3.6.2.

3.4 TEST FLUIDS FOR DENSITY AND VISCOSITY MEASUREMENTS

The density and viscosity measurements were performed using the light GTL sample supplied by the US DOE (from LaPorte facility). The light GTL sample consisted mostly of C5 to C12 and progressively decreasing amounts of the heavier alkanes (Table 3.1). The rationale for these tests was to establish trends in GTL properties with temperature and to estimate how mixing with crude oil will affect the properties. The GTL sample was used on "as-is" basis, i.e., the sample was not treated in any way at UAF because only preliminary results were desired as a screening tool. The composition of the GTL is shown in Table 3.1. The crude oil samples were supplied in pressurized 1000 cc, CP2-M Welker cylinders. The aliquots of the crude oil were subsequently drawn from the Welker sample cylinder, into glass receptacles for carrying out all the required tests. However, prior to the collection of samples from the Welker cylinders a crude oil reconditioning and aliquoting procedure was followed. The crude oil composition is provided in Table 3.2. This procedure is described in detail in the following section.

3.4.1 Crude Oil Reconditioning and Aliquoting

It is necessary to recondition the samples back to original pipeline sampling conditions before taking the sample out of the Welker cylinder. This is carried out to ensure that the original composition of the sample is retained in all the test aliquots produced from the Welker cylinder sample. Aliquot samples are the sub-samples produced from original test samples. A sequential procedure to recondition the crude oil followed by aliquoting is outlined in this section.

Welker constant pressure sample cylinders are used to maintain the sampled product at pipeline pressures, provide adequate mixers, and facilitate easy and safe removal of sample.

Welker cylinder has two ends that are separated internally by a floating piston. One end is marked "product inlet" or "sampling end" and the other is the "precharge end". It also has two pressure gauges to read the pressure at both the ends of the cylinder. Quick connects and disconnects are used on both the ends to allow easy removal of sample without any leak. On top of the precharged end is an indicator rod. The mixing rod is used to homogenize the sample by mixing.

In the crude oil reconditioning procedure, the Welker cylinder is immersed vertically in a 55-gallon drum filled with water. The water filled drum is heated using two industrial belt heaters that are wrapped around the drum. The re-conditioning temperature is raised between 70 to 80°C. The crude oil re-conditioning is carried out for a period of at least two hours. During heat up and reconditioning, the crude oil sample is mixed manually to ensure homogenization.

After completion of the re-conditioning procedure the Welker is removed from the water filled drum and nitrogen supply line is opened to the precharge end of the Welker cylinder. This pressure source from the nitrogen cylinder, which is set at the original Welker sampling pressure, acts as the driving force for expelling the sample. The whitey valve at the sample end of Welker cylinder is opened with the metering valve closed. Subsequently, the metering valve is opened and sample aliquots are directly transferred into the storage containers immediately and sealed with pressure tight caps. The crude oil re-conditioning and aliquoting assembly is shown in Figure 3.3.

3.5 TEST CONDITIONS FOR DENSITY AND VISCOSITY MEASUREMENTS

All density and viscosity measurements were carried out at atmospheric pressure. The density data were measured in the temperature range of 23.8 to 60°C, whereas the viscosity data were measured in the temperature range of 20 to 60°C.

3.6 EXPERIMENTAL PROCEDURES FOR DENSITY AND VISCOSITY MEASUREMENTS

3.6.1 Density Measurements

3.6.1.1 Calibration

Prior to carrying out any density measurements, the densitometer is calibrated as follows-

i. After a stable temperature is reached, the calibration constants A and B are determined and entered into the constant buffer before measurement is started. Both constants are dependent on temperature and must therefore be re-determined if a change in measuring temperature occurs.
ii. To calculate the calibration constants, the display selector (under the cover plate on top of the DMA 45 meter) is set to position T; the value of the period of oscillation "T" is then shown on the numerical display.
iii. The illumination light is turned on to observe sample through the observation window. Now, a small volume (about 0.7 cc) of de-ionized water is introduced into the sample

tube from the bottom opening using a suitable syringe. This can be observed through the observation window with the light being switched on.

iv. Filling is complete when the liquid has exceeded the upper of two thickenings on the oscillator. The syringe is left in the lower filling inlet and the light is switched off to maintain temperature stability. The temperature is allowed to reach an equilibrium value; this is indicated by a stable value on the display.

v. The reading is taken for the period of water and recorded. This value T_w corresponds to the period for the water-filled oscillator. For this first measurement, the water should be left in the oscillator for approximately 15 minutes, checking that no variation in the T_w value occurs during this time. If the value of T_w varies by a maximum of one unit in the last significant digit, then it is an indication that the temperature control is working efficiently.

vi. Next, the water is washed out of the measuring cell using alcohol. The air outlet is connected to the upper filling inlet using a piece of tubing. The pump is switched on and dry air is blown through the tubing into the sample tube until the displayed values remain constant for some time.

vii. Then, the pump is switched off and the dry air in the U-tube is allowed to come to thermal equilibrium with the test temperature. The value for the period of air, T_a is recorded. The density of air at the temperature of test is calculated using the following equation:

$$d_a, \text{g/ml} = 0.001293[273.15/T]*[P/760]$$

Where,

T = temperature, °K
P = barometric pressure, torr.

The density of water, d_w at the test temperature is determined by referring to Table 3.3.

Using the observed T-values and the reference density values for water and air, the values of the constants A and B are calculated using the following equations:

$$A = [T_w^2 - T_a^2]/[d_w - d_a]$$

$$B = T_a^2 - (A)\,(d_a)$$

where:
T_w = observed period of oscillation for cell containing water,
T_a = observed period of oscillation for cell containing air,
d_w = density of water at test temperature, and
d_a = density of air at test temperature.

viii. These values (A and B) and the corresponding measuring temperature should be noted down in pencil on the panel situated at the back of the cover of the constant buffer. The constants are stored in the buffer by adjusting the corresponding switches with a small screwdriver.

ix. The correct settings of the switches can be checked once more by adjusting the display selector (by checking the values of A, B separately).

x. If the selector switch is set at position "ρ", then the equipment may carry out density measurement.

The above calibration procedure was consistently followed for all the test temperatures.

3.6.1.2 Test Sample Density Measurement

The density measurements on GTL, crude oil, and their blends is carried out in the following manner –

i. The illumination light is turned on to observe the sample through the observation window.

ii. During measurement, a small amount (about 0.7 cc) of sample is introduced into the clean, dry sample tube of the instrument using a suitable syringe. At this point, it is made sure the sample introduced is enough to fill beyond the suspension point on the right-hand side.

iii. The sample is allowed to equilibrate to the test temperature before proceeding to evaluate the test sample for the presence of unseen air or gas bubbles.

iv. The sample tube is examined carefully. It is made sure that no bubbles are trapped in the tube, and that it is filled to just beyond the suspension point on the right-hand side. The sample must be homogeneous and free of even the smallest bubbles.

v. The illumination light is turned off immediately after verification, because the heat generation can affect the measurement temperature.

vi. After the instrument displays a steady reading to four significant figures for density and five for T-values, indicating that temperature equilibrium has been reached, the density value is recorded. This recorded value if the final result.

vii. The sample tube is flushed with a suitable solvent and dried and the calibration is checked as described previously prior to introducing another sample.

3.6.2 Viscosity Measurements

3.6.2.1 Calibration

The following calibration procedure is adopted for the LVDV-II+ Cone Plate Viscometer. In this work, Brookfield certified viscosity standards were used for calibration.

i. The sample cup inlet/outlet ports are connected to the water bath inlet and outlet and the bath is set to the desired test temperature.

ii. The appropriate sample volume is determined. For spindle CPE-40, the sample volume of 0.5 ml is used. For other types of spindles, Brookfield's Instruction Manual is referred to determine the correct sample volume required for the spindle to be used.

iii. A viscosity standard fluid that will give viscosity readings between 10% and 100% of full-scale range is selected. It is best to use a viscosity standard fluid which is closer to the maximum viscosity for a given cone spindle/speed combination.
iv. With the motor off, the sample cup is removed and the necessary volume of viscosity standard fluid is placed into the sample cup.
v. The sample cup is attached back to the viscometer and sufficient time is allowed for the sample, cup and the cone to reach the temperature equilibrium.
vi. The temperature of the bath fluid is measured using a calibrated thermometer and it is made sure that it is within ± 0.1°C of 25°C (or specific calibration temperature). A waiting period of at least 15 minutes is given to make sure that sample temperature is same as bath fluid temperature.
vii. The temperature is recorded.
viii. If the fluid is at the test temperature, the motor is turned on. For the desired speed(s), viscosity is measured and data recorded using the Brookfield Wingather Software Program. Note: The spindle must rotate at least five (5) times before readings are taken.
ix. The viscosity reading should equal the cP value on the fluid standard to within the combined accuracies of the viscometer and the viscosity standard, in steps shown below as the acceptable calibration.

STEP 1:The full-scale viscosity range (A) is calculated using the equation:

Full Scale Viscosity Range, "A" [cP] = TK * SMC * 10,000/RPM

Where,
TK = Viscometer torque constant, 0.09373
SMC = Current spindle multiplier constant, 0.327
The viscosity is accurate to ±1% of A (cP) = "X" cP

STEP 2: If the viscosity standard fluid is "B" cP, its accuracy is ±1% of B (cP) = "Y" cP

STEP 3: If the precision of the thermometers, above -50°C, is within ±0.3% and if the variation of Brookfield viscosity standards is approximately 2% with 0.3° C variations in temperature, let that variation (approximately ±2% of "B" cP) be "Z" cP.

STEP 4: So, total allowable error is (X+Y+Z) cP = ± (X+Y+Z) cP.

STEP 5: Therefore, a viscometer is assumed to be calibrated if the error in the viscosity reading lies within ±(X+Y+Z) cP of the standard fluid viscosity. Any reading outside these limits indicates a viscometer problem.

3.6.2.2 Test Sample Viscosity Measurement

A systematic procedure followed to (i) set up the cone plate viscometer, (ii) set the gap between the cone & plate and (iii) measure viscosity using cone plate viscometer is explained as follows:

Setting Up The Cone Plate Viscometer

i. It is made sure that the cone plate viscometer is securely mounted to the laboratory stand. The instrument is leveled by referring to the viscometer bubble level and adjusting the leveling screws. The viscometer is then zeroed with no cone or cup attached so that the face of the viscometer displays 0% torque.
ii. The sample cup inlet/outlet ports are connected to the water bath inlet and outlet.
iii. All measurements are made as close to target test temperature as possible. The initial water bath temperature is set to test temperature. Sufficient time is allowed for bath to reach the test temperature.
iv. The cone plane viscometer comes with a special cone spindle(s) (for example CPE-40 spindle) which contains the Electronic Gap Setting feature.
v. With the motor off, cone spindle is threaded by using the spindle wrench to secure the viscometer coupling nut; the spindle is gently pushed up on the coupling nut, which is held securely with the wrench. The cone spindle is threaded by hand. Note: Left Handed Threads.
vi. The cup is attached, taking care not to hit the cone with the cup.

Setting the "Gap" between the Cone and the Plate

i. The toggle switch is moved to the right; this turns on (enable) the Gap Setting Feature. The Pilot (red) light is illuminated.
ii. If the contact light (yellow) is illuminated, the micrometer adjustment ring is turned clockwise until the light is no longer illuminated.
iii. If the yellow contact light is not illuminated, the micrometer adjustment ring is slowly turned in small increments in the counter-clockwise direction. The micrometer adjustment ring is continuously moved slowly in the counter-clockwise direction until the contact light (yellow) first turns on. This is the "Hit Point".
iv. The sliding reference marker is adjusted, right or left, to the closest full-scale division mark.
v. The micrometer adjustment ring is adjusted one scale division to the left to meet the line on the sliding reference marker. The yellow contact light goes OFF.
vi. Now, the gap space needed for viscosity measurement is established. The toggle switch is turned OFF (left); the red pilot light goes off.
vii. The sample cup is carefully removed. The motor is turned OFF when the sample cup is being removed.

Viscosity Measurement using Cone and Plate Viscometer

i. The appropriate sample volume is determined. For spindle CPE-40, the sample volume of 0.5 ml is used.
ii. With the motor off, the sample cup is removed and appropriate sample volume is injected into the cup.
iii. The sample cup is attached to the viscometer and sufficient time is allowed for the sample, cup and cone to reach temperature equilibrium.

iv. The spindle/speed combination that will give a minimum scale reading of 10% (% torque reading displayed at the bottom right of the viscometer touch screen) at the lowest speed to be tested is selected.
v. The temperature is monitored by measuring the temperature of the bath fluid using a calibrated mercury thermometer. Sufficient time is given so that sample temperature is the same as the bath fluid temperature.
vi. When the stable test temperature is reached, the temperature is recorded.
vii. The motor is turned on. The desired speed(s) selected is set for the material under test. The viscometer is allowed to run until the reading has stabilized. The data is recorded using Wingather Software Program.
viii. The viscometer speed is increased stepwise and the viscometer reading is recorded after it stabilizes at each speed. After an observation has been made at the top speed, the speed is decreased in steps to the slowest speed, recording the viscometer reading after stabilizing at each speed. Note: It is preferable to change speed when the motor is running.
ix. After the last reading has been taken at the slowest speed, the viscometer is shut off and the viscometer and the specimen are allowed to stand undisturbed for 5 minutes. At the end of the rest period, the viscometer is started at the slowest speed and the initial maximum and equilibrium scale readings are recorded.
x. The Wingather program is stopped and the data is saved.
xi. If the data indicate that at the top speed, measured viscosity as a function of shear rate is stable, the measurements are complete. However, if the data indicate that viscosity is still decreasing as shear increases additional measurements are carried out, including a new sample with temperature pre-treatment, at higher shear rates.

3.7 EXPERIMENTAL RESULTS AND DISCUSSIONS

3.7.1 Density Measurements

The density data were measured in conjunction with the American Society For Testing and Materials (ASTM) D 4052 method using the Anton-Paar digital densitometer. All the density measurements were carried out at various temperatures in the range of ambient to 60 °C. The test temperatures were accurate to ± 0.1 %. The test samples were 100 % ANSC oil, three blends of ANSC: GTL in the volumetric proportions of 3:1, 1:1, and 1:3, and 100 % GTL. Sample requirements for the densitometer were as low as 0.7 cc. The measured density data are presented in Table 3.4 and represented in Figure 3.4. The reproducibility of the experimental density data is determined to be ± 0.005 g/cc.

For liquids, density decreases with increasing temperature, since the liquid molecules move away from each other. As seen in Table 3.4 and Figure 3.4 the reduction in density with temperature follows a similar trend for different samples tested. The presented data also indicate that as GTL proportion in the blend increases, the density gradually decreases because of the fact that lighter hydrocarbons are added to the heavier ANSC oil. Since density decreases with increasing GTL proportion, the pressure or horsepower requirements for commingled flow should fall within the feasible limits. Also, the effect of temperature on density appears to be fairly small, indicating that density is not likely to be a critical factor in low temperature pumpability of the material. The density data thus provide crucial information for determining the hydraulic parameters (Akwukwaegbu, 2001) that are required in studying the transportation of GTL products through the Trans Alaska Pipeline System (TAPS).

3.7.2 Viscosity Measurements

All viscosity measurements were carried out in an LVDV-II+ cone and plate Brookfield Viscometer. The electronic cone spindle CPE-40 was used. The cone angle and radius were 0.8° and 2.4 cm respectively. The test temperatures ranged from 20 to 60°C. The accuracy of temperature measurement was within ± 0.1 %. Similar to the density measurements, test samples were 100 % ANSC oil, ANSC: GTL blends in the volumetric proportions of 3:1, 1:1, and 1:3, and 100 % GTL. Sample requirements were as low as 0.5 cc. The measured viscosity data are furnished in Table 3.5 and graphically represented in Figure 3.5. The reproducibility of the experimental viscosity data is determined to be ± 0.05 mPa.s.

As seen from the data presented in Table 3.5 and Figure 3.5, viscosity decreases as temperature increases for all the samples. For the 100 % ANSC oil, the effect of temperature on viscosity is much more pronounced than in other test samples. At the lowest temperature of 20 °C, the 100 % ANSC oil viscosity is higher than the 100 % GTL by almost 13 times, whereas the difference is as low as 8 times when results at 60 °C are compared. The significantly high viscosity of 100 % ANSC oil at 20 °C does indicate an approach towards a non-Newtonian type behavior. However, the measured data clearly indicates that GTL addition to the ANSC oil significantly reduces the overall viscosity of the blend. This is attributed to the low viscosity of the 100 % GTL sample due to the absence of long chain of heavy hydrocarbon molecules unlike the ANSC oil, in which they dominate the composition and thus impart high viscosity characteristics. The measured viscosity data in conjunction with the density data will facilitate the calculations of friction factors, Reynolds numbers, and pressure drops required in comparing the calculations of batching or blending mode of transporting GTL products through TAPS (Akwukwaegbu, 2001).

In summary, it is observed that crude oil viscosity is a stronger function of temperature than light GTL viscosity. Viscosity of the light GTL being much smaller than crude oil viscosity and the effect of temperature on light GTL viscosity being small (Fig 3.5), it appears that viscosity is not likely to be a controlling factor GTL or GTL-crude blend pumpability.

3.8 CORRELATIONS OF THE MEASURED DENSITY AND VISCOSITY DATA

The measured density (ρ, in g/cc) and viscosity (μ, in mPa.s) data of ANSC, GTL, and their blends were correlated as a function of temperature (T, in °C) and ANSC oil composition by volume (x, in fraction) in the blend. The experimental data were correlated using non-linear regression technique (SigmaPlot 2000, v6.1).

The density data were correlated as shown below:

$$\rho= aT^2 + bT + c \qquad (1)$$

Where,

$$a = a_1x^2 + b_1x + c_1 \tag{2}$$

$$b = a_2x^2 + b_2x + c_2 \tag{3}$$

$$c = a_3x^2 + b_3x + c_3 \tag{4}$$

with the following values of the coefficients –

$a_1 = 1.48633e^{-5}$ $c_1 = 1.29317e^{-5}$ $b_1 = -1.83177e^{-5}$
$a_2 = -0.00146545$ $c_2 = -0.00159337$ $b_2 = 0.00188374$
$a_3 = -0.0581009$ $c_3 = 0.770151$ $b_3 = 0.207453$

The density correlation reproduced the experimental data with an average absolute deviation (AAD) of 0.3 % and the regression coefficient (R^2) of 0.998. A comparison of the correlated and measured density data is shown in Figure 3.6.

The viscosity data were correlated as shown below:

$$\mu = dx^2 + ex + f \tag{5}$$

Where,

$$d = d_1T^2 + e_1xT + f_1 \tag{6}$$

$$e = d_2T^2 + e_2T + f_2 \tag{7}$$

$$f = d_3T^2 + e_3T + f_3 \tag{8}$$

with the following values of the coefficients:

$d_1 = 0.000913208$ $f_1 = 3.23332$ $e_1 = -0.106364$

$d_2 = -0.000514859$ $f_2 = -0.213413$ $e_2 = 0.0668998$

$d_3 = 0.00020135$ $f_3 = 1.10379$ $e_3 = -0.036443$

The viscosity correlation reproduced the experimental data with an average absolute deviation (AAD) of 5.6 % and regression coefficient (R^2) of 0.997. A comparison of the correlated and measured viscosity data is given in Figure 3.7.

$$\frac{v^2}{2}+\frac{P}{\rho}+gz=C_e \qquad (4.2.11)$$

where C_e is a constant. Equation (4.2.11) is more commonly known as the Bernoulli equation of pressure in steady flow or the equation of energy for steady flow.

For flow between points 1 and 2, equation (4.2.11) is written as,

$$\left(\frac{V_2^2}{2g}+\frac{P_2}{\rho_2 g}+z_2\right)-\left(\frac{V_1^2}{2g}+\frac{P_1}{\rho_1 g}+z_1\right)=C_e \qquad (4.2.12)$$

In equation (4.2.12), $V^2/2g$, and $P/(\rho g)$ are the velocity and pressure heads respectively. The last term, z, is the elevation or geometric head of the fluid above an arbitrary reference plane (Kaufmann, 1963; Holland, 1973).

4.3.2.2.1 Energy Losses

Since most natural liquids are very nearly incompressible (i.e. constant density), they are not inviscid (frictionless). Internal friction (viscosity) converts part of the flow energy into other energy forms such as sound, heat etc. and it is "lost" (Kaufmann, 1963). This loss is normally considered as a "head", the friction head, h_f, and is given by the Darcy-Weisbach equation (Smith et al, 1960) as:

$$h_f=4f\frac{LV^2}{2gD} \qquad (4.2.13)$$

Therefore, equation (4.2.12) is re-written as,

$$\left(\frac{V_1^2}{2g}+\frac{P_1}{\rho\, g}+z_1\right)=\left(\frac{V_2^2}{2g}+\frac{P_2}{\rho g}+z_2\right)+h_f \qquad (4.2.14)$$

For steady incompressible flow through a pipe, between points 1 and 2, with a pump at one end, equation (4.2.14) can be re-written as,

$$\left(\frac{V_2^2}{2g}+\frac{P_2}{\rho g}+z_2\right)-\left(\frac{V_1^2}{2g}+\frac{P_1}{\rho g}+z_1\right)=\Delta h_p-h_f \qquad (4.2.15)$$

where Δh_p, is the head imparted to the fluid by the pump (Holland, 1973).

This then implies that the total pressure drop across the streamline is given as

3.9 TEST FLUIDS FOR GEL STRENGTH MEASUREMENTS

The gel strength measurements were carried out on two different GTL samples and crude oil. The properties of the two GTL samples are presented in the following sub-sections. The crude oil composition has already been presented in Table 2.

3.9.1 GTL 1

The first set of gel strength measurements were performed using the light GTL sample (from LaPorte) mixed with varying wax fractions. The wax and the light hydrocarbon GTL sample were supplied by the University of Alaska Fairbanks (UAF) to WTCI after receiving them from US DOE. The paraffin wax (heavier alkanes) was separated from Shellwax® 200 by a modified ASTM-1160 Vacuum Distillation process to produce only a 20% overhead fraction. This wax fraction was then gravimetrically mixed with the light hydrocarbon GTL liquid in the proportions of 25% wax distillate + 75 % light GTL and 50 % wax distillate + 50 % light GTL. The compositions of the light GTL and the blends with the wax are shown in Table 6.

The purpose of mixing the wax distillate with the light GTL in different proportions was to create GTL samples of varying wax content. Since gel strength has significant dependence on wax content, it was necessary to use samples with varying wax content so that the limiting conditions for flow through TAPS can be estimated.

3.9.2 GTL 2

The second GTL sample was a Fischer-Tropsch (FT) diesel sample, also supplied by US DOE. The characteristics of this GTL are presented in Table 7. A compositional analysis of this GTL sample (FT Diesel) was also carried out at UAF. The detailed composition of GTL 2 is provided in Table 8. A plot of the PIANO (Paraffins, Iso-paraffins, Aromatics, Naphthenes, Olefins) analysis of GTL 2 is presented in Figure 8. The FT diesel was used by itself (i.e. without mixing with wax fractions) in this set of tests. This represents a scenario where clean diesel is produced and transported from the North Slope.

3.10 GTL AND TAPS CRUDE OIL BLENDS

As far as GTL 1 is concerned, twenty-four samples were, gravimetrically prepared for gel strength measurements, prepared as per the ratios listed below:

(a) 25 % wax distillate + 75 % light hydrocarbon (LH) GTL
(b) 50 % wax distillate + 50 % light hydrocarbon GTL
(i) sample (a) + crude oil (1:4)
(ii) sample (a) + crude oil (1:3)
(iii) sample (b) + crude oil (1:4)
(iv) sample (b) + crude oil (1:3)
(v) LH sample + crude oil (1:4)
(vi) LH sample + crude oil (1:3)

The gel strength measurements were carried out on twenty-four test samples for the GTL 2. The samples were gravimetrically prepared, eight each at the three ratios listed below:

(a) 100% Light Hydrocarbon GTL
(b) 25% Light Hydrocarbon GTL + 75% Crude Oil
(c) 20% Light Hydrocarbon GTL + 80% Crude Oil

In the GTL:crude oil blend ratios, smaller proportions of GTL were used because it was assumed that GTL production in the North Slope will be far less than crude oil production in the foreseeable future. Thus, blends containing lower proportions of GTL are likely to flow through TAPS.

3.11 COMPOSITIONAL ANALYSIS OF GTL 1 AND CRUDE OIL BLENDS

The quantitative compositions of various GTL and crude oil blends and pure crude oil were determined by WTCI. Prior to the GC analysis of blends, the apparatus is subjected to an extensive quality control check using normal alkane standard, aromatic standard, reference gas oil, and two crude oil standards. The gas chromatographs on the GTL and crude oil blends were quantified by employing iso-octane as an internal standard. The Standard Laboratory Procedure (2001) of WTCI explains the GC analysis procedure in further details.

The compositions of GTL and crude oil blends (samples v and vi, Section 3.10) were not measured, these values were calculated from the individual GTL and crude oil compositions. All the compositional data are presented in Table 3.9. In order to assess the internal consistency of the measured compositional data on the blends, the TAPS crude oil composition was back calculated using a simple component mass balance approach as shown below (example for C30+):

$$C_{30+[50:50]GTL} * M_{[50:50]GTL} + C_{30+CRUDEOIL} * M_{CRUDEOIL} = C_{30+BLEND} * M_{BLEND}$$

or

$$C_{30+[25:75]GTL} * M_{[25:75]GTL} + C_{30+CRUDEOIL} * M_{CRUDEOIL} = C_{30+BLEND} * M_{BLEND}$$

Where,

$C_{30+[50:50]GTL}$ and $C_{30+[25:75]GTL}$ is the weight % of C30+ in 50:50 (wax:GTL) and 25:75 (wax:GTL) respectively

$C_{30+CRUDEOIL}$ and $C_{30+BLEND}$ is the weight % of C30+ in the crude oil and the blend respectively

$M_{[50:50]GTL}$ and $M_{[25:75]GTL}$ is the mass of 50:50 (wax:GTL) and 25:75 (wax:GTL) respectively

$M_{CRUDEOIL}$ and M_{BLEND} is the mass of crude oil and the blend respectively

The calculated crude oil composition and the ones measured on the crude oil were compared as shown in Figure 3.9. As seen in Figure 3.9, all the data lies neatly on a 45° line, which clearly indicates that the measured compositional data on GTL and crude oil blends is reliable, and internally consistent.

3.12 COMPOSITIONAL ANALYSIS OF GTL 2 AND CRUDE OIL BLENDS

Compositional data for the GTL 2 and TAPS crude oil blends were not measured. However, the compositions of the GTL 2 were measured using gas chromatography at UAF. For this purpose, a known calibration sample was analyzed over a wide range of solvent to sample concentrations. Based on this, a relationship between the molar composition, retention time, and the areas under the chromatograph peaks was developed. The known calibration sample is primarily normal paraffins. Although, this may not be a good relationship for other substances, it does not pose a problem for a substance like FT diesel as it is mainly composed of alkanes or saturates (Table 3.7 and 3.8). The developed correlation was applied to the area percents from a sample of GTL 2, which was run through the GCMS, to determine its composition.

The individually measured compositions of the GTL 2 and the TAPS crude oil were numerically recombined to determine the blend compositions. The calculated blend compositions are presented in Table 3.10.

3.13 TEST TEMPERATURES FOR GEL STRENGTH MEASUREMENTS

The GTL 1 and TAPS crude oil blend gel strength measurements were carried out at temperatures ranging from 60 to 0°F, whereas for the GTL 2 and TAPS crude oil blends the gel strength measurements were performed at temperatures in the range of 27 to –20°F.

These test temperatures were selected on the basis of the cold ramping of the GTL and crude oil blends from 90 to –20°F over a twenty one day period. The temperature decay curve used for the sample preparation and test temperature selection was based on the Trans Alaska Pipeline cold restart data supplied by the Alyeska Pipeline Service Company. The temperature ramp is presented in Figure 3.10, along with the selected test temperatures. The temperature ramp simulates cooling of the fluids inside TAPS under winter shutdown conditions. Thus, by choosing test temperatures from the TAPS cooling ramp, one would be able to estimate the feasibility of cold restart for a given GTL product or its blend.

3.14 GEL STRENGTH MEASUREMENT PROCEDURE

The gel strengths of various GTL crude oil blends were determined by the rotating vane method. The tests for determining the yield stress, or yield stress value, of the cooled crude oil blends, were performed following Westport's Standard Laboratory Procedure 307 (WTC, July 2000). This method is based on Brookfield rotary viscometers and vane spindles, which extend horizontally through a sample, minimizing the impact of slippage at the spindle wall. This method determines the minimum amount of torque necessary to initiate oil movement at low shear, and subsequent gel breakdown after initiation of flow.

The method basically consists of determining the yield stress value of a crude oil by measuring the torque on a spindle, using a Brookfield viscometer, rotating at 0.01 rpm in the material. The spindle to be used consists of four rectangular vanes dimensioned (0.75"w x 2.25"h) and oriented at 90 degree increments around the central axis. The sample cup is dimensioned (1.5" id x 4.0"h). Vertical orientation of vanes within the sample cup is dimensioned (1.00" from top and 0.75" from bottom).

The crude oil blends were initially heated to 150°F to destroy all temperature and shear histories and then cooled to 100°F at which stress value they were loaded into the vane closed-cup apparatus. The closed-cup apparatus holds the vanes rigidly during cooling and aging and prevents loss of light ends through evaporation. After loading into the cup apparatus the samples were cooled in an environmental chamber at a controlled rate to below 0°F. The cooling rate mimics the expected rate of cooling of the Trans-Alaska pipeline oil in the case of shut-in.

Samples were withdrawn from the environmental chamber at selected test temperatures and transferred to a refrigerated circulator that maintains the sample at test temperature. The spindle was attached to the Brookfield viscometer (LV, RV or HB) before the spindle clamping mechanism was released. The clamping mechanism was released and the viscometer was started at 0.01 rpm and torque as a function of time was measured, until a maximum reading was obtained. The maximum torque (dyne-cm) obtained is divided by a vane parameter constant K to obtain the yield stress (dynes/sq.cm). The constant K is calculated based on the dimensions of the vanes. (K=36.19 cm^3, for a Vane with D=0.75 inch (1.905 cm) and H=2.25 inch (5.715 cm).

3.15 EXPERIMENTAL RESULTS AND DISCUSSIONS

3.15.1 Gel Strength Measurements on GTL 1 and TAPS Crude Oil

The results on the gel strength measurements for the GTL 1 and TAPS crude oil mixtures are presented in Table 3.11 and Figure 3.11, respectively.

Initial test temperatures were set at 9, 0 and –20°F. However, tests at 9°F indicated gel strength beyond measurable limits of the viscometer for samples (i) to (iv) and relatively high strengths for samples (v) and (vi). Because of this the cold ramp was continued and testing resumed at 0°F for samples (v) and (vi). Similarly, due to the high yield stress values encountered, no tests were conducted at –20°F and the remaining samples were tested at higher temperatures in order to determine the gelation onset and build-up.

Thus, from the very high gel strengths of samples (i) to (iv) at 9°F, it appears that GTL products with moderate to high wax content are not likely to be acceptable for transporting via TAPS from the cold restart point of view. Even the pure light GTL-crude samples (v) and (vi), which did not have any added wax fraction, exhibited very high gel strength at 0°F. Cold restart may be a problem for even the light GTL.

All remaining samples were re-heated to 150°F and then cold ramped to a 21-day cycle. The high wax content/GTL samples (iii, iv) were tested at 60°F resulting in low yield values.

The tests at 40°F were performed on samples (i) to (iv). Samples (ii) and (iii) resulted in maximum torque readings beyond the limits of the initially selected viscometers. Therefore, repeat tests were performed for samples (ii) and (iii) using viscometers with higher spring ratings, which permitted the measurement of yield stress.

All the tests at 20°F on samples (i), (ii), (iv), (v) and (vi), were carried out using the strongest viscometer (HB). Due to the higher wax content, the test on sample (iv) was beyond the strongest viscometer limit, and yield stress is reported as > 1589 dyne/cm^2.

The gel strength measurements on sample (vi) at 9°F were repeated. The repeat measurements indicated some variability, as far as the results are concerned (229 vs. 438 dyne/cm^2). This variation is not attributed to procedural variations. Moreover, due to the lack of sample quantity a third repeat test could not be performed. However, the value of 438 dyne/cm2 is considered as more reliable as it falls within the data trend.

3.15.2 Gel Strength Measurements on GTL 2 and TAPS Crude Oil

The results on the gel strength measurements for the GTL 2 and TAPS crude oil mixtures are presented in Table 3.12 and Figure 3.12, respectively.

Initially, the planned test temperatures were set at 20°F, 0°F and –20°F. However, the simple spot test of the pure GTL sample (a) indicated possible gel strength onset at earlier temperatures. Therefore, tests were performed on the 100% GTL at 27°F and a yield stress of 171 dynes/sq.cm was obtained. At a temperature of 20°F the pure GTL sample had reached its pour point value. Therefore, no gel strength measurements could be carried out at the other temperatures of 20, 0, and –20°F as these were beyond the measurable limits of the strongest viscometers. Thus, these values are reported as >1589 dyne/sq.cm.

The gel strength measurements for sample (b) and (c) at 20°F resulted in averaged yield stress values of 2.91 dynes/sq.cm and 1.13 dynes/sq.cm respectively. At a temperature of 0°F sample (b) produced an average yield stress value of 694 dynes/sq.cm, whereas sample (c) produced an average yield stress value of 389 dynes/sq.cm.

All tests performed at a temperature of –20°F on sample (b) and (c) produced yield stress values beyond the measurable limits of the Vane test equipment, or values greater than 1589 dynes/sq.cm.

These results indicate that gel strength of FT diesel can increase abruptly once the temperature falls below a threshold. The threshold temperature can be as high as 20°F. From the pipeline cold restart point of view, this poses a serious problem. Since the pure GTL sample gels at a higher temperature than GTL-crude oil blends, batching of GTL could be more troublesome than commingled flow. Although these results are preliminary, they clearly indicate the need for further studies to identify exactly what amounts and molecular weights of paraffins in GTL will be acceptable for transportation through TAPS.

3.16 COMPARISON OF GEL STRENGTH MEASUREMENTS ON GTL 1 AND GTL 2 AND TAPS CRUDE OIL BLENDS

In order to evaluate the effect of GTL type or its characteristics on gel strength measurements of GTL and crude oil blends, a comparative study of the two GTL's, i.e., GTL 1 and GTL 2 was carried out. For the sake of fare comparison, gel strengths measured for the blends having the ratios of 1:3 (GTL:crude oil) and 1:4 (GTL:crude oil) or 25% GTL and 75% crude oil and 20% GTL and 80% crude oil, were compared. These results are shown Figure 3.13 and Figure 3.14 respectively. This comparison indicated that the trend of gel strengths were similar for samples (b) and (vi) and (c) and (v) having 1:3 and 1:4 GTL to crude oil ratios respectively.

3.17 CONCLUSIONS

3.17.1 Density and Viscosity Measurements

Based on the experimental study carried out at UAF on density and viscosity measurements of GTL, crude oil and their blends, the following main conclusions are drawn.

- Standard laboratory testing procedures are developed and used to determine the density and viscosity data of Alaskan North Slope Crude (ANSC) oil, Gas-to-Liquids (GTL), and their blends, in the temperature range of ambient to 60 ^{o}C at ambient pressure.
- A Quality Assurance Project Plan (QAPjP) has been developed.
- Appropriate calibration procedures are followed for calibrating the Anton-Paar densitometer and the cone and plate Brookfield viscometer used for measuring the density and viscosity respectively.
- The reproducibility of the measured density and viscosity data was found to be ± 0.005 g/cc and ± 0.05 mPa.s respectively.
- It was found that GTL and crude oil readily developed miscibility when mixed at ambient temperature and pressure conditions.
- The trend of both density as well as viscosity reduction as a function of increasing temperature is clearly evident for all the tested samples.
- The dilution of crude oil by GTL causes a major reduction in both density as well as viscosity.

- The measured density and viscosity data have also been correlated using non-linear regression techniques. It is demonstrated that the developed correlations are capable of reproducing the measured data with reasonable accuracy and reliability.
- Using the measured data and the developed correlations, the hydraulics of transporting GTL and crude oil fluids either commingled or batches through TAPS can be evaluated.

3.17.2 Gel Strength Measurements

Based on the test results at WTCI on gel strength measurements and compositional analysis of various GTL and crude oil blends, the following main conclusions are drawn.

- The trend of increasing yield stress with increasing wax content was clearly observed.
- Gel strength tests at –20°F for the GTL 1 and TAPS crude oil blends had to be abandoned owing to very high yield stress (beyond measurable limits of the apparatus) already encountered at temperatures higher than –20°F.
- The results indicate that light samples had measurable gel strength whereas significant gel strength problems were observed for heavier GTL and crude oil blends.
- The formation of weak gel structures at higher temperatures (sample vi, 9°F) posed some repeatability problems. The lack of additional samples precluded the possibility of further repetition of the test.
- The measured compositional data on GTL 1 and crude oil blends was found to be accurate and reliable.
- As far as the 100% GTL 2 sample is concerned, it produces high gel strength, but when it is blended with TAPS crude oil a significant reduction is observed.
- It is also evident that the decrease in GTL 2 in the blend ratio also contributes to lower yield stress values.
- No gel strength measurements could be reported at temperatures of –20°F for the GTL 2 and TAPS crude oil blends due to very high yield stress (beyond measurable limits of the apparatus).
- In general, the gel strength behavior observed with the GTL 2 and TAPS crude oil blends can be attributed to the chemical composition of the GTL 2, which indicates a highly paraffinic characteristic.

- The developed methodology of GCMS calibration at UAF was found to be accurate and reliable for the determination of FT diesel (GTL 2) compositions.

- It can be concluded that the ratio blending may be effective in lowering the ultimate yield stress values of GTL/crude oil blends. However, it will be worthwhile to determine if the effect of ratio blending is reproducible with varying crude oil composition.

- A similarity in the gel strength trend was observed when the results for GTL 1 and GTL 2 and TAPS crude oil blends were compared.

- This study indicates that even light GTL (LaPorte type) or FT diesel can pose problems for transportation through TAPS from the cold restart point of view. Rigorous studies are needed to identify the upper limit on the quantity and nature of paraffins in GTL that can be accepted for TAPS flow. Since high molecular weight paraffins are clearly not acceptable, it may be necessary to include a hydrocracking unit in the GTL plant considerations for the North Slope.

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