AN EXPERIMENTAL INVESTIGATION ON THERMAL ANALYSIS & COLD FLOW PROPERTIES OF VARIOUS BIODISEL SAMPLES

A THESIS SUBMITTED TO THE GRADUATE
SCHOOL OF APPLIED SCIENCES
OF
NEAR EAST UNIVERSITY

By
RENAS HASAN SAEED

In Partial Fulfilment of the Requirements for
the Degree of Master of Science
in
Mechanical Engineering

NICOSIA, 2019

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Approval of Director of Graduate School of
Applied Sciences

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ACKNOWLEDGMENTS

My deepest gratitude goes to my lecturer and supervisor Assoc. Prof. Dr. Hüseyin ÇAMUR and Assist. Prof. Dr. Youssef KASSEM for their help, encouragement and support throughout my master program especially their role in this thesis is uncountable. Without their consistent follow-up, support and advice this thesis could have been nothing.

I want to express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study. This accomplishment would not have been possible without them. Thank you.

To my parents…

ABSTRACT

Biodiesel is a source of energy derived from natural feedstocks. Either these feedstocks can be waste or used cooking oil. Via a transesterification process they were transformed to methyl esters. Biodiesels can be blended at distinct ages to enhance the fuel quality. Three different Biodiesel samples blended at different percentage. The study outputs are used to determine the biodiesel properties of the biofuel. This research focuses on waste cooking oil and used cooking oil of methyl ester. The blending ratios range from 100% biodiesel to 0% biodiesel per volume in 25% steps. Therefore, fifteen samples of biodiesel were prepared. The research aim was to determine the temperature effect on biodiesel sample properties. Kinematic viscosity of biodiesel samples were measured at 80℃ to 30℃ and from 20℃ to freezing point, and also density measured at the same conditions, according to ASTM standards. It was established that these properties decrease with increasing temperatures. Cold flow properties had been formulated via a thermal analysis. These were impacted in the correlating samples by the quantity of biodiesel samples. This had been supported by a Computer Aided Cooling Curve Analysis (CA-CCA).

Keywords: Biodiesel; Cold flow properties; Cloud point; Density; Kinematic viscosity; Pour point

ÖZET

Biyodizel doğal ham maddelerden elde edilen bir enerji kaynağıdır. Bu ham maddeler atık yağ veya kullanılmış pişirme yağı olabilirler ve transesterifikasyon yöntemi ile, metil esterlere dönüştürülürler. Bu çalışmada, biyodizeller'de yakıt kalitesini artırmak ve özelliklerini iyileştirmek için farklı yaşlardaki biyodizeller belirli oranlarda karıştırılıp elde edilmiştir. Bu çalışmada farklı üç biyodizel kullanılmıştır. Biyodizellerin karıştırma oranları 75%, %50 ve %25' dir ve toplam 12 numune hazırlanmıştır. Biyodizel numunelerin özelliklerini sıcaklığa bağlı olarak araştırılmıştır. Bu özellikler kinematik viskozite, yoğunluk ve soğuk akış özellikleridir. Biyodizel numunelerin kinematik viskozitesi, ASTM standartlarına göre, (30°C-80°C) sıcaklık aralığında ve 20°C' den donma noktasına kadar incelenmiştir. Ayni sıcaklık aralıkları için yoğunluk da hesaplanmıştır. Bu iki özellik sıcaklık artıkça azalıyor. Soğuk akış özellikleri de bu çalışmada incelenmiştir.

Anahtar Kelimeler: Biyodizel; Soğuk akış özellikleri; clod noktası; Yoğunluk; kinematik viskozite; Akma noktası

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LIST OF ABBREVIATIONS

ASTM:	American Society for Testing Materials
B100:	Biodiesel sample with %100 concentration
BD1:	Biodiesel type one
BD2:	Biodiesel type two
BD3:	Biodiesel type three
CA-CCA:	Computer Aided Cooling Curve Analysis
CaO:	Calcium oxide
CCA:	Cooling Curve Analysis
CFPP:	Cold filter plugging point
CP:	Cloud Point
EU:	European union
FAME:	Fatty Acid Methyl Ester
HHV:	Higher heating value
NTA:	Newtonian Thermal Analysis
PP:	Pour Point
Zn:	Newtonian Zero Curve

LIST OF SYMBOLS

A: Area (m^2)

D: Capillary diameter (m)

Dv: Changing in velocity (m/s)

Dx: Changing in separation height (m)

G: Acceleration due to gravity (m/s^2)

H: Capillary height (m)

K: Viscometer constant (mm^2/s^2)

L: Length of viscometer (mm)

P: Flow pressure (Pa)

Q: Flow rate (m^3/s)

R: Capillary radius (m)

T: Absolute temperature (℃)

t: Time (s)

V: Flow velocity (m^2/s)

V: Volume (m^3)

Y: Correction factor (--)

Z: Length in flow direction (mm)

Cp: Specific Heat (J/k)

L: Latent heat (J/kg)

Ti: Temperature at point i (℃)

To: Cooling bath temperature (℃)

cc: Cooling Curve First Derivative (--)

m: Mass (g)

m_e: Mass of the empty pycnometer (g)

m_f: Mass of the completely filled pycnometer (g)

t_e: End of Solidification (s)

t_s: Start of Solidification (s)

u: Velocity (m/s)

U: Overall heat transfer coefficient (Wm^{-2}K^{-1})

v_r: Velocity in radian direction (m/s)

v_z: Velocity in flow direction (m/s)

v_θ: Velocity in angular direction (rad/s)

GREEK SYMBOLS

$\boldsymbol{\dot{\gamma}}$**:** Rate of shear (1/s)

V: Kinematic viscosity (mm^2/s)

$\boldsymbol{\gamma}$**:** Strain (--)

$\boldsymbol{\theta}$**:** Angular length (rad)

$\boldsymbol{\mu}$**:** Dynamic viscosity (N. s/m)

$\boldsymbol{\rho}$**:** Density (kg/m^3)

$\boldsymbol{\tau}$**:** Shear stress (N/m^2)

CHAPTER 1
INTRODUCTION

1.1 Energy

Rapid population growth and the upgrade in production technologies have increased global energy demand. Energy is divided into two main groups: non-renewable energy and renewable energy. Non-renewable energy is limited and cannot be renewed in any way (Oxford, 2018). Limited amount of non-renewable energy sources, such as natural gas and coal, causes people to look for a new energy source. Some researchers showed that the remaining amount of fossil fuels will come out by 2040 (Showstack, 2016). Because of these facts, experts focus on alternative renewable resources such as hydropower, solar energy, tidal energy, biofuel, nuclear energy, biomass, wind energy, etc.

Renewable energy sources include; biofuel, biomass, and hydro, and wind, solar and geothermal energy. This type of energy sources replaced rapidly by a natural process.

Engineers are currently seeking a way to reduce the use of fossil fuels and other non-renewable energy sources using various techniques such as hybrid machines that use petrochemical fuel for ethanol driven vehicles and electric energy for solar-powered cars. Solar and wind energy have been on the rise as a possible long term solutions. The reason for the replacement is not only depletion, but a drive towards a more environmentally friendly means of energy. Energy which conforms to the idea of sustainability. A major alternative is biodiesel and its blends.

Renewable energy sources are useful for electric energy, but cannot be properly used in the transport sector. Biofuels are the most suitable renewable energy source used for transportation, and therefore biofuels are different from other types of renewable energy.

1.2 Definition of Biodiesel

Biodiesel mono-alkyl ester is obtained by transterification of oils and fats derived from plants and animals respectively (National Biodiversity Council, 2018). These oils and fat can be collected from restaurants and homes. The transterifictaion process ensures the interaction of raw materials (i.e, vegetable oils, animal fats or vegetable oils) with methanol; they are affected by the biodiesel catalyst, the fatty acid methyl esters (FAME) (Evcil et al., 2018).

Different feedstock or raw materials can be used with different catalysts. Basal / alkaline catalysts are mainly used at most sodium and potassium hydroxides because they produce the final product faster. A sodium hydroxide catalyst is used to produce biodiesel in one step using a bath of water or microwave (Loong and Idris, 2017).

Other catalysts are acid catalysts. They are used in the earlier start-up phase and is 4000 times slower than the major catalysts. However, the cement waste catalyst is a more inexpensive and environmentally friendly catalyst. Cement, concrete and mortar are used in the damaged construction sites. It is said that the concrete or mortar used is calcinated and is similar with calcium oxide (CaO) (Kumar et al., 2018).

Biodiesel is used rapidly in engines, cars and trucks worldwide. This is a very stable energy source controlled by ASTM D6751. Quality parameters can be used in different ways (Pratas, et al., 2010). Pure biodiesel are called B100. "B" indicates the ratio of literal biodiesel. This analytical reflects the percentage of biodiesel in the fuel. Conventional blends of biodiesel contain mixtures of petroleum chemistry. For B20 the mixture is used for engines without special modifications. The biodiesel blend can be made in different stages. These may be; mixing in reservoirs at the stage of manufacturing before transportation to trucks carrying petrol.

Some features have to be considered, when working with biodiesel; these include kinematic viscosity, density, and cold flow properties which are affected at different temperatures. The uses of biodiesel vary across the energy field. As the name indicates the major application of biodiesel is in diesel engines. However, due to its clean way of burning, the advantages has expanded to, heating and cooking.

1.3 Aim of the Thesis

The aim of the study was to determine the properties of 3 types of biodiesel blends at different percentages and produced from waste/used cooking oil at different temperatures (i.e, 0 ℃ - 80℃). Fuel properties that were examined are as follows;

- Kinematic viscosity
- Density
- Cold flow properties

1.4 Thesis Outline

Chapter 1 described the aim of this study, and general information about biodiesel.

Chapter 2 provides the concept and basic importance of some biodiesel properties such as viscosity, density, and cold flow properties.

Chapter 3 explains the measurement procedure and test preparation to measure the properties of biodiesel.

Chapter 4 shows the results obtained from the study discussed

Chapter 5 describes conclusions and recommendations for future activities

CHAPTER 2
LITERATURE REVIEW AND THEORIES

2.1 Concept of Viscosity

While examining a liquid, the most important property to check out is the viscosity. Viscosity is a measure of resistance to flow or shear. It is sometime refers to as the “thickness” of a fluid.

2.1.1 Dynamic viscosity

The ratio of the shear stress to the velocity gradient of a fluid is called Dynamic viscosity is also called absolute viscosity. Sometimes it refers to the shear viscosity. When they are multiplied by shear force operating in the same direction on both sides of the material, the shear stress is generated between the layers and the corresponding shear stress is generated. Shear strain is defined as follows;

$$\gamma = \frac{dx}{dy} \tag{2.1}$$

The rate of shear strain;

$$\dot{\gamma} = \frac{d\gamma}{dt} \tag{2.2}$$

The shear stress ratio is the relative shear stress between the layers of oil, air and water.

The formula for dynamic viscosity can be indicated as follows;

$$\mu = \frac{\tau}{\dot{\gamma}} = \tau \frac{dy}{du} \tag{2.3}$$

2.1.2 Kinematic viscosity

Kinematic viscosity is a measure of fluid-resistant flow under gravity. It is a dynamic viscosity divided by density. This expression mathematically is;

$$\mathrm{v} = \frac{\mu}{\rho} \tag{2.4}$$

The units of kinematic viscosity is mm^2/s.

The kinematic viscosity of biodiesel is highly dependent on composition and temperature. In the literature (Corach et al. 2017), there are many numerical models that attempt to define the viscosity of mixtures having a structure known as a function of temperature.

2.1.3 Measurement of viscosity

Means for measuring viscosity are known as viscometer. The viscometers are generally divided into six groups as follows;

- Capillary (U-Tube) Viscometers
- Falling Piston Viscometers
- Falling Sphere Viscometers
- Bubble Viscometers
- Rotational Viscometers
- Rheometers

2.1.4 Capillary viscometers and theory

Capillary viscometers are preferable utilized to measure fluids which conform to Newtonian theory of fluids. Due to their accurate calibration they are used widely. It measures the time of required of fluid to pass through a capillary. These instruments include in their range the Ubbelohde and Ostwald varieties alternatively referred to as U-tube viscometers. They are easy and also unpretentious to use, with a U-like shaped glass tube with two spheres, an upper and a lower. Fluids pass from the upper sphere down to the lower sphere through capillary and the viscosity is recorded by recording the time required for liquid to cross the tube (Saint Clair Systems Norcross, 2018). Figure 2.1 shows the ideal viscometer.

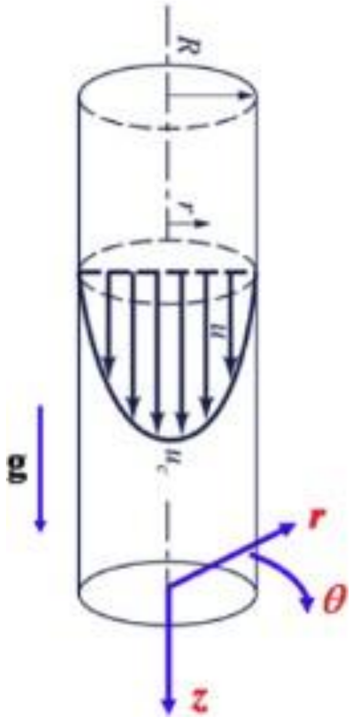


Figure 2.1: Hagen-poiseuilles fluid flow through a vertical pipe (Fox et al., 2012)

The viscosity calculation of the viscosity indicator data is followed by Poiseuilles' Newtonian fluid equation.

The particles travel through the z axis.

$$v_r \ = \ 0, v_z \ \neq \ 0, v_\theta \ = \ 0 \tag{2.5}$$

From the equation of continuity

$$\frac{v_r}{r} + \frac{\partial v_z}{\partial_z} + \frac{\partial v_r}{\partial_r} = 0 \tag{2.6}$$

Symmetry of rotation

$$\frac{\partial \mathrm{v}_\theta}{\partial_\theta}\frac{1}{\mathrm{r}} = 0; \quad \mathrm{v}_\mathrm{z}(\mathrm{r},\mathrm{t}) = \mathrm{v}_\mathrm{z} \qquad \text{or } \frac{\partial}{\partial_\theta} = 0 \tag{2.7}$$

Taking equation 2.5, 2.6 with 2.7 into the Navier Stoke's equation in cylindrical coordinates, the expression becomes;

$$\frac{\partial v_z}{\partial t} = v\left(\frac{\partial^3 v_z}{\partial r^3} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right) - \frac{1}{\rho}.\frac{\partial p}{\partial z}\ follow\ z\ direction \tag{2.8}$$

When flow is steady, equation will be as

$$\frac{1}{\mu}\frac{\partial_p}{\partial_z} = \frac{1}{r}\frac{\partial v_z}{\partial_r} + \frac{\partial^2 \partial_z}{\partial r^2} \tag{2.9}$$

Solving the equation 2.9 these boundary conditions will use

$$v_z\ is\ finite \text{ at } \quad r = 0 \tag{2.10}$$

$$v_z = 0; \quad \text{at} \quad R = r \tag{2.11}$$

It gives

$$\left(-\frac{\partial p}{\partial p}\right).\frac{R^3}{4\mu}.\left(1 - \frac{r^3}{R^3}\right) = v_z \tag{2.12}$$

while

$$-\frac{\Delta p}{L} = \frac{\partial p}{\partial z} \tag{2.13}$$

Volume flow rate discharge is

$$Q = \int_0^R 2\pi v_z r dr \tag{2.14}$$

Putting 2.12 and 2.13 in 2.14

$$Q = \pi \left(\frac{\Delta p}{L}\right) \frac{R^3}{8\mu} \tag{2.15}$$

and

$$\frac{V}{t} = Q \tag{2.16}$$

Overall flow rate is Q, V is the volume and t is the time

$$v = \frac{\mu}{\rho} \tag{2.17}$$

$$\Delta p = \rho g h \tag{2.18}$$

Therefore

$$v = \frac{\pi g H R^4}{8LV}.t \tag{2.19}$$

K Calibration constant

$$v = \frac{\pi g H R^4}{8LV}.t \tag{2.20}$$

So, the equation will be

$$v = Kt \tag{2.21}$$

Equation 2.21 kinematic viscosity equation is absolutely conformable to ASTM 446-07, but only expecting the correction factor.

$$v = \frac{10\pi g D^4 t H}{138 L V} - \frac{E}{t^3} \tag{2.21}$$

E presences the correction factor.

2.1.4.1 Types of capillary viscometers

Appendix 1 shows the list and technical characteristics of various devices for measuring capillary viscosity. The following sections will explain in detail the viscosity scale of Ubbelohde users.

2.2 Density of Biodiesel

This is the mass of any material depending on the material's unit size (Giacomas and Sarkatsans, 2018). It is the principle of Archimedes and expressed in the formula,

$$\rho = \frac{m}{V} \tag{2.22}$$

Where ρ is density in (kg/ml), or (kg/m^3)

m is biodiesels' mass in (kg)

V is biodiesels' volume in (m^3)

Petrochemical diesel has a less value than density compared to Methyl esters. This will cause fuel pumps of diesel engine which are based solely on volume operations (Agarwal, 2007), to spray less weight of petrochemical diesel than biodiesel into the engine (Gabrowski and McCormick, 1998). So then the air / fuel ratio will be directly affected (Demirbas, 2005 and Giakoumis et al., 2012).

The apparatus that is used for measuring the density of biodiesel according to the standards is called pycnometer. Using a sensitive scale to measure the mass of it, after filling the pycnometer with fuel. The mass of the pycnometer should be recorded when it's empty and must be used in determination of the density according to ASTM D941-88 (Appendix 2).

2.3 Cold Flow Properties of Biodiesel

Biodiesel liquidity can be explained by biodiesel properties and cold flow properties at low temperatures. Fuel is often a problem in low temperature ignition due to low flow properties. Cold flow properties are divided into three properties which are cloud point (CP), and pour point (PP) and cold filter plugging point (CFPP).

2.3.1 Cloud point

The temperature at which the wax crystals become visible is called cloud point. Fuel begins to appear cloudy or transparent. The petrochemical diesel has a lower cloud point than biodiesel; ASTM D2500 (Appendix 3) should be followed when measuring the Cloud Point.

2.3.2 Pour point

Pour point is the flow property at which the temperature of fuel is partially loses and hardened. The minimum pour point can be determined as the temperature at which the vehicle can operate. Biodiesel contains most of the crystals collected at this stage that are actually jellied and can no longer flow. It is known that Cloud point is always higher than pour point. Petro-diesel has lower pour point than biodiesel when we compare biodiesel and petro-diesel, ASTM D97-05 (Appendix 4) was used for the PP measurements.

2.3.3 Cold filter plugging point

The lowest temperature at which a vehicle will seize to operate. The wax particles begin to clog the fuel filters. The vehicle's operability will become almost obsolete. For naked eye is hard to measure this point. It’s usually between cloud point and pour point.

2.4 Thermal Analyses

Thermal analysis is an indication that the temperature of the material on which the properties of the material are studied with various temperature. The measured property usually uses many different techniques (Paulik et al., 1966).

2.4.1 Newtonian thermal analysis

It can be shortened as NTA, the heat flow generated during sample solidification is expressed from heat equation equilibrium as (Kierkus & J. H. Sokolowski, 1999)

$$-MC_P\frac{dT}{dt}+\frac{dQ}{dt}=(T-T_0)UA \quad (2.23)$$

Where M is mass of the sample in (kg), C_P is specific heat of the sample in (J/K), and T is the temperature of sample in (K), T_0 is the cooling bath temperature in kelvin, t is the time taken in (s), Q is the latent heat of solidification in (J/kg), U is overall heat transfer coefficient in ($Wm^{-2}K^{-1}$), A is the sample surface area in (m^2).

Assume that there is no phase change in the cooling course $\frac{\mathrm{dQ}}{\mathrm{dt}}=0$. The cooling rate for the biodiesel sample can be written.

$$\frac{dT}{dt}=-\frac{UA(T-T_0)}{MC_P}=Z_N \quad (2.24)$$

Z_N being termed the zero curve of Newtonian or simply, the baseline

Therefore, the total of the latent heat L is determined as

$$L=\frac{Q}{M}=CP\int_{t_s}^{t_e}[(\frac{dT}{dt}_{CC}-Z_N)]\,dt \quad (2.25)$$

With t_e and t_s are the times for end and start of solidification. The first derivative of the cooling curve with t_e and t_s shows as the times for ending and starting solidification.

The biofuel sample solidification latent heat can be as,

$$L=\mathrm{Cp}\ \times(Area\ in-between\ cooling\ curve\ and\ baseline) \quad (2.26)$$

Equation 2.26 is useful when the Cp of the biofuel is known. The total area inside the rate curve and the Newtonian baseline, as a fraction of total area between these two curves, the solid fraction at time t during freezing can be obtained (Evcil, et al., 2018).

2.5 Required Standards for Biodiesel

The quality of physical and chemical properties of the biodiesel is controlled by incorporating them into adequate standard requirements. Changes in engines, emission standards, and reassessment of raw materials used to produce biodiesel, etc. Due to biodiesel standards are constantly being updated. The biodiesel generated must fulfill the global standard requirements for biodiesel. The requirements provide producers with an opportunity to determine how the fuel will impact their products ' efficiency and lifetime. These specifications include the European Union standards and American Standards for Testing and Materials Association, and some other standards in the world such as ON in Austria DIN 51606 in Germany, CSN in Czech Republic and others,. Table 2.1 shows some standards of biodiesel used in the worldwide.

Table 2.1: Biodiesel quality standards (Brabas, 2011)

Standards	Place	Caption
EN 14213	EU	Heating fuels- FAME-Requirements and test methods
EN 14214	EU	EN 14214 Automotive fuels-Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods
ASTM D6751	U.S	ASTM D6751 – 11astandard specification for Biodiesel Fuel Blend Stock (B100) For Middle Distillate Fuels
	Australia	Fuel standard (Biodiesel) Determination 2003
ANP42	Brazil	Brazilian Biodiesel Standard
IS15607	India	Bio-diesel (B100) blend stock for diesel fuel Specification
JASO M360	Japan	Automotive fuel – Fatty acid methyl ester (FAME) as blend stock
SANS 1925	South Africa	Automotive biodiesel fuel

CHAPTER 3

MATERIALS AND METHODS

3.1 Material and Method

In this chapter the experiment techniques and set-ups were discussed in detail. Strict adherence to the standards was followed. These standards include kinematic viscosity ASTM D 445 (Appendix 1), density ASTM D 941-88 (Appendix 2), cold flow properties and D2500 – 09 (Appendix 3) and ASTM D 97- 05 (Appendix 4). The techniques of blend preparing were described initially. This is followed by setting up the fundamental properties experiments. The setup of the cooling curve was described and pictures of all materials used in the method are given.

3.2 Biodiesel Blends

In this study, we did the experiments with three types of biodiesel produced from waste and used cooking oil were conducted to measure their properties. The three different biodiesels are;

- BD1 (8 months old)
- BD2 (0 months old)
- BD3 (30 months old)

Three types of biodiesels were blended to each other at certain percentages and 12 different blends were obtained. The blends with their mixing percentages were shown in Table 3.1.

Table 3.1: Biodiesel types in 12 different blends with different percentages

BD1 - BD2	BD1 - BD3	BD2 - BD3
100% BD1 - 0%BD2	100%BD1 - 0% BD3	100% BD2 - 0% BD3
75% BD1 - 25%BD2	75% BD1 - 25% BD3	75% BD2 - 25% BD3
50% BD1 - 50%BD2	50% BD1 - 50% BD3	50% BD2 - 50% BD3
25% BD1 - 75%BD2	25% BD1 - 75% BD3	25% BD2 - 75% BD3
0% BD1 - 100% BD2	0% BD1 - 100% BD3	0% BD2 - 100% BD3

3.2.1 Procedure of preparation of biodiesel blend sample

As previously noted, 12 blends of biodiesel sample of three different types of biodiesel were prepared, as following steps;

Step 1

Preparing the bottles (750 ml), for storage the biodiesel sample blends. Be sure the bottles are dry and clean.

Step 2

Start with two types of biodiesel, measure the volume required by appropriate percentage for each type using the measuring cylinder (Figure3.1).

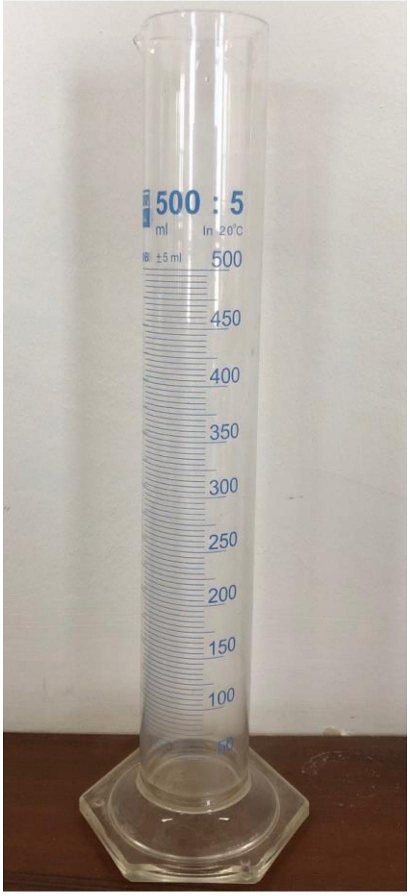


Figure 3.1: Measuring cylinder

Step 3

Blend the two types of biodiesel at certain percentage measured in step.

Step 4

Fill the bottles with these blends as shown in Figure 3.2.

Figure 3.2: Biodiesel samples blend ready for experiments

Step 5

Repeat and continue the process, from step 2 with other two types of biodiesel.

Step 6

Blends of biodiesel are tabulated in Table 3.1 and they are ready for experiments.

3.2.2 Apparatus used for preparation of biodiesel blend sample

The following instruments and equipmentms were used in the preparation of the biodiesel sample;

- Measuring cylinder, 500 ml
- Funnel
- Beaker
- Storage Bottles, 750 ml
- Calculator

3.3 Kinematic Viscosity

The Ubbelohde viscometer Figure 3.3 is a tool using a capillary technique to measure kinematic viscosity and is recommended for high viscosity cellulose polymer solutions application. This sort of viscometer has the benefit that obtained values are independent of the total size.The instrument was created by Leo Ubelohade, a German chemist (1877-1964) (Viswanath, 2007).

Figure 3.3: Ubbelohde Viscometer

The viscometer of Ubbelohde, as shown in Figure 3.3, is intimately linked to the Ostwald viscometer. Both are U-shaped glassware parts with a measuring sphere and a capillary on one hand and a reservoir on the other hand.

A liquid is inserted into the reservoir and subsequently sucked through the capillary and measuring sphere. The time that it requires for the liquid to traverse two calibrated points is the measure of viscosity after the liquid is allowed to pass again through the measuring sphere. The Ubbelohde viscometer comprises a third arm extending from the tip of the capillary and opening into the atmosphere. In this manner the pressure head there is no longer depends on the total volume of liquid but only depends on a fixed height. Ubbelohde viscometer was selected because of its broad range of accuracy. It can be measured transparently and at high temperatures.

Two viscometers of type I and Ic were selected in this work to measure kinematic viscosity according to their kinematic viscosity spectrum. The manufacturer calibrated these viscometers.

The constant of the ubbelohde viscometer, K, (mm^2/s)/s was determined by the manufacturer's and giving in Table 3.2.

Table 3.2: Ubbelohde viscometer technical specifications

Capillary No.	**Capillary Dia. I ± 0.01[mm]**	**Constant, K (mm^2/s)/s**	**Measuring range [mm^2/s]**
I	0.58	0.009820	2 ………10
Ic	0.78	0.02944	6 ………30

For absolute measurement, the flow time between the two timing marks multiplied by the constant viscometer K gives the direct kinematic viscosity mm^2/s as shown in Equation 3.1.

$$v = K(t - y) \tag{3.1}$$

Where ν is the kinematic viscosity in (mm^2/s)

K is the calibration constant in (mm^2/s^2)

t is the measured time of flow in (s)

y is kinetic energy correction factor

As shown in Table 3.3 below, the kinetic energy correction is provided by the source in terms of fluid flow time and adjusted to each viscometer.

Table 3.3: Correction factor of kinematic energy for a range of viscometers

Flow Time (s)	**Capillary no**						
	0	**0c**	**0a**	**I**	**Ic**	**Ia**	**1**
40	B	B	B	1.03	0.45	0.15	-
50	B	B	B	3.96	0.66	0.29	0.10
60	B	B	B	2.75	0.46	0.20	0.07
70	B	B	B	2.02	0.34	0.15	0.05
80	B	B	4.78^B	1.55	0.26	0.11	0.04
90	B	B	3.78^B	1.22	0.20	0.09	0.03
100	B	7.07^B	3.06^B	0.99	0.17	0.07	0.02
110	B	5.84^B	2.53	0.82	0.14	0.06	0.02
120	B	4.91^B	2.13	0.69	0.12	0.05	0.02
130	B	4.18^B	1.81	0.59	0.10	0.04	0.01
140	B	3.61^B	1.56	0.51	0.08	0.04	0.01
150	B	3.14^B	1.36	0.44	0.07	0.03	0.01

Table 3.3: Continued

Flow	**Capillary no**						
Time (s)	**0**	**0c**	**0a**	**I**	**Ic**	**Ia**	**1**
160	B	2.76	1.20	0.39	0.06	0.03	0.01
170	B	2.45	1.06	0.34	0.06	0.02	0.01
180	B	2.18	0.94	0.30	0.05	0.02	0.01
190	B	1.96	0.85	0.28	0.05	0.02	0.01
200	10.33[B]	1.77	0.77	0.25	0.04	0.02	0.01
225	8.20	1.40	0.60	0.20	0.03	0.01	0.01
250	6.64	1.13	0.49	0.16	0.03	0.01	<0.01
275	5.47	0.93	0.40	0.13	0.02	0.01	<0.01
300	4.61	0.79	0.34	0.11	0.02	0.01	<0.01
325	3.90	0.66	0.29	0.09	0.02	0.01	
350	3.39	0.58	0.25	0.08	0.01	0.01	
375	2.95	0.50	0.22	0.07	0.01	0.01	
400	2.59	0.44	0.19	0.06	0.01	<0.01	
425	2.30	0.66	0.29	0.09	0.01	<0.01	
450	2.05	0.58	0.25	0.08	0.01	<0.01	
475	1.84	0.50	0.22	0.07	0.01		
500	1.66	0.44	0.19	0.06	0.01		
550	1.37	0.23	0.1	0.03	0.01		
600	1.15	0.20	0.09	0.03	0.01		

Table 3.3: Continued

Flow Time (s)	0	0c	0a	I	Ic	Ia	1
650	0.98	0.17	0.07	0.03	<0.01		**650**
800	0.65	0.11	0.05				
850	0.51	0.10	0.04				
900	0.46	0.09	0.04				
950	0.42	0.08	0.03				
1000	3.39	0.07	0.03				

[A] The correction seconds stated are related to the respective theoretical constant

[B] For precision measurement, these flow times should not be applied.

3.3.1 Procedure of measuring the kinematic viscosity using ubbelohde viscometer

As previously noted, Ubbelohde viscometer was used for measuring the kinematic viscosity. Procedure of measuring the kinematic viscosity is as following;

Step 1

Use the washing products to clean the viscometer. The content of cleaning material must have the correct ratios (15% muriatic acid, 15% sulfur peroxide, 70% distilled oil). Then add acetone to complete the method of washing. The capillary tube must be drained to begin the experiment method.

Step 2

Fill in the viscometer with a fix amount of biodiesel. The biodiesel is should place between the two lines on the tube so that the amount of liquid loaded does not block the air tube during use.

Step 3

Insert the viscometer in a liquid bath at a desired temperature. Sample fluid will takes about 20 minutes to reach the same temperature in the bath.

Step 4

Sucking up the fluid inside the capillary viscometer with suction syringe that is shown in Figure 3.4, until liquid fill up the pre-run sphere.

Figure 3.4: Suction instrument

Step 5

Then let the liquid flow and record the flow time in seconds between to calibrated marks. Be sure to use the same edges of the two marks, upper and lower. The time required for the liquid to pass through the two marks is a flow time for calculating the kinematic viscosity.

Step 6

Use equation 3.1 to calculate the kinematic viscosity of the biodiesel sample. In order to get precise results, repeat the process 3 times for the same temperature. Calculate the average of the measurements and apply the same procedure to measure the kinematic viscosity at a different temperature value.

3.3.2 Kinematic viscosity setup for cooling

Figure 3.5 shows the experimental setup for measuring the kinematic viscosity at low temperature. It contains the following components:

- Cooling bath
- Compressor
- Radiator
- Thermostat with thermocouple
- Viscometer holder
- Capillary viscometer
- Time recorder
- Coil
- Alcohol

Figure 3.5: The experimental setup for measuring the viscosity of a biodiesel sample in the temperature range 20℃ - 0℃

Same procedure was applied for measuring kinematic viscosity from 20℃ up to freezing point until the biodiesel gets gel formation that there is no more for fluid to flow. Alcohol (ethanol) was utilized as liquid for cooling bath because alcohol did not freeze up to -114 °C, but water freezes to 0 °C. The 97% was the purity of alcohol, that was took up from Northern Cyprus in a local alcohol manufactory. Thick Styrofoam layer was used to isolate the cooling bath to keep the bath temperature constant as match as possible. Thermostat is used to control the bath temperature using a compressor by automatically shutting down and starting up. To cool down the liquid inside the cooling bath a coil connected between the compressor and the bath, and a radiator used to cool down the compressor.

3.3.3 Kinematic viscosity setup for heating

Figure 3.6 shows the experimental setup for measuring the kinematic viscosity from 20℃ to 80℃.

It contains the following components:

- Thermocouple
- Capillary viscometer
- Viscometer holder
- Electromagnetic hot plate
- Water
- Heat resistant beaker thermometer
- Time recorder
- Biodiesel sample

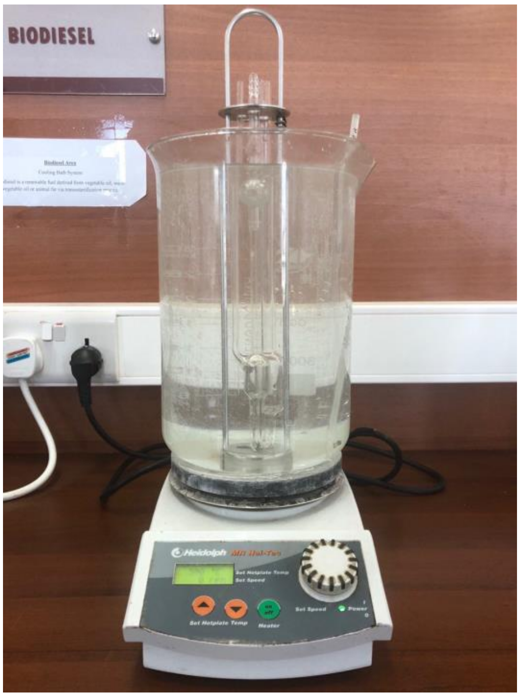


Figure 3.6: The experimental setup for measuring the viscosity of a biodiesel sample in the temperature range 20℃ - 80℃

Same procedure was applied for measuring kinematic viscosity from 20℃ to 80℃ and increase the temperature by 10℃ in steps. Water was used as a heating bath liquid .The water inside the baker is heated by using electronic hot plate to increase the biodiesel sample temperature. The temperature was controlled by a digital standard thermometer.

3.4 Density

Pycnometer is a device which is used for measuring the density of liquid (biodiesel sample). Usually a pycnometer is produced of glass, with a close-fitting ground glass stopper with a capillary tube through it, so the device will allow the surplus fluid and air bubbles to escape from it. This device can accurately measure the density of the fluid with reference to a suitable working fluid, such as water, using an electronic scale. The density of the biodiesel sample was measured for heating and cooling the biodiesel sample. For measuring the biodiesel sample mass, we subtract the empty pycnometer mass from the filled pycnometer mass of biodiesel sample. Dividing the mass of the biodiesel sample by the volume of the pycnometer, we get the density of the biodiesel sample in kg/m^3 as given in Equation 3.2.

$$\rho = \frac{(m_{\mathrm{full}} - m_{\mathrm{empty}})}{V} \qquad (3.2)$$

where ρ is the density of the biodiesel sample in (kg/ m^3)

m_{empty} is the mass of the empty pycnometer in (kg)

m_{full} is the mass of the full pycnometer in (kg)

V is the volume of the pycnometer in (m^3)

3.4.1 Procedure of measuring the density using pycnometer

As previously noted, pycnometer was used for measuring the density. Procedure of measuring the density occurs in following steps;

Step 1

Use the washing products to clean the pycnometer. Cleaning content must have the correct ratios. (15% muriatic acid, 15% sulfur peroxide, 70% distilled oil). Then add acetone to complete the method of washing. The pycnometer must be drained to begin the experiment method.

Step 2

Measure the filled pycnometer mass of biodiesel sample. But before that, we must measure the empty pycnometer mass, using an electronic balance scale as shown in Figure 3.7. We will use Equation 3.2, for measuring the density.

Figure 3.7: Measuring mass of empty pycnometer

Step 3

The pycnometer should be fully filled with biodiesel. As shown in Figure 3.8, air gaps and excess biodiesel will leak from the pycnometer.

Figure 3.8: The pycnometer over flow gap

Step 4

Locate the pycnometer in cooling bath and heating bath, and wait for the needed temperature. Wait for at least 15 minutes at the necessary temperature until the temperature in the beaker or cooling bath becomes homogeneous.

Step 5

Using an electronic balance as shown in Figure 3.9, to measure the mass of the pycnometer with biodiesel sample at desired temperature.

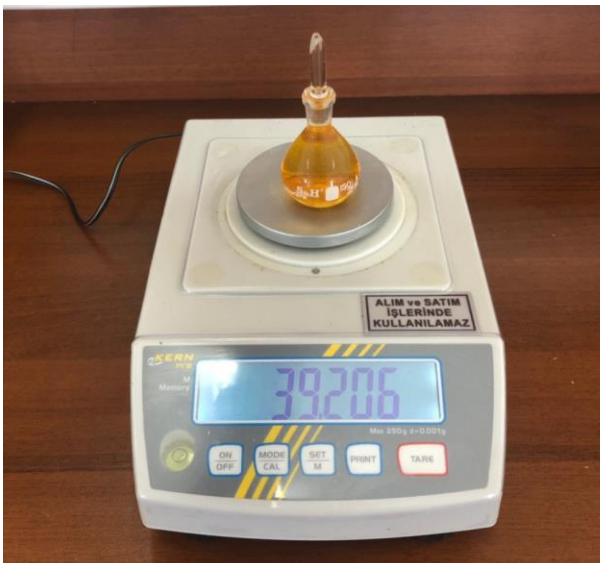


Figure 3.9: Electronic balance for measuring the pycnometr mass

Step 6

Using Equation 3.2 to calculate the density of biodiesel at prefer temperature. Repeat these steps to calculate the average density value.

3.4.2 Density setup for cooling

Figure 3.10 shows the experimental setup for measuring the density for low temperatures, it contains the components:

- Cooling bath
- Compressor

- Radiator
- Thermostat with Thermocouple
- Pycnometer
- Coil
- Alcohol

Figure 3.10: Experimental setup used for measuring the density of biodiesel sample in the temperature range 20℃ - 0℃

Same procedure was applied for measuring density from 20℃ to the temperature by specific steps until the biodiesel sample gets gel formation. The same components as we used for measuring the kinematic viscosity. Utilize an electronic balance scale for measuring the mass of pycnometer, when it was fully filled and also empty of biodiesel.

3.4.3 Density setup for heating

Figure 3.11 shows the experimental setup for measuring the density for high temperatures, it contains the following components:

- Thermometer
- Pycnometer
- Electromagnetic hot plate
- Water
- Heat resistant beaker thermometer
- Biodiesel sample
- Electronic Balance Scale

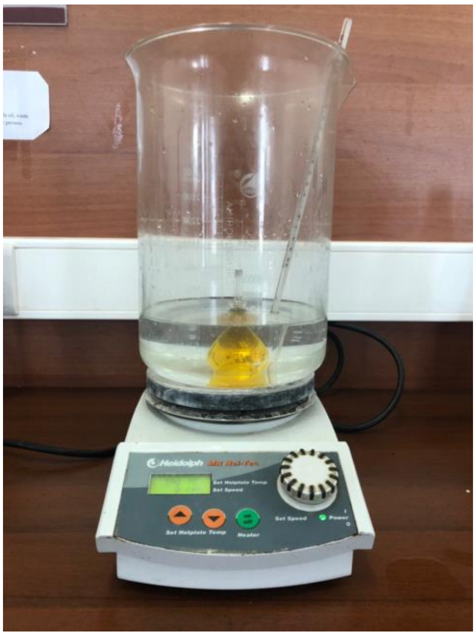


Figure 3.11: Experimental setup used for measuring the biodiesel sample in the temperature range 20℃ – 80℃

Same procedures were applied for measuring density from 20℃ to 80℃ and increase the temperature in step of 10℃ . Water was used as a heating bath liquid, was set to the baker using electronic hot plate to increase the temperature of the biodiesel sample. The temperature was controlled by a digital standard thermometer. Utilize an electronic balance scale for measuring the mass of pycnometer, when it was fully filled and also empty of biodiesel.

3.5 Cold Flow Properties

Cloud Point and Pour Point are the cold flow properties and can be measured with a special glass jar test in the cooling bath. The data logger with four thermocouples was utilized. Both the ASTM 2500 and the ASTM D 97-05 have been pursued for these properties. It is possible to do both experiments concurrently.

3.5.1 Procedure of measuring the cold flow properties

As previously noted, a special glass test jar and a data logger with four thermocouples were used for measuring the cold flow properties. Procedure of measuring the cloud point and pour point was as follows;

Step 1

Measuring a 45 ml of the biodiesel sample using a measuring cylinder as shown in Figure 3.1, and then claim it in a special glass test jar for measuring the cloud point and pour point. The thermocouples must be arranged as shown in Figure 3.12.

Figure 3.12: Glass jar test with thermocouples

In this setup four thermocouples were placed at the bottom, middle, and upper layer of the glass test jar to measure the cloud point, cooling curve and the pour point respectively. Cold filter plugging point can be determined using the cooling curve. Fourth thermocouple was placed in the alcohol bath to measure the temperature of the alcohol bath which is the same function with the compressor systems thermostat.

Step 2

When the temperature inside the bath becomes -16℃, then the special glass jar is put in the jacket cylinder, and the level of alcohol must be noted before place the glass jar.

Step 3

We have to check the biodiesel sample inside the glass jar every 2 or 3 minutes (every 1 ℃ temperature drop) continuously.

Step 4

The cloud point will be reached when we see small grains like crystals at the bottom of the glass jar test. We record the temperature according to the thermocouple shown on the computer.

Step 6

The pour point will be reached, when the sample gets a gel formation and is no longer to flow as shown on Figure 3.13. We record the temperature according to the t thermocouple shown on the computer.

Figure 3.13: The formation of biodiesel sample when reaching the Pour Point

Step 7

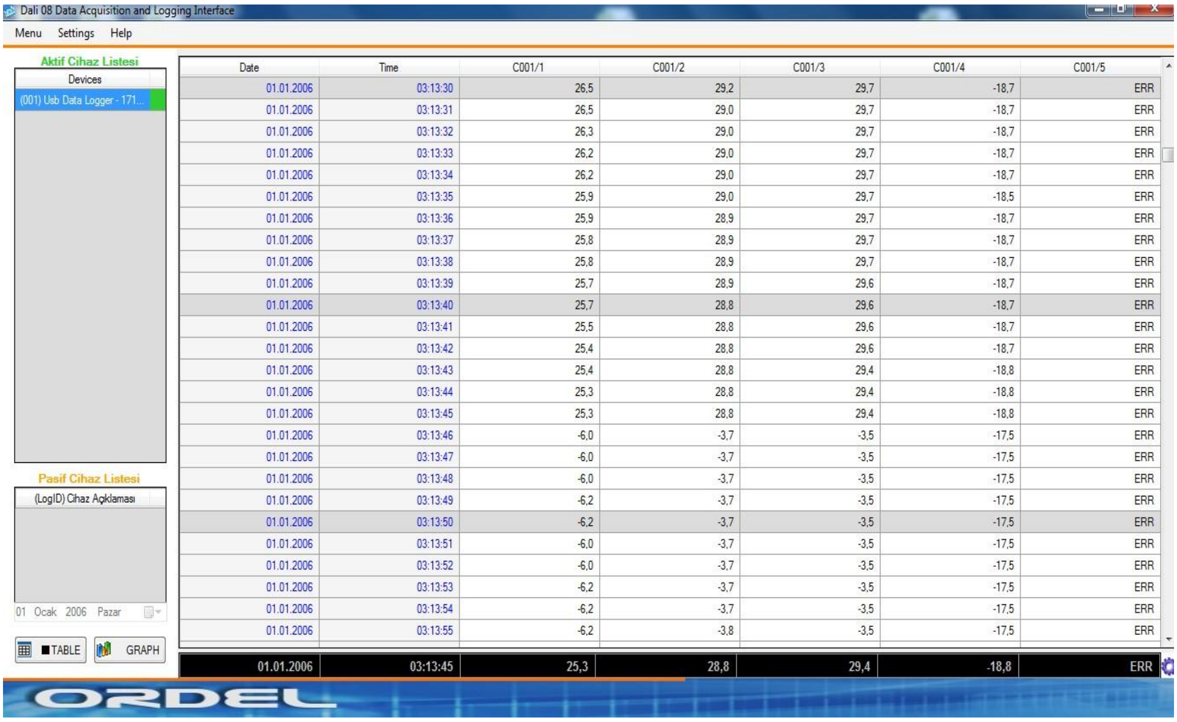
The data acquired digitally from the data logger will constant and compare with the outcomes results of the cooling curve.

3.5.2 The cold flow properties setup

Figure 3.15 shows the experimental setup for measuring the cold flow properties, it contains the following particular components:

- Cooling bath
- Compressor
- Radiator
- Thermostat with thermocouple
- Glass test jar
- Four thermocouples
- Coil
- Alcohol

The same procedure was applied for measuring the cold flow properties. Alcohol was used as liquid for cooling bath. For isolating the cooling bath, a thick Styrofoam layer was used to remain the bath temperature. Thermostat was used to control the bath temperature, and a compressor to cool the bath by a coil connected to it. A special glass test jar applied with four thermocouples as shown in Figure 3.12. Equipment used for saving data from thermocouples called Data logger, and activated over the process, and using an unique software program from the computer to see the data as shown in Figure 3.14, and the results were measured every 30 seconds. Third column represents the cloud point, the fourth column shows the results of pour point, and the fifth column represent cooling curve temperature, and sixth column shows the cooling bath temperature.



Date	Time	C001/1	C001/2	C001/3	C001/4	C001/5
01.01.2006	03:13:30	26,5	29,2	29,7	-18,7	ERR
01.01.2006	03:13:31	26,5	29,0	29,7	-18,7	ERR
01.01.2006	03:13:32	26,3	29,0	29,7	-18,7	ERR
01.01.2006	03:13:33	26,2	29,0	29,7	-18,7	ERR
01.01.2006	03:13:34	26,2	29,0	29,7	-18,7	ERR
01.01.2006	03:13:35	25,9	29,0	29,7	-18,5	ERR
01.01.2006	03:13:36	25,9	28,9	29,7	-18,7	ERR
01.01.2006	03:13:37	25,8	28,9	29,7	-18,7	ERR
01.01.2006	03:13:38	25,8	28,9	29,7	-18,7	ERR
01.01.2006	03:13:39	25,7	28,9	29,6	-18,7	ERR
01.01.2006	03:13:40	25,7	28,8	29,6	-18,7	ERR
01.01.2006	03:13:41	25,5	28,8	29,6	-18,7	ERR
01.01.2006	03:13:42	25,4	28,8	29,6	-18,7	ERR
01.01.2006	03:13:43	25,4	28,8	29,4	-18,8	ERR
01.01.2006	03:13:44	25,3	28,8	29,4	-18,8	ERR
01.01.2006	03:13:45	25,3	28,8	29,4	-18,8	ERR
01.01.2006	03:13:46	-6,0	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:47	-6,0	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:48	-6,0	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:49	-6,2	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:50	-6,2	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:51	-6,0	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:52	-6,0	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:53	-6,2	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:54	-6,2	-3,7	-3,5	-17,5	ERR
01.01.2006	03:13:55	-6,2	-3,8	-3,5	-17,5	ERR
01.01.2006	03:13:45	25,3	28,8	29,4	-18,8	ERR

Figure 3.14: Software program for data logger

Figure 3.15: Complete cooling curve analysis setup

3.6 Cooling Curve

Cooling curve is used to analyse the liquid sample behaviour with respect to falls in temperature. Liquid and solid fractions are determined; also from this experiment the cold flow properties are determined.

1. ***Cooling bath:*** It's made of dense glass that's a poor heat conductor. Glass forums are combined as a sealant with silicone to avoid loss the bath of alcohol.
2. ***Compressor:*** Used to cool the alcohol bath by a connect coil between them.
3. ***Radiator:*** We utilized to cool down the compressor.
4. ***Thermostat with Thermocouples:*** Use to regulate the temperature of the cooling bath. It is linked in combination with the compressor to a thermostat.
5. ***Glass test jar:*** Is as special glass jar test use for measuring the cold flow properties, and also for prepare the cooling curve, according to the standards.
6. ***Four thermocouples:*** They are used to collect sample temperature and the cooling bath of alcohol. Three thermocouples are used to measure the sample temperature, and the fourth measures the temperature of the cooling bath.

7. ***Coil:*** This is the device that takes the cooling gas for heat exchange to the compressor. It requires the heat to the surrounding area from the alcohol bath.
8. ***Styrofoam layer:*** This is a very bad conductor of heat. We covered the entire bath with this sty foam, just a small area to show the process inside.
9. ***Alcohol inside the bath:*** The main reason for using the alcohol, because it freezes at -114°C a very low temperature.

3.6.1 Procedure of operating the cooling curve

As previously noted, cooling curve used to analyse the biodiesel sample when it falls in temperature. Procedure of running the cooling curve was as following steps;

Step 1

Set the thermostat at -16°C and let the cooling process start, and then wait until the temperature inside the bath reaches the required temperature.

Step 2

Measuring 45ml of the biodiesel sample by cylinder measurement Figure 3.1, and then put it into the glass test jar.

Step 3

Set up the thermocouples as shown in Figure 3.12 where the second thermocouple represent the cooling curve. This is done in accordance with the standards for performing a Newtonian Thermal Analysis and a Fourier Thermal Analysis.

Step 4

Put the glass test jar inside a baker of water, then heat the water with the biodiesel sample until the temperature of the sample reaches 70°C.

Step 5

Place the heated sample inside the jacket cylinder in the cooling bath -16°C and wait about 4 hours. Be sure that thermocouples are at the same level after placed in the cooling bath.

Step 6

While monitoring the cooling process, when the temperature of the heated sample reaches 65°C, after placing it to the cooling to the cooling bath, we must save the result data every 10-15 minutes, in order to remove any fault which can occur during the process.

Step 7

Use Matlab or Microsoft Excel to evaluate the collected data.

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Kinematic Viscosity

In this experimental study, I and Ic were used as a capillary viscometers which were calibrated by manufacturers. An accuracy and repeatability test was undertaken to verify the precision of the outcome values.

Pure water was utilized as the main standard for kinematic viscosity. Kinematic viscosity is measured as 0.80908 mm^2/s for pure water at 30˚C as in literature (Streeter et al., 1998). With the same experimental conditions, at 30˚C pure water was used for determination of kinematic viscosity and the value was calculated as 0.803 mm^2/s. The percent error was determined to be below than 1%, which means capillary viscometers were great for calibration.

4.1.1 Effect of temperature on kinematic viscosity of biodiesel blends

This chapter focuses on determining the impact of temperature on the kinematic viscosity of the various biodiesel blends. Several measurements were performed to confirm that the kinematic viscosity values were accurate. To show the findings, a number of plots have been prepared to guarantee the necessary precision. In the figures, the kinematic viscosities have been plotted versus temperature.

The experimental data on the kinematic viscosity in mm^2/s, for biodiesel blends were measured at different temperatures from 30℃ to 80℃ and from 20℃ and decrease until the biodiesel blend gets gel formation.

The biodiesel blends vary in the range of 13.55192 mm^2/s to 2.1486 mm^2/s, in the temperature range of 80℃ until it freezes.

The kinematic viscosities of twelve biodiesel samples have been determined and reported in Table 4.1. The relationships are given in Figures 4.1 to 4.3, respectively. For known temperatures, any measurement of viscosity can be simply obtained from Table 4.1 to Table 4.3.

The measurements show that when all samples are cooled down, they have the same empirical action, getting them more viscous, but all samples are smooth at temperatures reaching crystallization due to unique chemical structure. From the Figures 4.1 to 4.3 it is seen that when temperature decrease, the viscosity rapidly increases. For each biodiesel the viscosity at the same temperature is distinct from another form of biodiesel, depending on its blended percentages and chemical structure for example the viscosity of 75% BD1+25% BD2 at 20 °C is 6.6621826 mm^2/s, while the viscosity of 25% BD1+75% BD2 at the same temperature is 6.991363 mm^2/s. Viscosity of BD1-BD2 and BD2-BD3 could not be determined less than 0 °C and the viscosity of BD1-BD3 could not be determined less than 6 °C, because they are approaching to become gel and no longer to flow. Thus by mixing any two portions of BD1 and BD2, and BD3, the lowest temperature was between 6°C and 0°C for determining the biodiesel properties.

Table 4.1: Kinematic viscosity measurements for BD1-BD2 blend in mm^2/s

Temperature [℃]	**Kinematic Viscosity** $[\mathbf{mm^2/s}]$				
	100%BD1 - 0%BD2	**75%BD1 - 25%BD2**	**50%BD1 - 50%BD2**	**25%BD1 - 75%BD2**	**0%BD1 - 100%BD2**
0					13.55192
2			12.472452	12.5804	12.69816
4			11.265412	11.75608	11.94253
6	10.828326	10.887501	10.961199	10.92195	11.02008
8	10.066125	10.211264	10.568666	10.2252	9.999492
10	9.4349312	9.4670208	9.8912512	9.616478	9.518345
15	7.9346688	7.9161216	9.4987179	8.213171	8.252425
20	6.704508	6.6621826	8.1641045	6.917797	6.991363
30	5.810003	5.2794611	7.3689301	5.379003	5.649348
40	4.4643684	4.2513726	6.704508	4.40267	4.534385
50	3.5012228	3.4758577	5.810003	3.622008	3.697426
60	2.9961475	2.9136922	4.4643684	2.98208	3.101843
70	2.574378	2.5224634	3.5012228	2.578045	2.631073
80	2.21904	2.1876014	2.9961475	2.230122	2.284967

Table 4.2: Kinematic viscosity measurements for BD1-BD3 blend in mm^2/s

Temperature [℃]	**Kinematic Viscosity** $[\mathbf{mm^2/s}]$				
	100%BD1 - 0%BD3	**75%BD1 - 25%BD3**	**50%BD1 - 50%BD3**	**25%BD1 - 75%BD3**	**0%BD1 - 100%BD3**
6	10.828326	10.392026	10.176132	10.36259	10.43179
8	10.066125	9.7244245	9.2963787	9.704798	9.783304
10	9.4349312	9.1650645	8.3014912	9.037491	9.096371
15	7.9346688	7.8402645	7.3983701	7.869705	7.882957
20	6.704508	6.998714	6.6514798	6.775996	6.857011
30	5.810003	5.5003784	5.5785456	5.502883	5.465154
40	4.4643684	4.4556286	4.5007024	4.440948	4.403386
50	3.5012228	3.651076	3.6816162	3.589063	3.611943
60	2.9961475	3.0385044	3.0177844	3.004069	3.010223
70	2.574378	2.598372	2.6073082	2.578928	2.55973
80	2.21904	2.272348	2.2391564	2.220744	2.225261

Table 4.3: Kinematic viscosity measurements for BD1-BD2 blend in mm^2/s

Temperature [℃]	**Kinematic Viscosity $[\mathrm{mm}^2/s]$**				
	100%BD2 - 0%BD3	**75%BD2 - 25%BD3**	**50%BD2 - 50%BD3**	**25%(BD2) - 75%BD3**	**0%BD2 - 100%BD3**
0	13.551919				
2	12.698159	13.422			
4	11.942532	12.5	12.598	11.835	
6	11.020079	11.479	11.577	10.912	10.43179
8	9.9994923	10.998	11.096	9.892	9.783304
10	9.5183445	9.732	9.830	9.411	9.096371
15	8.2524245	8.2524245	8.569	8.145	7.882957
20	6.9913627	7.1291	7.2273	6.8836	6.857011
30	5.6493478	5.548	5.6102	5.5348	5.465154
40	4.534385	4.5034	4.4641	4.1432	4.403386
50	3.6974264	3.5999	3.5705	3.5279	3.611943
60	3.1018434	2.9318	2.9678	2.9384	3.010223
70	2.6310726	2.5582	2.496	2.5124	2.55973
80	2.2849667	2.2205	2.1878	2.1486	2.225261

In Table 4.1 – Table 4.2 the increment for determining the kinematic viscosity for heating 20°C-80°C was in step of 10°C and for cooling was in step of 5°C but after that the step-wise was decreased to 1°C or 2°C before getting freezing point in order to determine the maximum kinematic viscosity of the samples as shown in Figure 4.1 – Figure 4.3.

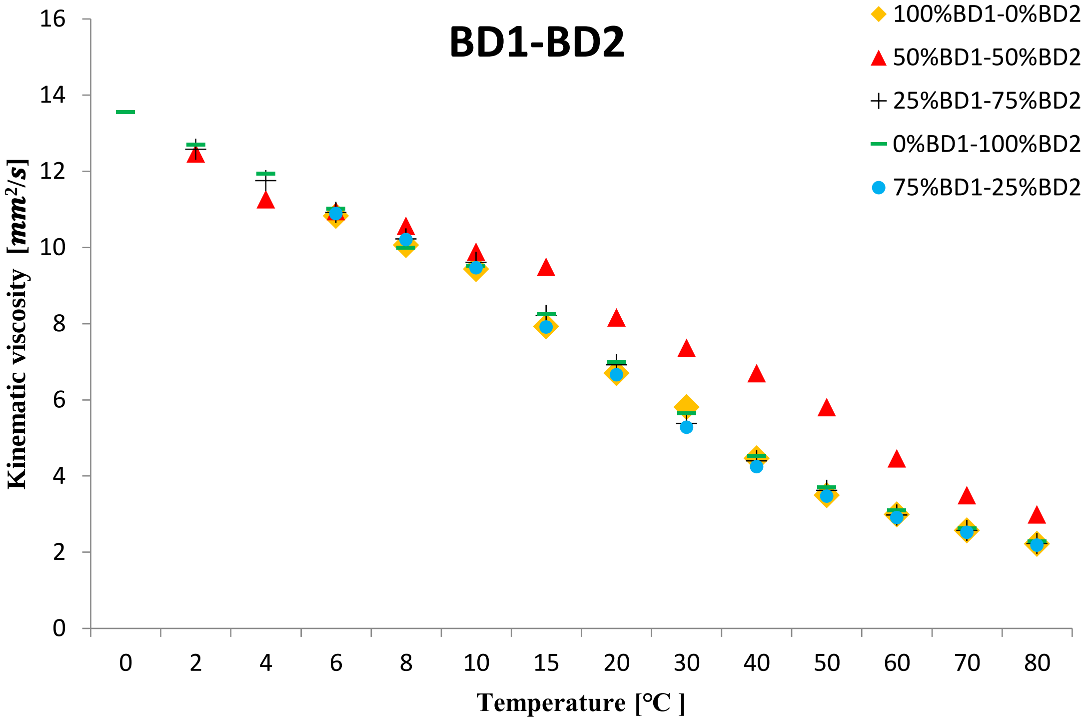


Figure 4.1: Kinematic viscosity vs temperature relationship of BD1-BD2 blend

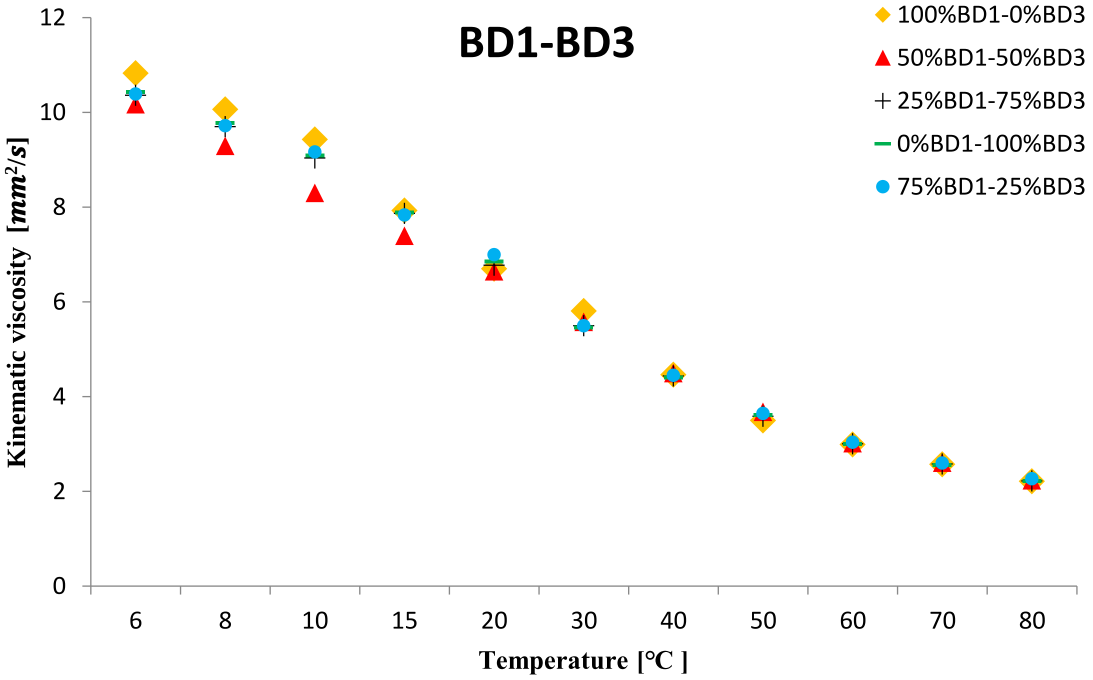


Figure 4.2: Kinematic viscosity vs temperature relationship of BD1-BD3 blend

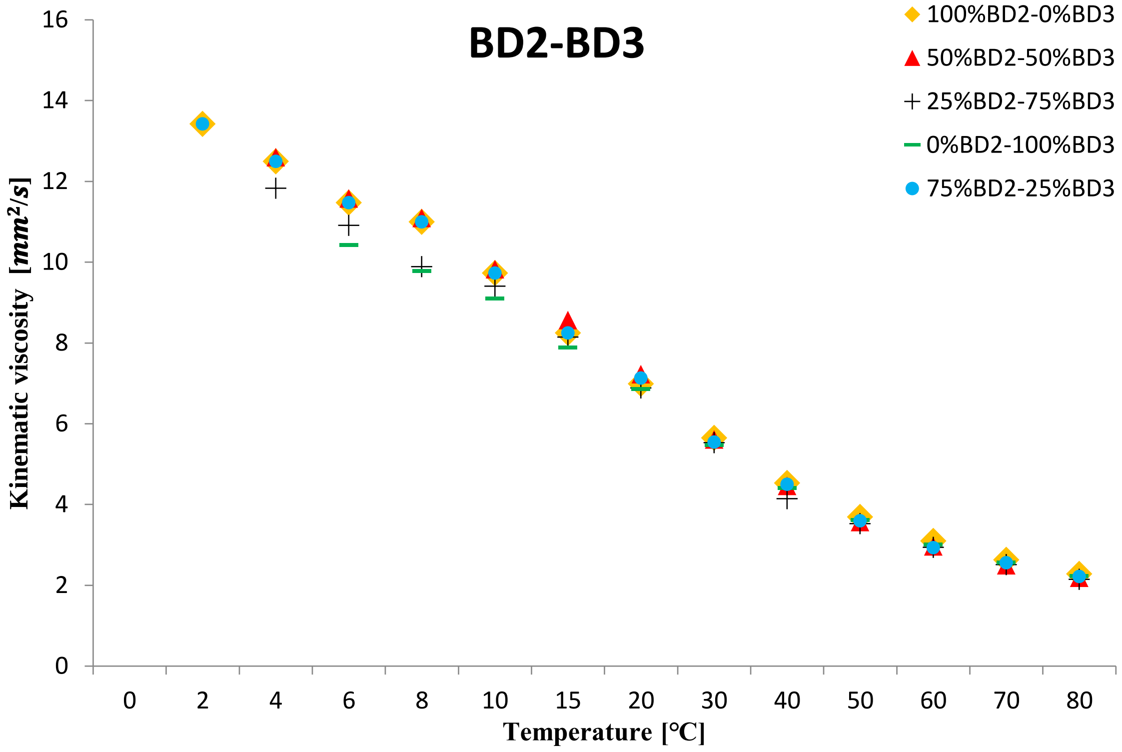


Figure 4.3: Kinematic viscosity vs temperature relationship of BD2-BD3

According to the above figures, it can be seen that the kinematic viscosity is quickly rising as the temperature decreases and this rise is distinct from one biodiesel to another. This increase in viscosity is in general agreement with all the other works that were reported in the literature reported earlier.

4.2 Density

Biodiesel is more at danger due to assault and breakdown from oxygen exposure because it is produced from animal fat or vegetable. Although chemically assessed to burn in an engine like diesel fuel, the composition of biodiesel molecules is not precisely the same as in petrochemical molecules. Their molecular structure has more regions that are weaknesses for free radicals and oxygen to strike, react and break away from each other. Biodiesel density was anticipated to improve with the creation of fresh impurities in the sample during temperature reduction. The density of the biodiesel was measured using a pycnometer with a bulb capacity of 25ml. The weighing was done by using a high precision electronic balance with a precision of ± 0.1mg. The density values of the samples were measured for temperatures between 20℃ to 80℃. The density of biodiesel blend was estimated according to the ASTM standards (Appendix 2).

We can examine the increase in the values of density of biodiesel sample with temperature, in Table 4.4 to Table 4.6, experimental density measurements for temperature ranges from 80°C to 0°C were performed.

Table 4.4: Density measurements for BD1-BD2 blend in kg/m^3

Temperature [℃]	**Density [kg/m^3]**				
	100%BD1 - 0%BD2	**75%BD1 - 25%BD2**	**50%BD1 - 50%BD2**	**25%BD1 - 75%BD2**	**0%BD1 - 100%BD2**
0					911.89
2			911.84	911.92	911.68
4			911.60	911.76	911.40
6	910.00	910.64	911.44	911.32	911.04
8	909.72	910.48	911.28	910.92	910.84
10	909.36	910.04	910.76	910.60	910.68
15	908.56	909.88	910.32	910.04	909.96
20	908.42	909.72	909.84	908.20	909.35
30	907.36	909.52	908.20	906.16	909.01
40	901.08	904.13	902.28	902.80	903.53
50	894.08	892.97	894.27	896.00	894.72
60	886.79	886.31	887.39	887.72	888.733
70	879.16	878.17	878.87	880.40	880.40
80	872.04	870.89	871.73	873.68	874.29

Table 4.5: Density measurements for BD1-BD3 blend in kg/m^3

Temperature [℃]	**Density [kg/m^3]**				
	100%BD1 - 0%BD3	**75%BD1 - 25%BD3**	**50%BD1 - 50%BD3**	**25%BD1 - 75%BD3**	**0%BD1 - 100%BD3**
0	910.00	907.52	908.00	908.79	907.80
2	909.72	906.76	907.00	908.28	907.65
4	909.36	906.58	906.82	907.80	907.36
6	908.56	906.24	906.36	907.32	906.88
8	908.42	906.04	901.13	903.40	902.20
10	907.36	905.05	893.87	900.53	896.65
15	901.08	897.97	883.04	893.87	889.85
20	894.08	890.57	875.12	886.44	882.44
30	886.79	882.93	867.19	879.28	875.56
40	879.16	875.69	860.05	872.06	867.92
50	872.04	868.05	852.37	864.72	860.35
60	910.00	907.52	908.00	908.79	907.80
70	909.72	906.76	907.00	908.28	907.65
80	909.36	906.58	906.82	907.80	907.36

Table 4.6: Density measurements for BD2-BD3 blend in kg/m^3

Temperature [°C]	**Density** $[\mathbf{kg/m^3}]$				
	100%BD2 **-** **0%BD3**	**75%BD2** **-** **25%BD3**	**50%BD2** **-** **50%BD3**	**25%BD2** **-** **75%BD3**	**0%BD2** **-** **100%BD3**
0	911.89	13.551919	13.551919	13.55192	
2	911.68	12.698159	12.698159	12.69816	
4	911.4	11.942532	11.942532	11.94253	
6	911.04	11.020079	11.020079	11.02008	907.8
8	910.84	9.9994923	9.9994923	9.999492	907.65
10	910.68	9.5183445	9.5183445	9.518345	907.36
15	909.96	8.2524245	8.2524245	8.252425	906.88
20	909.35	878.98	875.48	873.00	902.20
30	909.01	873.58	873.84	864.47	896.65
40	903.53	870.15	867.54	855.53	889.853
50	894.72	864.52	861.69	853.54	882.44
60	888.73	860.42	854.73	836.04	875.56
70	880.40	841.49	848.44	835.65	867.92
80	874.29	839.47	837.93	834.85	860.35

In Table 4.1 to Table 4.3 the increment for determining the density for cooling was 5°C, but for lowest determined temperature, the stepwise decrease was made to 1°C or 2°C to determine the maximum density of the samples, and for heating 20°C-80°C was 10°C as shown if Figure 4.4 to Figure 4.6 .

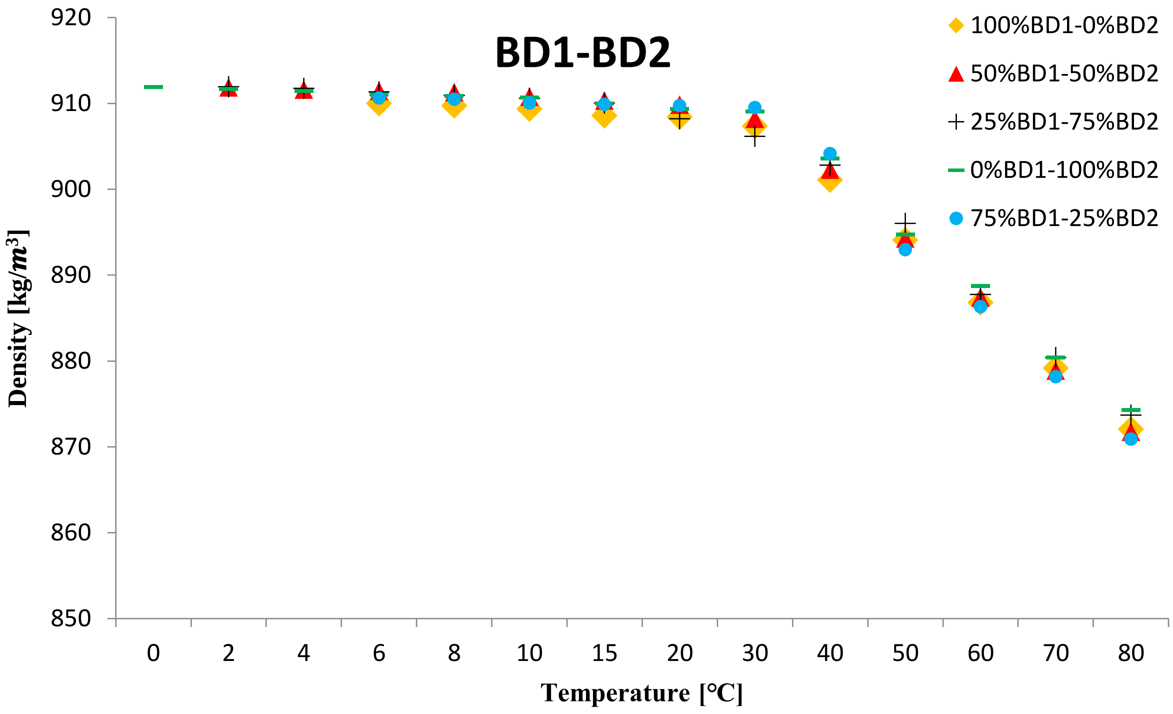


Figure 4.4: Density vs temperature relationship of BD1-BD2

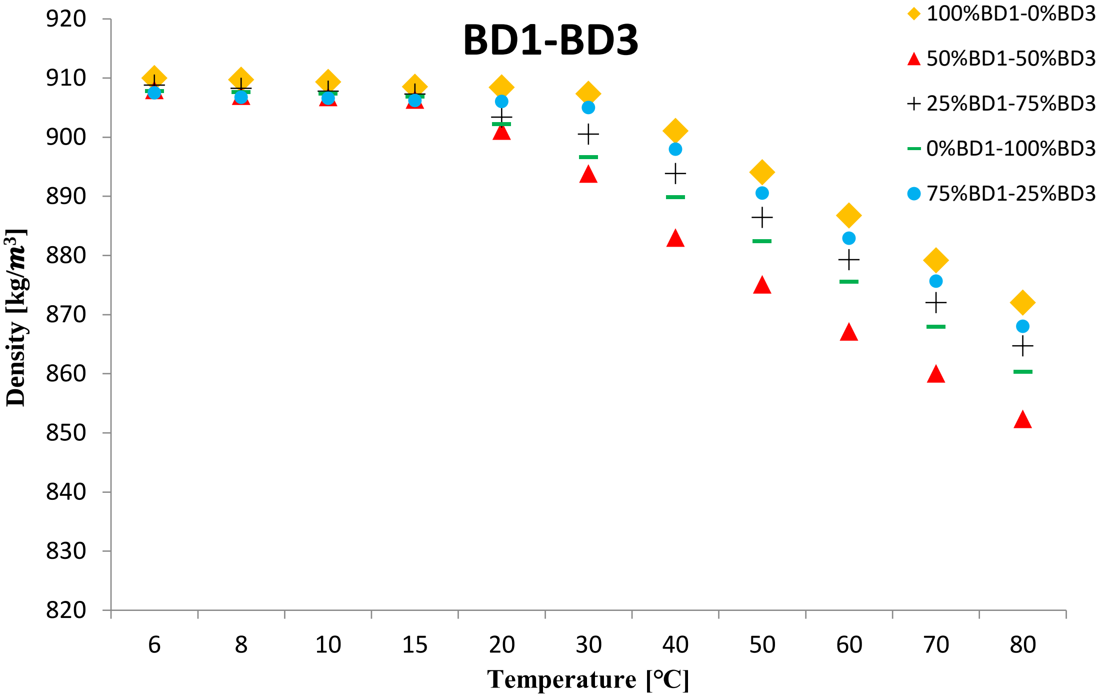


Figure 4.5: Density vs temperature relationship of BD1-BD3

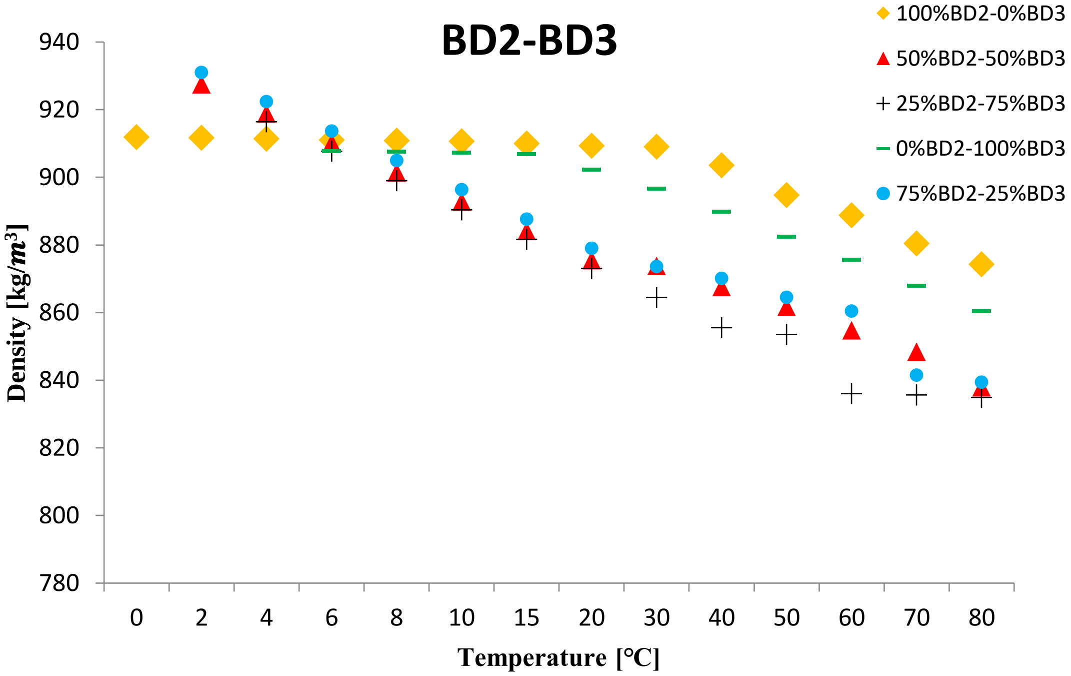


Figure 4.6: Density vs temperature relationship of BD2-BD3

The above figures show that the density is increasing rapidly as the temperature reduces and this increase is different from one biodiesel to another. In particular, this rise in density agrees with all the other works previously reported in the literature.

4.3 Cooling Curve

Computer-aided thermal analysis of the cooling curve CA-CCA provides useful knowledge about the latent heat of solidification, fraction of solid during solidification, and also the number of different phases. CA-CCA can be categorized into both the Fourier and Newtonian analysis.

In this study, the Newtonian analysis was undertaken in this work with the test jar produced from glass with the biodiesel sample size of 45ml. In addition, two thermocouples are positioned, to measure the temperature of the sample of biodiesel T_1, and the temperature of the cooling bath T_2. It must be observed which the thermocouples were calibrated. Leading up to the collection of data for CA-CCA, The bath was cooled to -16 ° C and the sample of biodiesel was heated up to 70 °C as shown in Figure 4.7 to Figure 4.12.

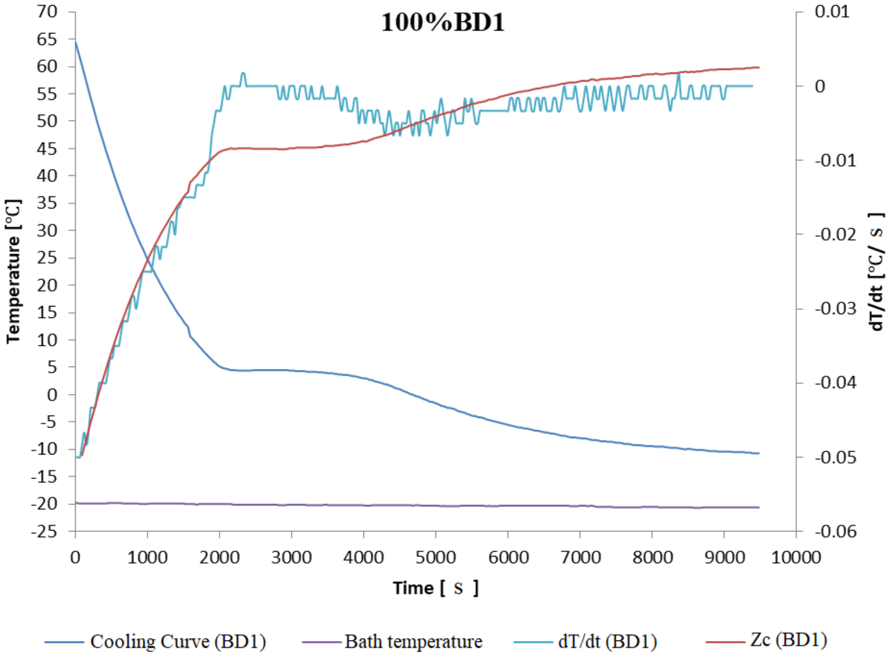


Figure 4.7: CCA for 100% BD1 biodiesel sample

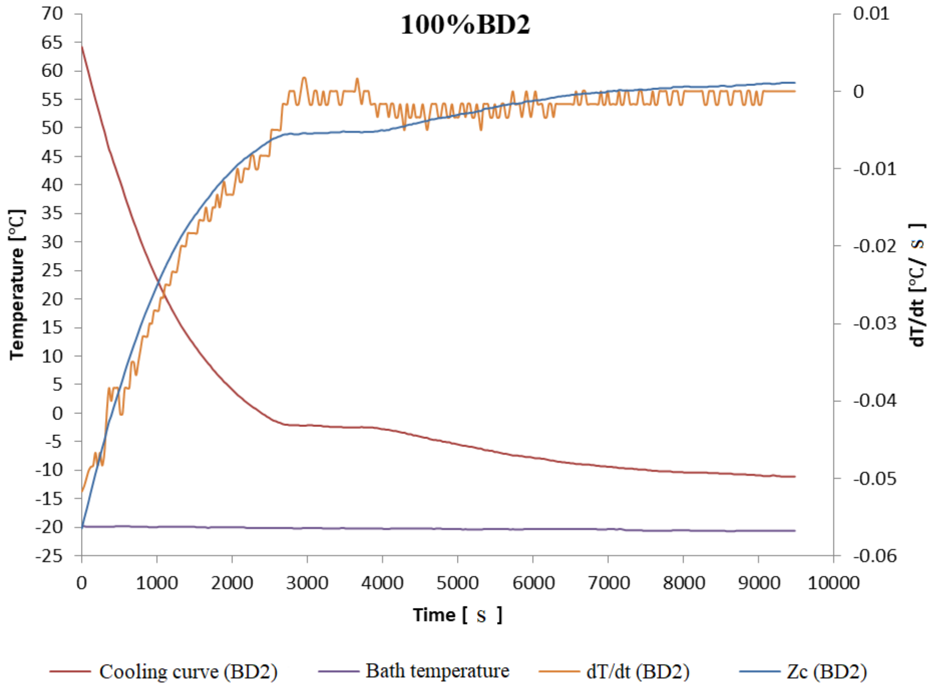


Figure 4.8: CCA for 100% BD2 biodiesel sample

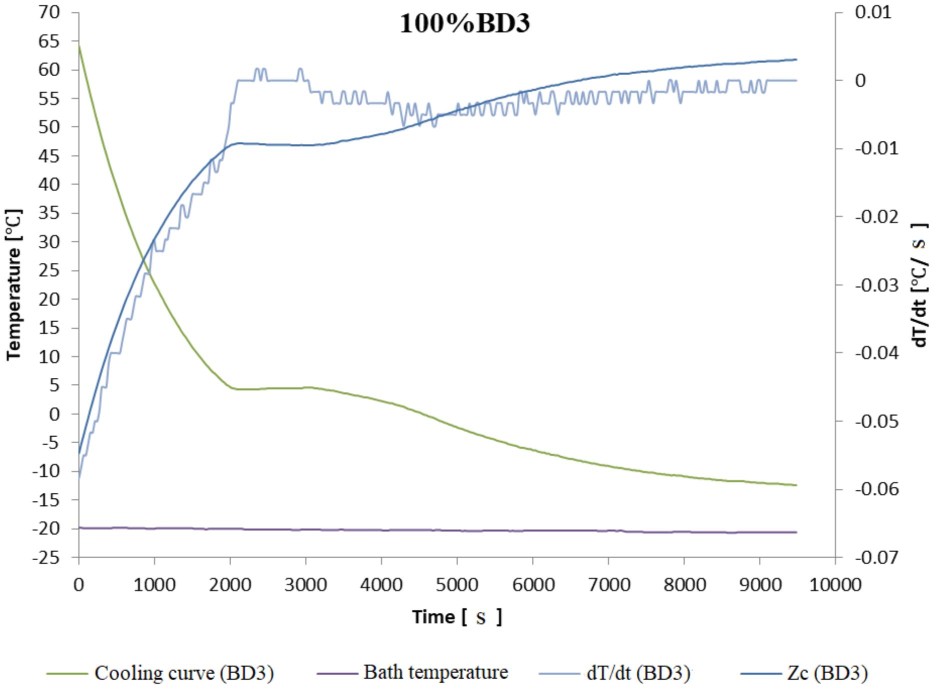


Figure 4.9: CCA for 100% BD3 biodiesel sample

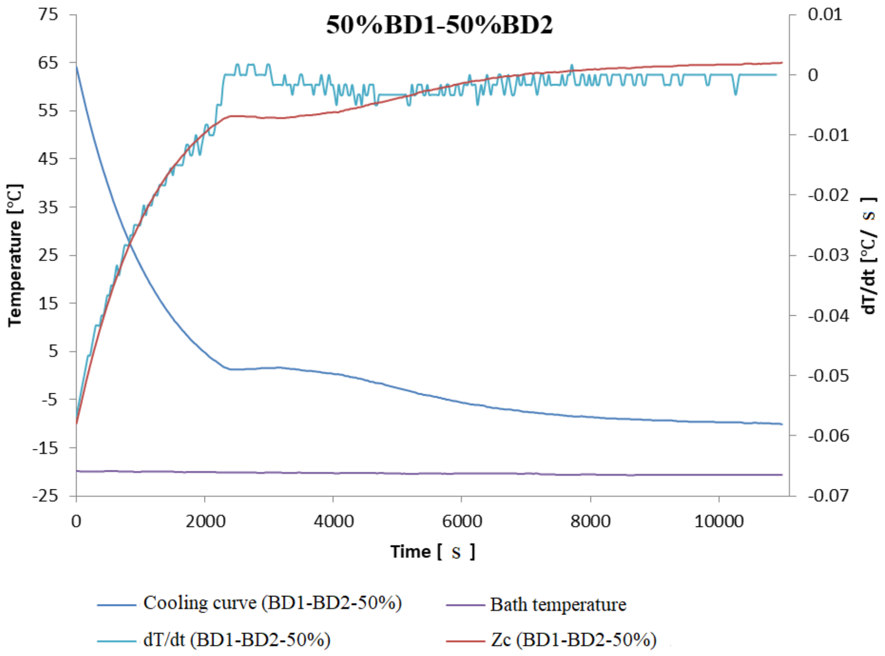


Figure 4.10: CCA for 50% BD1 – 50% BD2 biodiesel sample

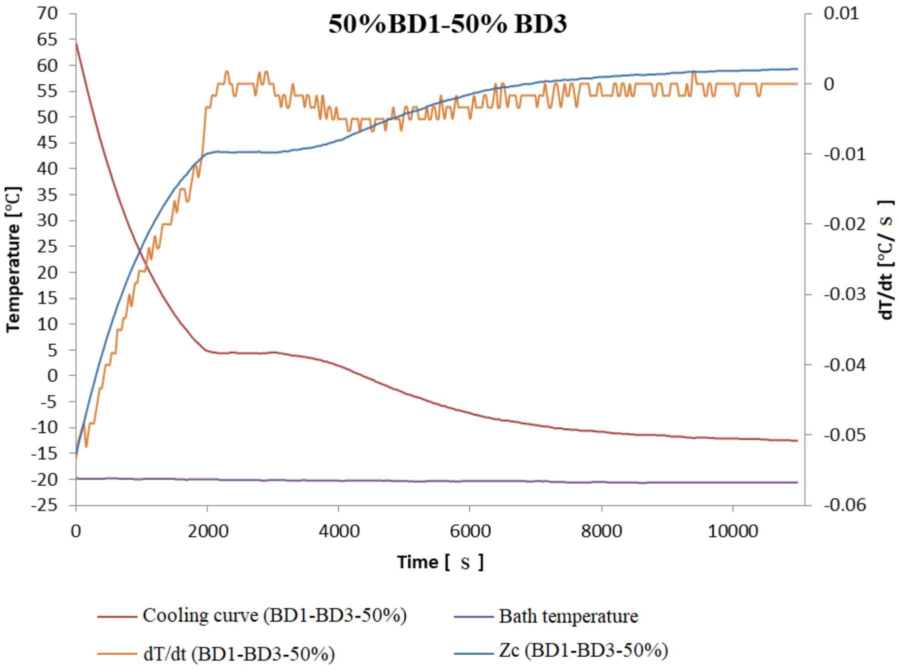


Figure 4.11: CCA for 50% BD1 – 50% BD3 biodiesel sample

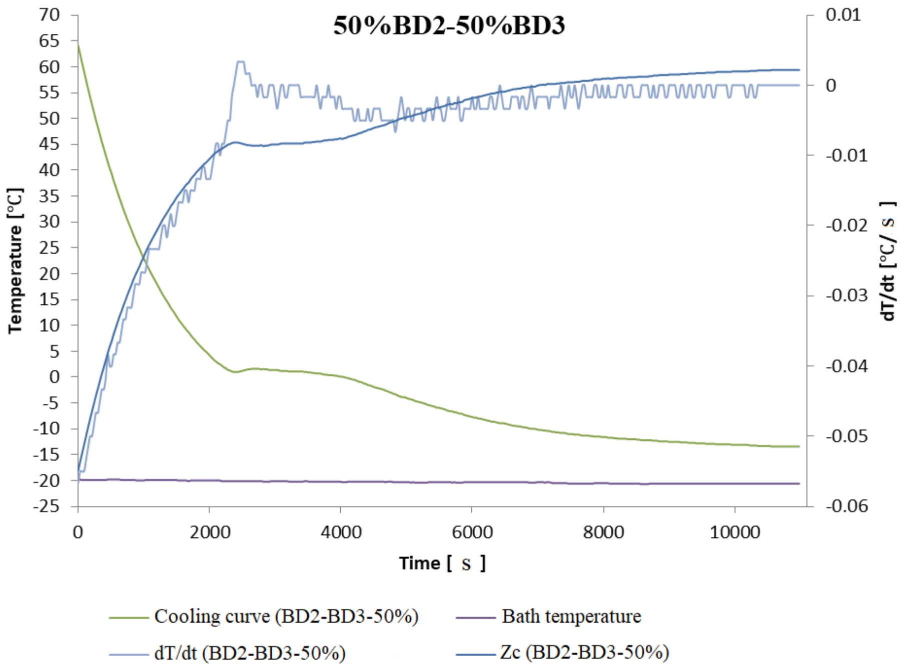


Figure 4.12: CCA for 50% BD2 – 50% BD3 biodiesel sample

We see from Figures 4.7 to 4.12 respectively, the rate move and the Newtonian Zero curve together to the stage where solidification begins.

This is the solid-liquid phase of the two phases. The region between both the two curves has a direct correlation to the solidification latent heat value. After the solidification, the graphs actually nearly take part and proceed in the solid stage.

3.5 Cold Flow Properties

The cloud point is of interest when plugging cold filters, so this is a calculation of functionality at low temperatures. Pour point is important at low temperatures for improving or managing bulk fuels. All outcomes of the pour point and cloud point were evaluated optically. By checking the biodiesel sample at any degree of temperature, the cloud point was evaluated, until the wax crystal cloud was apparent, as well as the pour point was calculated by cooling down the samples until the biodiesel was completely frozen and the degree was measured before the point disappeared. The cloud point and pour point of twelve different percentages of blending BD1 and BD2, and BD3, are shown in Figures 4.13 to 4.15 respectively. The measured cloud point and pour point are presented in Table 4.7.

Table 4.7: CP and PP of different percentages of BD1-BD2-BD3

Properties	**100%BD1 - 0%BD2**	**75%BD1 - 25%BD2**	**50%BD1 - 50%BD2**	**25%BD1 - 75%BD2**	**0%BD1 - 100%BD2**
CP [°C]	5.2	3.4	1.6	-0.2	-2.0
PP [°C]	-2.0	-2.46	-3.2	-4.2	-5.5
Properties	**100%BD1 - 0%BD3**	**75%BD1 - 25%BD2**	**50%BD1 - 50%BD2**	**25%BD1 - 75%BD3**	**0%BD1 - 100%BD3**
CP [°C]	5.2	5.0	4.8	4.6	4.5
PP [°C]	-2.0	-0.1	1	1.3	1.4
Properties	**100%BD2 - 0%BD3**	**75%BD2 - 25%BD3**	**50%BD1 - 50%BD2**	**25%BD2 - 75%BD3**	**0%BD2 - 100%BD3**
CP [°C]	-2.0	0.2	2.0	3.4	4.5
PP [°C]	-5.5	-4.1	-2.5	-0.9	1.4

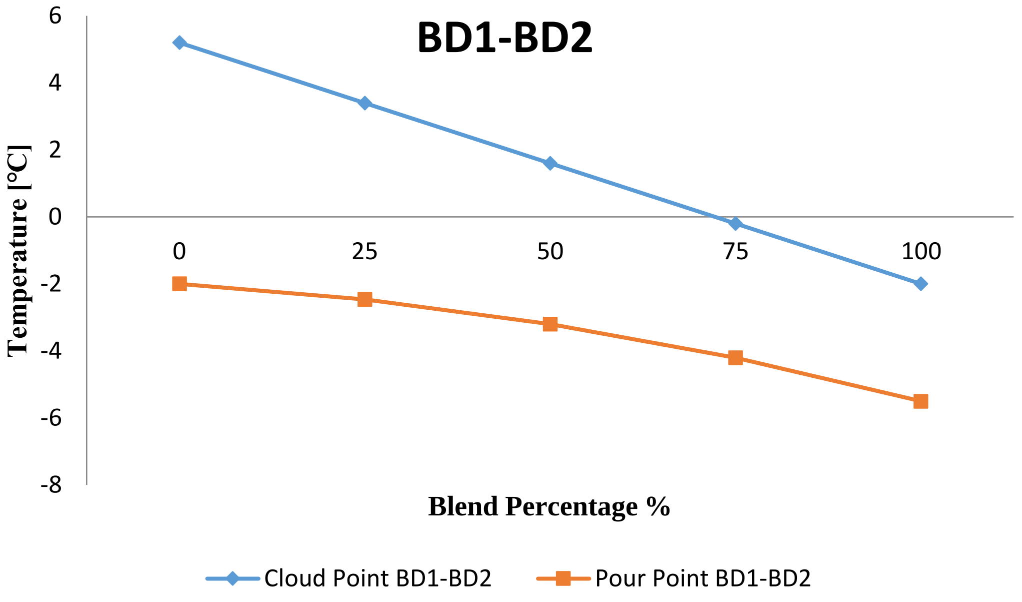


Figure 4.13: CP and PP values of five different percentages BD1-BD2 blend

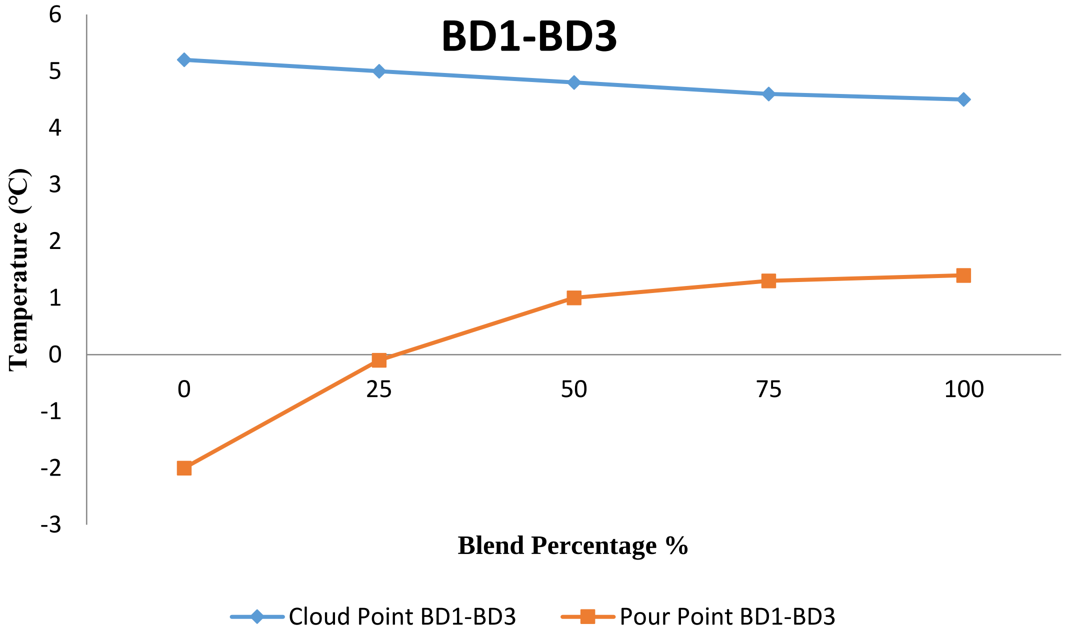


Figure 4.14: CP and PP values of five different percentages BD1-BD3 blend

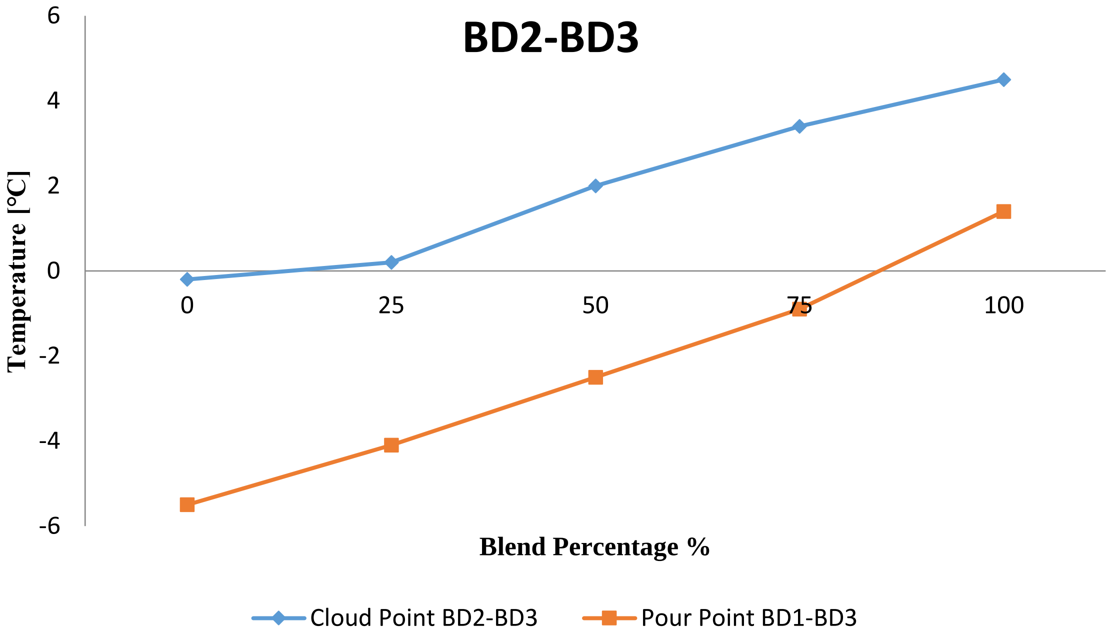


Figure 4.15: CP and PP values of five different percentages BD2-BD3 blend

CHAPTER 5
CONCLUSIONS

5.1 Conclusions

The kinematic viscosity of twelve biodiesel samples at different percentages were determined from 20°C and decrease until it freezes and from 30°C up to 80°C by using Ubbelohde viscometer per ASTM D445-09. Density of biodiesel sample was measured at same conditions of measuring the viscosity using pycnometer according to standard ASTM D 941-88 and the experimental data were recorded. Also the cloud point and pour point of the biodiesel samples were tested per ASTM D2500-09 and ASTM D97-05 respectively. Based on the results obtained, the following conclusions can be drawn:

- The samples kinematic viscosity differs by simply changing the proportion of the blend. The maximum kinematic viscosity at every degree of temperature is in %100BD2 sample.
- The kinematic viscosity of BD1-BD3 blend cannot be measured below 6 °C because the sample gets solidification.
- Also for BD1-BD3 and BD2-BD3 blends, the kinematic viscosity cannot be determined below 0˚C.
- The kinematic viscosity of biodiesel blend samples increases logarithmically when the temperature decrease in all instances.
- The biodiesel blend density also increases against the temperature.
- Results indicate that somehow the obtained values from the cooling curve for cold flow properties were approximately equal to experiments data.
- CP of biodiesel blend samples are always a few degrees above PP
- We cannot use these biodiesel samples straight in an engine at these temperatures because the cloud point and kinematic viscosity are high.

The experiments were conducted as correctly as possible, but a few aspects affect the results such as:

1- Error during averaging and readings.
2- Equipment's inaccuracy probability, particularly electronic balance calibration.
3- The temperature inside the cooling bath is not homogenous everywhere.
4- It is impossible always to get the precise temperature within the capillary tube.
5- In the cooling bath, the temperature is rapidly changing, particularly at low temperatures.
6- Vibration in the experiment area can lead to mistakes in measurements.

REFERENCES

Argawal, AK., (2007). Biofuels (alcohols and biodiesel) applications as fuels in internal combustion engines. *Progr Energy Combust Sci*, 233–271.

Barabás, I., & Todoru, I. (2011). Biodiesel Quality, Standards and Properties. *Biodiesel Quality, Emissions and By-Products*. doi:10.5772/25370

Corach, J., Colman, M., Sorichettic, P.A., & Romano, S.D. (2017). Kinematic viscosity of soybean biodiesel and diesel fossil fuel blends: Estimation from permittivity and temperature. *Fuel Volume 207*, 488-492.

Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and non- catalytic supercritical methanol transesterification methods. *Progr Energy Combust Sci*, 466-487.

Evcil, A., Al-Shanableh, F., & Savas, M. A. (2018). Variation of solid fraction with cold flow properties of biodiesel produced from waste frying oil. *Fuel*, 522-527.

Fox, R. W., McDonald, A. T., Pritchard, P. J. (2012). *Fluid Mechanics*. Asia: Wiley and Sons

Gabroski, M.S & McCormick, RL. (1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Progr Energy Combust Sci*, 125–64.

Giakoumis, E. G., & Sarakatsanis, C. K. (2018). Estimation of biodiesel cetane number, density, kinematic viscosity and heating values from its fatty acid weight composition. *Fuel 222 (2018) Science direct.*, 574–585.

Giakoumis, E., Rakopoulos, C., Dimaratos, A., & Rakopoulos, D. (2012). Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends. *Progr Energy Combust Sci*, 691-715.

Kierkus, W., & J. H. Sokolowski. (1999). Recent Advances in CCA: A New Method of Determining 'Baseline' Equation. *AFS Transactions v66*, 161-167.

Kumar, D., Singh, B., Banerjee, A., & Chatterjee, S. (2018). Cement wastes as transesterification catalysts for the production of biodiesel from Karanja oil. *Journal of Clean-*

er Production, 26-34.

Loong, T. C., & Idris, A. (2017). One step transesterification of biodiesel production using simultaneous cooling and microwave heating. *Journal of Cleaner Production*, 57-62.

National Biodiesel Board. (2018, March 31). *Biodiesel Americas Advanced Biofuels*. Retrieved from http://www.biodiesel.org

Oxford. (2018, April 4). *Oxford living Dictionaries*. Retrieved from https://en.oxforddictionaries.com/definition/non-renewable

Paulik, F., Paulik, J., & Erdey, L. (1966). Derivatography A complex method in thermal analysis. *Talanta 13*, 1405-1430.

Pratas, M. J., Freitas, S., Oliveira, M. B., Monteiro, S. C., Lima, A. S., & Coutinho, J. (2010). Densities and Viscosities of fatty acid methyl and ethyl esters. . *Journal of Chemical and Engineering Data, 55(4),*, 83–90.

Showstack, R. (2016). High Energy Growth, Fossil Fuel Dependence Forecast Through 2040. *Eos, 97*. doi:10.1029/2016eo052301

Streeter, V. L., Bedford, K. W., & Wylie, E. B. (1998). *Fluid mechanics*. Boston: McGraw-Hill.

Viswanath, D. S., Ghosh, T. K., Prasad, D. H., Dutt, N. V., & Rani, K. Y. (2007). *Viscosity of Liquids: Theory, Estimation, Experiment, and Data*. Dordrecht: Springer.

APPENDICES

APPENDIX 1

ASTM D 445-09

Designation: D 445 – 09

British Standard 2000: Part 71:1990

Designation: 71/1/97

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)[1]

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid.

NOTE 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

NOTE 2—ISO 3104 corresponds to Test Method D 445.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.

1.3 The range of kinematic viscosities covered by this test method is from 0.2 to 300 000 mm^2/s (see Table A1.1) at all temperatures (see 6.3 and 6.4). The precision has only been determined for those materials, kinematic viscosity ranges and temperatures as shown in the footnotes to the precision section.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers

D 1193 Specification for Reagent Water

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer

D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer

D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer

D 2162 Practice for Basic Calibration of Master Viscometers and Viscosity Oil Standards

D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)

D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer

D 6071 Test Method for Low Level Sodium in High Purity Water by Graphite Furnace Atomic Absorption Spectroscopy

D 6074 Guide for Characterizing Hydrocarbon Lubricant Base Oils

D 6617 Practice for Laboratory Bias Detection Using Single Test Result from Standard Material

E 1 Specification for ASTM Liquid-in-Glass Thermometers

E 77 Test Method for Inspection and Verification of Thermometers

2.2 *ISO Standards:*[3]

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved July 1, 2009. Published August 2009. Originally approved in 1937. Last previous edition approved in 2006 as D 445–06.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

***A Summary of Changes section appears at the end of this standard.**

ISO 3104 Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity
ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions
ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods
ISO 5725 Accuracy (trueness and precision) of measurement methods and results.
ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use
ISO 17025 General Requirements for the Competence of Testing and Calibration Laboratories

2.3 *NIST Standards:*[4]

NIST Technical Note 1297, Guideline for Evaluating and Expressing the Uncertainty of NIST Measurement Results
NIST GMP 11
NIST Special Publication 819

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *automated viscometer*, *n*—apparatus which, in part or in whole, has mechanized one or more of the procedural steps indicated in Section 11 or 12 without changing the principle or technique of the basic manual apparatus. The essential elements of the apparatus in respect to dimensions, design, and operational characteristics are the same as those of the manual method.

3.1.1.1 *Discussion*—Automated viscometers have the capability to mimic some operation of the test method while reducing or removing the need for manual intervention or interpretation. Apparatus which determine kinematic viscosity by physical techniques that are different than those used in this test method are not considered to be Automated Viscometers.

3.1.2 *density*, *n*—the mass per unit volume of a substance at a given temperature.

3.1.3 *dynamic viscosity*, *n*—the ratio between the applied shear stress and rate of shear of a liquid.

3.1.3.1 *Discussion*—It is sometimes called the coefficient of dynamic viscosity or, simply, viscosity. Thus dynamic viscosity is a measure of the resistance to flow or deformation of a liquid.

3.1.3.2 *Discussion*—The term dynamic viscosity can also be used in a different context to denote a frequency-dependent quantity in which shear stress and shear rate have a sinusodial time dependence.

3.1.4 *kinematic viscosity*, *n*—the resistance to flow of a fluid under gravity.

3.1.4.1 *Discussion*—For gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, ν, where $\nu = \eta/\rho$, and η is the dynamic viscosity coefficient.

4. Summary of Test Method

4.1 The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity (determined value) is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values.

5. Significance and Use

5.1 Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications.

6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.

6.1.1 Viscometers listed in Table A1.1, whose specifications meet those given in Specifications D 446 and in ISO 3105 meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in Table A1.1. Annex A1 gives further guidance.

6.1.2 *Automated Viscometers*—Automated apparatus may be used as long as they mimic the physical conditions, operations or processes of the manual apparatus. Any viscometer, temperature measuring device, temperature control, temperature controlled bath or timing device incorporated in the automated apparatus shall conform to the specification for these components as stated in Section 6 of this test method. Flow times of less than 200 s are permitted, however, a kinetic energy correction shall be applied in accordance with Section 7 on Kinematic Viscosity Calculation of Specifications D 446. The kinetic energy correction shall not exceed 3.0 % of the measured viscosity. The automated apparatus shall be capable of determining kinematic viscosity of a certified viscosity reference standard within the limits stated in 9.2.1 and Section 17. The precision shall be of statistical equivalence to, or better (has less variability) than the manual apparatus.

NOTE 3—Precision and bias of kinematic viscosity measurements for flow times of less than 200 s has not been determined. The precision stated in Section 17 is not know to be valid for kinematic viscosity measurements with flow times less than 200 s.

6.2 *Viscometer Holders*—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see Specifications D 446 and ISO 3105).

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[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

6.2.1 Viscometers shall be mounted in the constant temperature bath in the same manner as when calibrated and stated on the certificate of calibration. See Specifications D 446, see Operating Instructions in Annexes A1–A3. For those viscometers which have Tube L (see Specifications D 446) held vertical, vertical alignment shall be confirmed by using (*1*) a holder ensured to hold Tube L vertical, or (*2*) a bubble level mounted on a rod designed to fit into Tube L, or (*3*) a plumb line suspended from the center of Tube L, or (*4*) other internal means of support provided in the constant temperature bath.

6.3 *Temperature-Controlled Bath*—Use a transparent liquid bath of sufficient depth such, that at no time during the measurement of flow time, any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1 *Temperature Control*—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C, the temperature of the bath medium does not vary by more than ±0.02°C of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed ±0.05°C.

6.4 *Temperature Measuring Device in the Range from 0 to 100°C*—Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of ±0.02°C or better, or any other thermometric device of equal or better accuracy.

6.4.1 If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C.

6.4.2 Outside the range from 0 to 100°C, use either calibrated liquid-in-glass thermometers of an accuracy after correction of ±0.05°C or better, or any other thermometric device of equal or better accuracy. When two temperature measuring devices are used in the same bath, they shall agree within ±0.1°C.

6.4.3 When using liquid-in-glass thermometers, such as those in Table A2.1, use a magnifying device to read the thermometer to the nearest ⅕ division (for example, 0.01°C or 0.02°F) to ensure that the required test temperature and temperature control capabilities are met (see 10.1). It is recommended that thermometer readings (and any corrections supplied on the certificates of calibrations for the thermometers) be recorded on a periodic basis to demonstrate compliance with the test method requirements. This information can be quite useful, especially when investigating issues or causes relating to testing accuracy and precision.

6.5 *Timing Device*—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better and has an accuracy within ±0.07 % (see Annex A3) of the reading when tested over the minimum and maximum intervals of expected flow times.

6.5.1 Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05 % or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled. When used to actuate electrical timing devices, such control can cause large errors in kinematic viscosity flow time measurements.

7. Reagents and Materials

7.1 *Chromic Acid Cleaning Solution*, or a nonchromium-containing, strongly oxidizing acid cleaning solution. (**Warning—**Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.)

7.2 *Sample Solvent*, completely miscible with the sample. Filter before use.

7.2.1 For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3 *Drying Solvent*, a volatile solvent miscible with the sample solvent (see 7.2) and water (see 7.4). Filter before use.

7.3.1 Acetone is suitable. (**Warning—**Extremely flammable.)

7.4 *Water*, deionized or distilled and conforming to Specification D 1193 or Grade 3 of ISO 3696. Filter before use.

8. Certified Viscosity Reference Standards

8.1 Certified viscosity reference standards shall be certified by a laboratory that has been shown to meet the requirements of ISO 17025 by independent assessment. Viscosity standards shall be traceable to master viscometer procedures described in Test Method D 2162.

8.2 The uncertainty of the certified viscosity reference standard shall be stated for each certified value ($k = 2$, 95% confidence). See ISO 5725 or NIST 1297.

9. Calibration and Verification

9.1 *Viscometers*—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

9.2 *Certified Viscosity Reference Standards (*Table A1.2*)*—These are for use as confirmatory checks on the procedure in the laboratory.

9.2.1 If the determined kinematic viscosity does not agree within the acceptable tolerance band, as calculated from Annex A4, of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

NOTE 4—In previous issues of Test Method D 445, limits of ±0.35% of the certified value have been used. The data to support the limit of ±0.35% cannot be verified. Annex A4 provides instructions on how to determine the tolerance band. The tolerance band combines both the uncertainty of the certified viscosity reference standard as well as the uncertainty of the laboratory using the certified viscosity reference standard.

9.2.1.1 As an alternative to the calculation in Annex A4, the approximate tolerance bands in Table 1 may be used.

9.2.2 The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

9.3 The calibration constant, C, is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization laboratory together with the instrument constant. Where the acceleration of gravity, g, differs by more that 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \qquad (1)$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

10. General Procedure for Kinematic Viscosity

10.1 Adjust and maintain the viscometer bath at the required test temperature within the limits given in 6.3.1 taking account of the conditions given in Annex A2 and of the corrections supplied on the certificates of calibration for the thermometers.

10.1.1 Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

10.1.2 In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see 6.4).

10.1.3 They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

10.2 Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time for manual viscometers shall not be less than 200 s or the longer time noted in Specifications D 446. Flow times of less than 200 s are permitted for automated viscometers, provided they meet the requirements of 6.1.2.

10.2.1 The specific details of operation vary for the different types of viscometers listed in Table A1.1. The operating instructions for the different types of viscometers are given in Specifications D 446.

10.2.2 When the test temperature is below the dew point, fill the viscometer in the normal manner as required in 11.1. To ensure that moisture does not condense or freeze on the walls of the capillary, draw the test portion into the working capillary and timing bulb, place rubber stoppers into the tubes to hold the test portion in place, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, and the remove the stoppers. When performing manual viscosity determinations, do not use those viscometers which cannot be removed from the constant temperature bath for charging the sample portion.

10.2.2.1 The use of loosely packed drying tubes affixed to the open ends of the viscometer is permitted, but not required. If used, the drying tubes shall fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument.

10.2.3 Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

TABLE 1 Approximate Tolerance Bands

NOTE—The tolerance bands were determined using Practice D 6617. The calculation is documented in Research Report RR: D02–1498.[A]

Viscosity of Reference Material, mm²/s	Tolerance Band
< 10	±0.30%
10 to 100	±0.32%
100 to 1000	±0.36%
1000 to 10 000	±0.42%
10 000 to 100 000	±0.54%
> 100 000	±0.73%

[A] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1498.

11. Procedure for Transparent Liquids

11.1 Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. If the sample is thought or known to contain fibers or solid particles, filter through a 75 µm screen, either prior to or during charging (see Specifications D 446).

NOTE 5—To minimize the potential of particles passing through the filter from aggregating, it is recommended that the time lapse between filtering and charging be kept to a minimum.

11.1.1 In general, the viscometers used for transparent liquids are of the type listed in Table A1.1, A and B.

11.1.2 With certain products which exhibit *gel-like* behavior, exercise care that flow time measurements are made at sufficiently high temperatures for such materials to flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

11.1.3 Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring a flow time.

11.1.4 Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

11.1.4.1 Thirty minutes should be sufficient except for the highest kinematic viscosities.

11.1.5 Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

11.2 Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. If this flow time is less than the specified minimum (see 10.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

11.2.1 Repeat the procedure described in 11.2 to make a second measurement of flow time. Record both measurements.

11.2.2 From the two measurements of flow time, calculate two determined values of kinematic viscosity.

11.2.3 If the two determined values of kinematic viscosity calculated from the flow time measurements agree within the stated determinability figure (see 17.1.1) for the product, use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If not, repeat the measurements of flow times after a thorough cleaning and drying of the viscometers and filtering (where required, see 11.1) of the sample until the calculated kinematic viscosity determinations agree with the stated determinability.

11.2.4 If the material or temperature, or both, is not listed in 17.1.1, use 1.5% as an estimate of the determinability.

12. Procedure for Opaque Liquids

12.1 For steam-refined cylinder oils and black lubricating oils, proceed to 12.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 12.1.1-12.2.2 shall be followed to minimize this.

12.1.1 In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

12.1.2 Heat in the original container, in an oven, at 60 ± 2°C for 1 h.

12.1.3 Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

12.1.4 Recap the container tightly and shake vigorously for 1 min to complete the mixing.

12.1.4.1 With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

12.2 Immediately after completing 12.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

12.2.1 Immerse the flask in a bath of boiling water for 30 min. (**Warning—**Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.)

12.2.2 Remove the flask from the bath, stopper tightly, and shake for 60 s.

12.3 Two determinations of the kinematic viscosity of the test material are required. For those viscometers that require a complete cleaning after each flow time measurement, two viscometers may be used. A single viscometer in which an immediate, repeat flow time measurement can be made without cleaning may also be used for the two measurements of flow time and calculation of kinematic viscosity. Charge two viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube viscometers for opaque liquids, filter the sample through a 75-µm filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

12.3.1 Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

12.3.2 After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D 446).

12.3.3 Allow the charged viscometers enough time to reach the test temperature (see 12.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring flow time.

12.4 With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the measurement.

12.4.1 In the case of samples requiring heat treatment described in 12.1 through 12.2.1, complete the measurements of flow time within 1 h of completing 12.2.2. Record the measured flow times.

12.5 Calculate kinematic viscosity, ν, in mm^2/s, from each measured flow time. Regard these as two determined values of kinematic viscosity.

12.5.1 For residual fuel oils, if the two determined values of kinematic viscosity agree within the stated determinability figure (see 17.1.1), use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If the calculated kinematic viscosities do not agree, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering of the sample. If the material or temperature, or both, is not listed in 17.1.1, for temperatures between 15 and 100°C use as an estimate of the determinability 1.0 %, and 1.5 % for temperatures outside this range; it must be realized that these materials can be non-Newtonian, and can contain solids which can come out of solution as the flow time is being measured.

13. Cleaning of Viscometer

13.1 Between successive determinations of kinematic viscosity, clean the viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

13.2 Periodically clean the viscometer with the cleaning solution (**Warning—**see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (see 7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected. (**Warning—**It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.)

14. Calculation

14.1 Calculate each of the determined kinematic viscosity values, ν_1 and ν_2, from the measured flow times, t_1 and t_2, and the viscometer constant, C, by means of the following equation:

$$\nu_{1,2} = C \cdot t_{1,2} \tag{2}$$

where:

$\nu_{1,2}$ = determined kinematic viscosity values for ν_1 and ν_2, respectively, mm²/s,
C = calibration constant of the viscometer, mm²/s², and
$t_{1,2}$ = measured flow times for t_1 and t_2, respectively, s.

Calculate the kinematic viscosity result, ν, as an average of ν_1 and ν_2 (see 11.2.3 and 12.5.1).

14.2 Calculate the dynamic viscosity, η, from the calculated kinematic viscosity, ν, and the density, ρ, by means of the following equation:

$$\eta = \nu \times \rho \times 10^{-3} \tag{3}$$

where:

η = dynamic viscosity, mPa·s,
ρ = density, kg/m³, at the same temperature used for the determination of the kinematic viscosity, and
ν = kinematic viscosity, mm²/s.

14.2.1 The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D 1217, D 1480, or D 1481.

15. Expression of Results

15.1 Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

16. Report

16.1 Report the following information:

16.1.1 Type and identification of the product tested,

16.1.2 Reference to this test method or a corresponding international standard,

16.1.3 Result of the test (see Section 15),

16.1.4 Any deviation, by agreement or otherwise, from the procedure specified,

16.1.5 Date of the test, and

16.1.6 Name and address of the test laboratory.

17. Precision

17.1 *Comparison of Determined Values*:

17.1.1 *Determinability (d)*—The difference between successive determined values obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C[5]	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C[6]	0.0013 y	(0.13 %)
Formulated oils at 150°C[7]	0.015 y	(1.5 %)
Petroleum wax at 100°C[8]	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C[9]	0.011 (y + 8)	
Residual fuel oils at 50°C[9]	0.017 y	(1.7 %)
Additives at 100°C[10]	0.00106 $y^{1.1}$	
Gas oils at 40°C[11]	0.0013 (y+1)	
Jet fuels at –20°C[12]	0.0018 y	(0.18 %)

where: y is the average of determined values being compared.

17.2 *Comparison of Results*:

17.2.1 *Repeatability (r)*—The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C[5]	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C[6]	0.0026 x	(0.26 %)
Formulated oils at 150°C[7]	0.0056 x	(0.56 %)
Petroleum wax at 100°C[8]	0.0141 $x^{1.2}$	
Residual fuel oils at 80 and 100°C[9]	0.013 (x + 8)	
Residual oils at 50°C[9]	0.015 x	(1.5 %)
Additives at 100°C[10]	0.00192 $x^{1.1}$	
Gas oils at 40°C[11]	0.0043 (x+1)	
Jet fuels at –20°C[12]	0.007 x	(0.7 %)

where: x is the average of results being compared.

17.2.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D02-1331 and RR:D02-1132. These precision values were obtained by statistical examination of interlaboratory results from six mineral oils (base oils without additive package) in the range from 8 to 1005 mm²/s at 40°C and from 2 to 43 mm ²/s at 100°C, and were first published in 1989. Request See Guide D 6074.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1332. These precision values were obtained by statistical examination of interlaboratory results from seven fully formulated engine oils in the range from 36 to 340 mm ²/s at 40°C and from 6 to 25 mm²/s at 100°C, and were first published in 1991. See Guide D 6071.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1333. These precision values were obtained by statistical examination of interlaboratory results for eight fully formulated engine oils in the range from 7 to 19 mm² /s at 150°C, and first published in 1991. See Guide D 6074.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1334. These precision values were obtained by statistical examination of interlaboratory results from five petroleum waxes in the range from 3 to 16 mm²/s at 100°C, and were first published in 1988.

[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1198. These precision values were obtained by statistical examination of interlaboratory results from fourteen residual fuel oils in the range from 30 to 1300 mm²/s at 50°C and from 5 to 170 mm²/s at 80 and 100°C, and were first published in 1984.

[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1421. These precision values were obtained by statistical examination of interlaboratory results from eight additives in the range from 145 to 1500 mm²/s at 100°C and were first available in 1997.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1422. These precision values were obtained by statistical examination of interlaboratory results from eight gas oils in the range from 1 to 13 mm²/s at 40°C and were first available in 1997.

[12] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1420. These precision values were obtained by statistical examination of interlaboratory results from nine jet fuels in the range from 4.3 to 5.6 mm²/s at– 20°C and were first available in 1997.

Base oils at 40 and 100°C[5]	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C[6]	0.0076 x	(0.76 %)
Formulated oils at 150°C[7]	0.018 x	(1.8 %)
Petroleum wax at 100°C[8]	$0.0366\,x^{1.2}$	
Residual fuel oils at 80 and 100°C[9]	0.04 (x + 8)	
Residual oils at 50°C[9]	0.074 x	(7.4 %)
Additives at 100°C[10]	$0.00862\,x^{1.1}$	
Gas oils at 40°C[11]	0.0082 (x+1)	
Jet fuels at –20°C[12]	0.019 x	(1.9 %)

where: *x* is the average of results being compared.

17.3 The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

17.4 The precision for specific automated viscometers has not been determined. However, an analysis has been made of a large data set including both automated and manual viscometers over the temperature range of 40 to 100°C. The reproducibility of automated viscometer data is not statistically significantly different than the reproducibility of manual viscometer data. It is also shown that there is no bias of the automated data in comparison to the manual data.[13]

18. Keywords

18.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

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[13] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1498.

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES AND CERTIFIED VISCOSITY REFERENCE STANDARDS

A1.1 Viscometer Types

A1.1.1 Table A1.1 lists capillary viscometers commonly in use for viscosity determinations on petroleum products. For specifications, operating instructions, and calibration, refer to specifications in Specifications D 446.

A1.1.2 Table A1.2 lists certified viscosity reference standards.

TABLE A1.1 Viscometer Types

Viscometer Identification	Kinematic Viscosity Range,[A] mm^2/s
A. Ostwald Types for Transparent Liquids	
Cannon-Fenske routine[B]	0.5 to 20 000
Zeitfuchs	0.6 to 3 000
BS/U-tube[B]	0.9 to 10 000
BS/U/M miniature	0.2 to 100
SIL[B]	0.6 to 10 000
Cannon-Manning semi-micro	0.4 to 20 000
Pinkevitch[B]	0.6 to 17 000
B. Suspended-level Types for Transparent Liquids	
BS/IP/SL[B]	3.5 to 100 000
BS/IP/SL(S)[B]	1.05 to 10 000
BS/IP/MSL	0.6 to 3 000
Ubbelohde[B]	0.3 to 100 000
FitzSimons	0.6 to 1 200
Atlantic[B]	0.75 to 5 000
Cannon-Ubbelohde(A), Cannon Ubbelohde dilution[B](B)	0.5 to 100 000
Cannon-Ubbelohde semi-micro	0.4 to 20 000
C. Reverse-flow Types for Transparent and Opaque Liquids	
Cannon-Fenske opaque	0.4 to 20 000
Zeitfuchs cross-arm	0.6 to 100 000
BS/IP/RF U-tube reverse-flow	0.6 to 300 000
Lantz-Zeitfuchs type reverse-flow	60 to 100 000

[A] Each range quoted requires a series of viscometers. To avoid the necessity of making a kinetic energy correction, these viscometers are designed for a flow time in excess of 200 s except where noted in Specifications D 446.

[B] In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

TABLE A1.2 Certified Viscosity Reference Standards

Designation	Approximate Kinematic Viscosity, mm²/s					
	20°C	25°C	40°C	50°C	80 °C	100°C
S3	4.6	4.0	2.9	...	...	1.2
S6	11	8.9	5.7	...	...	1.8
S20	44	34	18	...	...	3.9
S60	170	120	54	...	...	7.2
S200	640	450	180	...	...	17
S600	2400	1600	520	280	67	32
S2000	8700	5600	1700	...	...	75
S8000	37 000	23 000	6700	...	...	...
S30 000	...	81 000	23 000	11 000	...	...

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

A2.1.1 Use a short-range specialized thermometer conforming to the generic specification given in Table A2.1 and Table A2.2 and to one of the designs shown in Fig. A2.1.

A2.1.2 The difference in the designs rests mainly in the position of the ice point scale. In Design A, the ice point is within the scale range, in Design B, the ice point is below the scale range, and in Design C, the ice point is above the scale range.

A2.2 Calibration

A2.2.1 Use liquid-in-glass thermometers with an accuracy after correction of 0.02°C or better, calibrated by a laboratory meeting the requirements of ISO 9000 or ISO 17025, and carrying certificates confirming that the calibration is traceable to a national standard. As an alternative, use thermometric devices such as platinum resistance thermometers, of equal or better accuracy, with the same certification requirements.

A2.2.2 The scale correction of liquid-in-glass thermometers can change during storage and use, and therefore regular re-calibration is required. This is most conveniently achieved in a working laboratory by means of a re-calibration of the ice point, and all of the main scale corrections altered for the change seen in the ice point.

TABLE A2.1 General Specification for Thermometers

NOTE—Table A2.2 gives a range of ASTM, IP, and ASTM/IP thermometers that comply with the specification in Table A2.1, together with their designated test temperatures. See Specification E 1 and Test Method E 77.

Immersion		Total
Scale marks:		
Subdivisions	°C	0.05
Long lines at each	°C	0.1 and 0.5
Numbers at each	°C	1
Maximum line width	mm	0.10
Scale error at test temperature, max	°C	0.1
Expansion chamber:		
Permit heating to	°C	105 up to 90, 120 between 90 and 95 130 between 95 and 105, 170 above 105
Total length	mm	300 to 310
Stem outside diameter	mm	6.0 to 8.0
Bulb length	mm	45 to 55
Bulb outside diameter	mm	no greater than stem
Length of scale range	mm	40 to 90

TABLE A2.2 Complying Thermometers

Thermometer No.	Test Temperature		Thermometer No.	Test Temperature	
	°C	°F		°C	°F
ASTM 132C, IP 102C	150		ASTM 128C, F/IP 33C	0	32
ASTM 110C, F/IP 93C	135	275	ASTM 72C, F/IP 67C	−17.8	0
ASTM 121C/IP 32C	98.9,	210,	ASTM 127C/IP 99C	−20	−4
	100	212	ASTM 126C, F/IP 71C	−26.1	−20
ASTM 129C, F/IP 36C	93.3	200	ASTM 73C, F/IP 68C	−40	−40
ASTM 48C, F/IP 90C	82.2	180	ASTM 74C, F/IP 69C	−53.9	−65
IP 100C	80				
ASTM 47C, F/IP 35C	60	140			
ASTM 29C, F/IP 34C	54.4	130			
ASTM 46C F/IP 66C	50	122			
ASTM 120C/IP 92C	40				
ASTM 28C, F/IP 31C	37.8	100			
ASTM 118C, F	30	86			
ASTM 45C, F/IP 30C	25	77			
ASTM 44C, F/IP 29C	20	68			

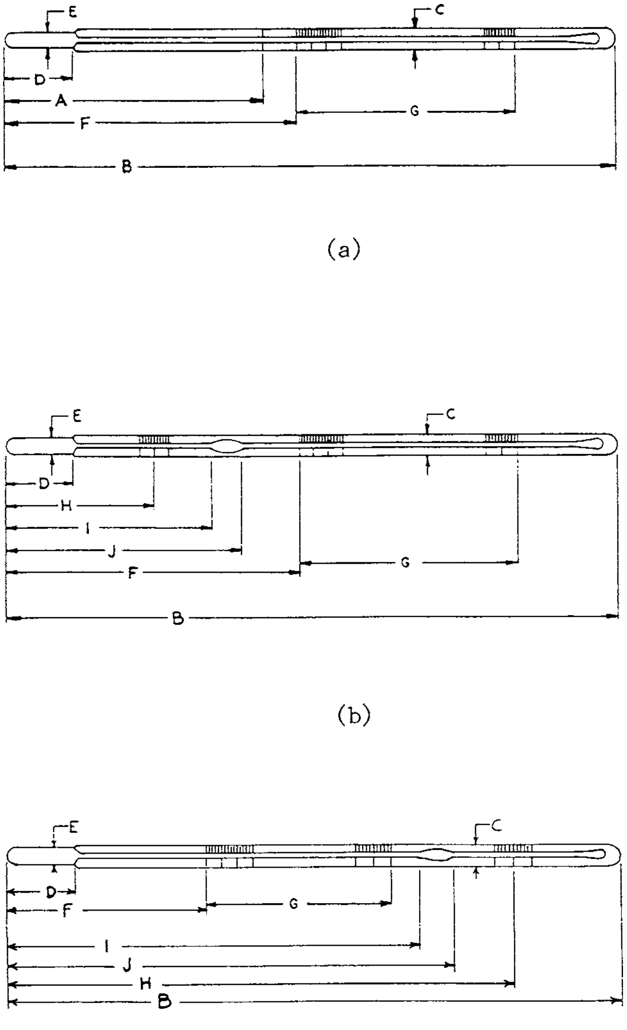
A2.2.2.1 The interval for ice-point recalibration shall be no longer than six months (see NIST GMP 11). For new thermometers, monthly checking for the first six months is recommended. A change of one or more scale divisions in the ice point means that the thermometer may have been overheated or damaged, and it may be out of calibration. Such thermometers shall be removed from service until inspected, or recalibrated, or both. A complete recalibration of the thermometer, while permitted, is not necessary in order to meet the accuracy ascribed to this design thermometer (see NIST Special Publication 819). Any change in ice-point correction shall be added to the other corrections of the original Report of Calibration.

A2.2.2.2 Other thermometric devices, if used, will also require periodic recalibration. Keep records of all recalibration.

A2.2.3 *Procedure for Ice-point Recalibration of Liquid-in-glass Thermometers.*

A2.2.3.1 Unless otherwise listed on the certificate of calibration, the recalibration of calibrated kinematic viscosity thermometers requires that the ice-point reading shall be taken within 60 min after being at test temperature for not less than 3 min.

A2.2.3.2 Select clear pieces of ice, preferably made from distilled or pure water. Discard any cloudy or unsound portions. Rinse the ice with distilled water and shave or crush into small pieces, avoiding direct contact with the hands or any chemically unclean objects. Fill the Dewar vessel with the



(a)

(b)

(c)

FIG. A2.1 Thermometer Designs

crushed ice and add sufficient water to form a slush, but not enough to float the ice. As the ice melts, drain off some of the water and add more crushed ice. Insert the thermometer, and pack the ice gently about the stem, to a depth approximately one scale division below the 0°C graduation.

A2.2.3.3 After at least 3 min have elapsed, tap the thermometer gently and repeatedly at right angles to its axis while making observations. Successive readings taken at least 1 min apart shall agree within 0.005°C.

A2.2.3.4 Record the ice-point readings and determine the thermometer correction at this temperature from the mean reading. If the correction is found to be higher or lower than that corresponding to a previous calibration, change the correction at all other temperatures by the same value.

A2.2.3.5 During the procedure, apply the following conditions:

(*1*) The thermometer shall be supported vertically.

(*2*) View the thermometer with an optical aid that gives a magnification of approximately five and also eliminates parallax.

(*3*) Express the ice-point reading to the nearest 0.005°C.

A2.2.4 When in use, immerse the thermometric device to the same depth as when it was fully calibrated. For example, if a liquid-in-glass thermometer was calibrated at the normal total immersion condition, it shall be immersed to the top of the mercury column with the remainder of the stem and the expansion volume at the uppermost end exposed to room temperature and pressure. In practice, this means that the top of the mercury column shall be within a length equivalent to four scale divisions of the surface of the medium whose temperature is being measured.

A2.2.4.1 If this condition cannot be met, then an extra correction may be necessary.

A3. TIMER ACCURACY

A3.1 Regularly check timers for accuracy and maintain records of such checks.

A3.1.1 Time signals as broadcast by the National Institute of Standards and Technology are a convenient and primary standard reference for calibrating timing devices. The following can be used to an accuracy of 0.1 s:

WWV	Fort Collins, CO	2.5, 5, 10, 15, 20 MHz
WWVH	Kauai, HI	2.5, 5, 10, 15, MHz
CHU	Ottawa, Canada	3.33, 7.335, 14.67 MHz

A3.1.2 Radio broadcast of voice and audio on a telephone line at phone 303-499-7111. Additional time services are available from the National Institute of Standards and Technology.

A4. CALCULATION OF ACCEPTABLE TOLERANCE ZONE (BAND) TO DETERMINE CONFORMANCE WITH A CERTIFIED REFERENCE MATERIAL

A4.1 Determine the standard deviation for site uncertainty, σ_{site}, from a laboratory quality control program.

A4.1.1 If the standard deviation for site uncertainty, σ_{site}, is not known, use the value 0.19%.

A4.2 Determine the combined extended uncertainty (CEU) of the accepted reference value (ARV) of the certified reference material (CRM) from the supplier's label or included documentation.

A4.3 Calculate the standard error of the accepted reference value (SEARV) by dividing the CEU by the coverage factor, *k*, listed on the supplier's label or included documentation.

A4.3.1 If the coverage factor, *k*, is not known, use the value 2.

A4.4 Construct the acceptable tolerance zone:

$$TZ = \pm 1.44\sqrt{\sigma_{site}^2 + SE_{ARV}^2}$$

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 445–06) that may impact the use of this standard.

(*1*) Change determinability requirements for materials of unknown precision in 11.2.4 as a temporary measure pending revision of the Precision and Bias section.

APPENDIX 2

ASTM D941-88

Designation: D 941 – 88

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An American National Standard

Standard Test Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer[1]

This standard is issued under the fixed designation D 941; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense to replace Method 402 of Test Method Standard No 791b. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This test method covers the measurement of the density of any hydrocarbon material that can be handled in a normal fashion as a liquid at the specified test temperatures of 20 to 25°C. Its application is restricted to liquids having vapor pressures less than 80 kPa (600 mm Hg) and having viscosities less than 15 mm^2/s (cst) at 20°C.

1.2 Two procedures are covered as follows:

1.2.1 *Procedure A*, for pure compounds and mixtures which are not highly volatile.

1.2.2 *Procedure B*, for highly volatile mixtures.

1.3 This test method provides a calculation procedure for converting density to relative density.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Notes 1, 2, 6 and Annex A1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1250 Petroleum Measurement Tables[2]

E 1 Specification for ASTM Thermometers[3]

3. Terminology

3.1 *density*—mass per unit volume.

3.1.1 *Discussion*— In this test method, the measurement is at any given temperature and the units are grams per millilitre.

3.1.2 *relative density*—the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

4. Summary of Test Method[4]

4.1 The liquid sample is drawn into the pycnometer and weighed. It is then equilibrated at the test temperature, and the positions of the liquid levels are observed. The density or relative density of the sample is then calculated from its weight, a calibration factor proportional to an equal volume of water, and a term that corrects for the buoyancy of air.

5. Significance and Use

5.1 Density is a fundamental physical property which can be used in conjunction with other properties to characterize both the light and heavy fractions of petroleum and to assess the quality of crude oils.

5.2 Determination of the density or relative density of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperatures of 15°C or 60°F.

6. Apparatus

6.1 *Pycnometer*—A pycnometer conforming to the dimensions given in Fig. 1, constructed of borosilicate glass, and having a total weight not exceeding 30 g.

6.2 *Constant-Temperature Bath*—A water bath having a depth of at least 12 in. (305 mm), provided with means for maintaining a temperature of 20 ± 0.02°C or 25 ± 0.02°C.

6.3 *Bath Thermometer*—No suitable ASTM Celsius thermometers are available; ASTM Kinematic Viscosity Thermometers 44F and 45F designed for tests at 68°F (20°C) and 77°F (25°C) and conforming to the requirements prescribed in Specification E 1 are therefore specified. Ice point and bore corrections must be known to the nearest 0.02°F. In use, the thermometers must be immersed to a point at least 2°F above the test temperature.

6.4 *Pycnometer Holder*—Figure 2 shows the structural details of the holder proper. It can be made of brass or any other available metal that can be hard- or soft-soldered and that will not corrode in the thermostat liquid. Figure 3 illustrates a convenient mounting for suspending the holders in the thermostat. It consists of a brass bar ⅛ in. (3.2 mm) in thickness by 1 in. (25 mm) in width, of a length suitable for

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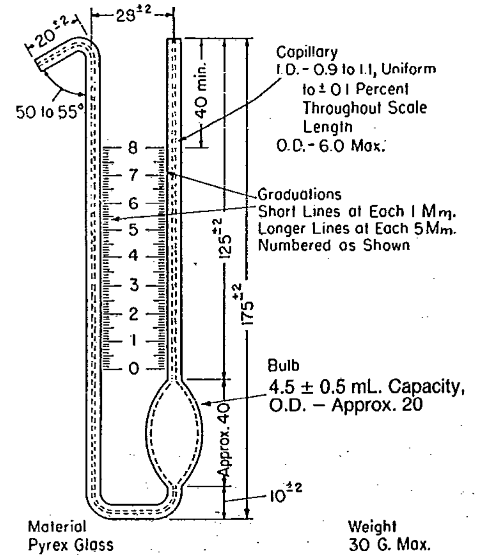
[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved Oct 31, 1988. Published December 1988. Originally published as D 941 – 47. Last previous edition D 941 – 83.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vols 05.03 and 14.01.

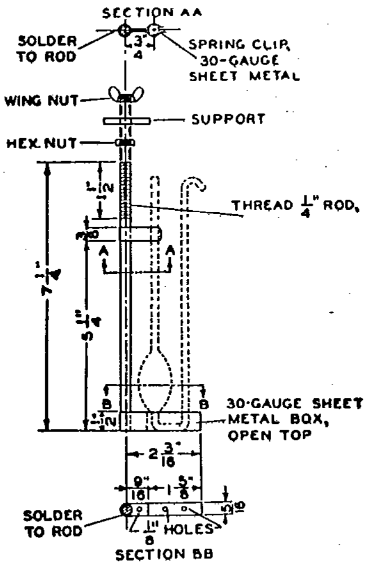
[4] For a more complete discussion of this method, see Davidson, J. A., Harvey, T., Kurtz, S. S., Jr., Lipkin, M. R., "Pycnometer for Volatile Liquids," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA Vol 16, No. 1, 1944, p. 55 and H. M. Smith, and Cooperators, "Measurement of Density of Hydrocarbon Liquids by the Pycnometer," *Analytical Chemistry*, ANCHA Vol 22, Nov. 1952, p. 1452.



All Dimensions in Millimetres

NOTE—The graduation lines shall extend around the entire circumference of the pycnometer at the integral numbers 0, 1, 2 cm, etc., half way around at the half divisions 0.5, 1.5, etc., and shorter lines for the intermediate subdivisions.

FIG. 1 Pycnometer



Metric Equivalents

in.	mm	in.	mm
5/16	7.94	3/4	19
9/16	14.3	1 1/2	38
1/8	3.2	1 5/8	41.3
3/8	9.53	2 3/16	55.6
1/4	6.4	5 1/4	133.4
1/2	12.7	7 1/4	184.2

FIG. 2 Pycnometer Holder

the bath used, and with seven 9/32-in. (7.144 mm) holes drilled 1½ in. (38.1 mm) apart to accommodate the threaded ends of the holders. Two nuts support each holder and permit regulation of the depth of immersion of the pycnometers.

6.5 *Balance*—A balance able to reproduce weighings within 0.1 mg when carrying a load of 30 g or less on each pan. The balance is to be located in a room shielded from drafts and fumes and in which the temperature changes between related weighings (empty and filled pycnometer) do not cause a significant change in the ratio of the balance arms. Otherwise weighings must be made by the substitution method in which the calibrated weights and pycnometer are alternately weighed on the same balance pan. The same balance shall be used for all related weighings.

6.6 *Weights*—Weights are to be used whose relative values are known to the nearest 0.05 mg, or better. The same set of weights shall be used for the calibration of the pycnometer and the determination of the densities, or the sets of weights shall be calibrated relative to each other.

7. Preparation of Apparatus

7.1 Thoroughly clean the pyncometer with hot chromic acid. (**Warning**—See Note 1.) Chromic acid solution is the most effective cleaning agent. However, surfactant cleaning fluids have also been used successfully. Rinse well with distilled water and dry at 105 to 110°C for at least 1 h, preferably with a slow current or filtered air passing through the pycnometer. Cleaning is to be done in this manner whenever the pycnometer is to be calibrated or whenever liquid fails to drain cleanly from the walls of the pycnometer or its capillary. Ordinarily, the pyncometer can be cleaned between determinations by washing with a suitable solvent, such as isopentane or acetone (**Warning**—See Note 2.) and vacuum drying. If acetone is used as the wash liquid, the pycnometer is then to be rinsed with isopentane.

NOTE 1: **Warning**—Causes severe burns. A recognized carcinogen. See Annex A1.1.

NOTE 2: **Warning**—Extremely flammable. See Annexes A1.2, A1.3.

8. Calibration of Apparatus

8.1 Proceeding as directed in Section 9, determine the weight of freshly boiled distilled water held by the pycnometer when equilibrated at the test temperature (20 or 25°C) with the water level at each of three different scale points on the graduated arms, two of which are to be at opposite ends of the scale. Prepare a calibration curve by plotting the sum of the scale readings on the two arms of the pycnometer against the corresponding apparent volume. If this curve is not a straight line, and subsequent checks do not correct the curvature, discard the pycnometer as imperfect, unless a line conforming to 8.2 can be obtained. Obtain the apparent volume in millilitres by dividing the weight of the water held in the pycnometer by the density of water at 20°C (0.99823 g/mL), or at 25°C (0.99707 g/mL).

NOTE 3—The apparent volume differs from the true volume by the amount of the air buoyancy correction on the weight of water contained in the pycnometer.

8.2 If a straight line cannot be drawn through the three points, determine enough additional points so that a straight line calibration can be drawn which does not lie more than 0.0002 mL in units from the points used to determine the line.

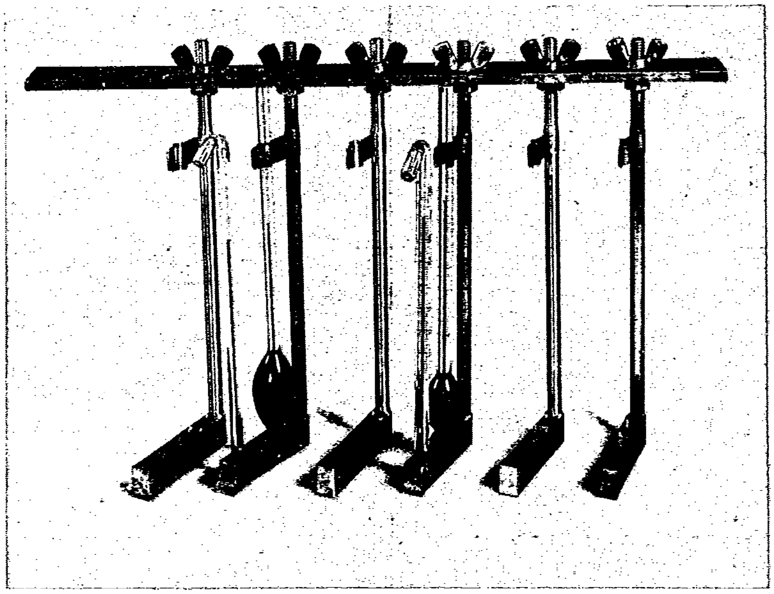


FIG. 3 Holder Mounting

9. Procedure A

9.1 Procedure A is intended for pure compounds and mixtures that are not highly volatile, that is, which are essentially free from materials boiling below 20°C.

9.2 Weigh the clean, dry pycnometer to 0.1 mg and record the weight.

9.3 Fill the pycnometer with the sample at approximately the test temperature by holding it in an upright position and placing the hooked tip in the sample, allowing the liquid to be drawn over the bend in the capillary by surface tension. Allow the pycnometer to fill by siphoning (requiring about 1 min) and break the siphon when the liquid level in the bulb arm of the pycnometer reaches the lowest calibration mark.

9.4 Wipe off the wet tip thoroughly (Note 4) with a chemically clean, lint-free cloth slightly damp with water and weigh to the nearest 0.1 mg.

NOTE 4—In atmospheres of low humidity (60 % or lower) drying the pycnometer by rubbing with dry cotton cloth will induce static charges equivalent to a loss of about 1 mg or more in the weight of the pycnometer. If this charge is not dissipated in less than ½ h it can be detected by touching the pycnometer to the wire hook on the balance and then drawing it away slowly. If the pycnometer exhibits an attraction for the wire hook, it may be considered to have a static charge.

9.5 Place the pycnometer in the holder in a constant temperature bath adjusted to the test temperature (20 to 25°C) within ±0.02°C. When the liquid level has reached equilibrium (usually in about 10 min), read the scale to the nearest 0.2 small division at the liquid level in each arm.

TABLE 1 Air Buoyancy Corrections

W/V	Correction,[A] plus	W/V	Correction,[A] plus
0.70	0.00036	0.85	0.00018
0.71	0.00035	0.86	0.00017
0.72	0.00033	0.87	0.00016
0.73	0.00032	0.88	0.00014
0.74	0.00031	0.89	0.00013
0.75	0.00030	0.90	0.00012
0.76	0.00029	0.91	0.00011
0.77	0.00028	0.92	0.00010
0.78	0.00026	0.93	0.00009
0.79	0.00025	0.94	0.00007
0.80	0.00024	0.95	0.00006
0.81	0.00023	0.96	0.00005
0.82	0.00022	0.97	0.00004
0.83	0.00020	0.98	0.00003
0.84	0.00019	0.99	0.00001

[A] This table applies for all air density values between 0.0011 and 0.0013 g/mL. For air densities outside this range, the air buoyancy correction, C, should be calculated as follows:

$$C = (d_a/0.99823) \times [0.99823 - (W/V)]$$

where:

C = air buoyancy correction,
d_a = density of air in the balance case, g/mL
W = weight of sample in pycnometer, and
V = volume of sample in pycnometer.

10. Procedure B

10.1 Procedure B is intended for highly volatile mixtures that contain appreciable amounts of material boiling below 20°C, or for any material where there is uncertainty concerning loss due to evaporation during the density determination.

10.2 Weigh the pycnometer as described in 9.2.

10.3 Cool the sample and pycnometer to a temperature of 0 to 5°C before filling. If the determination must be made when the dew point is high enough to cause condensation of moisture in the pycnometer, proper precautions should be taken to avoid this. Fill the pycnometer according to the procedure described in 9.3.

10.4 Place the pycnometer in the bath and read the volume as described in 9.5.

NOTE 5—If at any time during equilibration the level of the liquid rises above the scale graduations, cautiously apply air pressure to the opening of the bulb arm of the pycnometer and force a few drops of the sample from the bent arm.

10.5 Remove the pycnometer from the bath, rinse the outside with acetone, then with clean isopentane (**Warning—**

TABLE 2 Density of Water

Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL	Temperature, °C	Density, g/mL
0	0.99987	21	0.99802	40	0.99224
3	0.99999	22	0.99780	45	0.99025
4	1.00000	23	0.99756	50	0.98807
5	0.99999	24	0.99732	55	0.98573
10	0.99973	25	0.99707	60	0.98324
15	0.99913	26	0.99681	65	0.98059
15.56	0.99904	27	0.99654	70	0.97781
16	0.99897	28	0.99626	75	0.97489
17	0.99880	29	0.99597	80	0.97183
18	0.99862	30	0.99567	85	0.96865
19	0.99843	35	0.99406	90	0.96534
20	0.99823	37.78	0.99307	100	0.95838

See Note 6.) and dry thoroughly (see Note 4) with a chemically clean, lint-free cloth, slightly damp with water. Weigh to the nearest 0.1 mg.

NOTE 6: **Warning**—Extremely flammable. See Annex A1.2, A1.3.

11. Calculation

11.1 Calculate the density of the sample as follows:

$$D = (W/V) + C$$

where:

D = density, g/mL at 20 or 25°C,

W = weight, g, in air of sample contained in the pycnometer at the test temperature (20 or 25°C),

V = apparent volume, mL, corresponding to the sum of the scale readings on the two arms of the pycnometer, as obtained from the calibration curve, and

C = air buoyancy correction, as obtained from Table 1.

11.2 Calculate the relative density of the sample at t_1/t_2 by dividing the density as calculated in 11.1 by the density of water at the reference temperature, t_2, as obtained from Table 2. Relative density at t_1/15.56°C (t_1/60°F where t is expressed in degrees F) can be changed to the conventional 15.56/15.56°C (60/60°F) by use of the appropriate relative density Table 23 in Standard D 1250, provided that the glass expansion factor has been excluded.

12. Report

12.1 In reporting density, give the test temperature and the units (For example: Density at 20°C = x.xxxx g/mL). In reporting relative density, give both the test temperature and the reference temperature, but no units (For example: relative density, 15.56/15.56°C = x.xxxx). Carry out all calculations to five figures, and round off the final result to four figures.

13. Precision and Bias

13.1 The precision and bias of the test method as obtained by statistical examination of interlaboratory test results is as follows.

13.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed 0.0001 g/mL only in one case in twenty.

13.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed 0.0002 g/mL only in one case in twenty.

13.1.3 *Bias*—The subcommittee is presently working on the development of a bias statement.

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Chromic Acid (Cleaning Solution)

Do not get in eyes, on skin, or on clothing.
Avoid breathing vapor or mist.
Keep container closed.
Use with adequate ventilation.
Do not take internally.
Wash thoroughly after handling.
Use protective clothing and goggles when handling.

A1.2 Isopentane

Harmful if inhaled. Vapors may cause flash fire.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid build-up of vapors and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

A1.3 Acetone

Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Vapors may spread long distances and ignite explosively.
Avoid build-up of vapors, and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid contact with eyes or skin.

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APPENDIX 3

ASTM D 2500

Designation: D 2500 – 09

An American National Standard
British Standard 4458

Designation: 219/82

Standard Test Method for Cloud Point of Petroleum Products[1]

This standard is issued under the fixed designation D 2500; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C.

NOTE 1—The interlaboratory program consisted of petroleum products of Test Method D 1500 color of 3.5 and lower. The precisions stated in this test method may not apply to samples with ASTM color higher than 3.5.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standard:*[3]

Specifications for IP Standard Thermometers

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *biodiesel*, *n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.1.1 *Discussion*—Biodiesel is typically produced by a reaction of vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-esters and glycerin. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME).

3.1.2 *biodiesel blend*, *n*—a blend of biodiesel fuel with petroleum-based diesel fuel designated BXX, where XX is the volume % of biodiesel.

3.1.3 *cloud point*, *n—in petroleum products and biodiesel fuels,* the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions.

3.1.3.1 *Discussion*—To many observers, the cluster of wax crystals looks like a patch of whitish or milky cloud, hence the name of the test method. The cloud appears when the temperature of the specimen is low enough to cause wax crystals to form. For many specimens, the crystals first form at the lower circumferential wall of the test jar where the temperature is lowest. The size and position of the cloud or cluster at the cloud point varies depending on the nature of the specimen. Some samples will form large, easily observable, clusters, while others are barely perceptible.

3.1.3.2 *Discussion*—Upon cooling to temperatures lower than the cloud point, clusters of crystals will grow in multiple directions; for example, around the lower circumference of the test jar, towards the center of the jar, or vertically upwards. The crystals can develop into a ring of cloud along the bottom circumference, followed by extensive crystallization across the bottom of the test jar as temperature decreases. Nevertheless, the cloud point is defined as the temperature at which the crystals first appear, not when an entire ring or full layer of wax has been formed at the bottom of the test jar.

3.1.3.3 *Discussion*—In general, it is easier to detect the cloud point of samples with large clusters that form quickly, such as paraffinic samples. The contrast between the opacity of the cluster and the liquid is also sharper. In addition, small brightly-reflective spots can sometimes be observed inside the cluster when the specimen is well illuminated. For other more difficult samples, such as naphthenic, hydrocracked, and those samples whose cold flow behavior have been chemically

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved April 15, 2009. Published April 2009. Originally approved in 1966. Last previous edition approved in 2005 as D 2500–05.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

***A Summary of Changes section appears at the end of this standard.**

altered, the appearance of the first cloud can be less distinct. The rate of crystal growth is slow, the opacity contrast is weak, and the boundary of the cluster is more diffuse. As the temperature of these specimens decrease below the cloud point, the diffuse cluster will increase in size and can form a general haze throughout. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature of the specimen decreases, can also be caused by traces of water in the specimen instead of crystal formation (see Note 3). With these difficult samples, drying the sample prior to testing can eliminate this type of interference.

3.1.3.4 *Discussion*—The purpose of the cloud point method is to detect the presence of the wax crystals in the specimen; however trace amounts of water and inorganic compounds may also be present. The intent of the cloud point method is to capture the temperature at which the liquids in the specimen begin to change from a single liquid phase to a two-phase system containing solid and liquid. It is not the intent of this test method to monitor the phase transition of the trace components, such as water.

4. Summary of Test Method

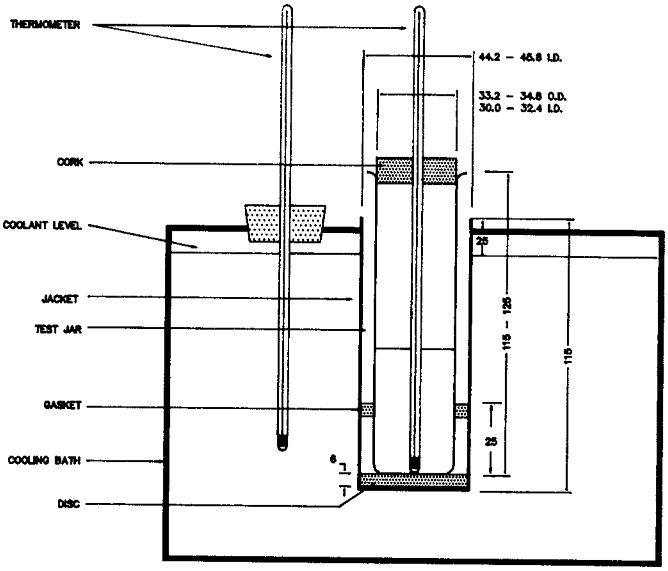
4.1 The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

5. Significance and Use

5.1 For petroleum products and biodiesel fuels, cloud point of a petroleum product is an index of the lowest temperature of their utility for certain applications.

6. Apparatus (see Fig. 1)

6.1 *Test Jar*, clear, cylindrical glass, flat bottom, 33.2 to 34.8-mm outside diameter and 115 and 125-mm height. The inside diameter of the jar may range from 30 to 32.4 mm within the constraint that the wall thickness be no greater than 1.6 mm. The jar should be marked with a line to indicate sample height 54 ± 3 mm above the inside bottom.



NOTE—All dimensions are in millimetres.

FIG. 1 Apparatus for Cloud Point Test

6.2 *Thermometers*, having ranges shown below and conforming to the requirements as prescribed in Specification E 1 or Specifications for IP Standard Thermometers.

Thermometer	Temperature Range	Thermometer Number ASTM	Thermometer Number IP
High cloud and pour	–38 to +50°C	5C	1C
Low cloud and pour	–80 to +20°C	6C	2C

6.3 *Cork*, to fit the test jar, bored centrally for the test thermometer.

6.4 *Jacket*, metal or glass, watertight, cylindrical, flat bottom, about 115 mm in depth, with an inside diameter of 44.2 to 45.8 mm. It shall be supported free of excessive vibration and firmly in a vertical position in the cooling bath of 6.7 so that not more than 25 mm projects out of the cooling medium.

6.5 *Disk*, cork or felt, 6-mm thick to fit loosely inside the jacket.

6.6 *Gasket*, ring form, about 5 mm in thickness, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

6.7 *Bath or Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable cooling mixtures. Cooling mixtures commonly used for bath temperatures shown are in Table 1.

7. Reagents and Materials

7.1 *Acetone*—Technical grade acetone is suitable for the cooling bath, provided it does not leave a residue on drying. (**Warning—**Extremely flammable.)

7.2 *Carbon Dioxide (Solid) or Dry Ice*—A commercial grade of dry ice is suitable for use in the cooling bath.

7.3 *Petroleum Naphtha*—A commercial or technical grade of petroleum naphtha is suitable for the cooling bath. (**Warning—**Combustible. Vapor harmful.)

7.4 *Sodium Chloride Crystals*—Commercial or technical grade sodium chloride is suitable.

7.5 *Sodium Sulfate*—A reagent grade of anhydrous sodium sulfate should be used when required (see Note 3).

TABLE 1 Cooling Mixtures and Bath Temperatures

	Bath Temperature
Ice and water	0 ± 1.5°C
Crushed ice and sodium chloride crystals, or acetone or petroleum naptha (see 7) with solid carbon dioxide added to give the desired temperature	–18 ± 1.5°C
Acetone or petroleum naptha (see 7) with solid carbon dioxide added to give the desired temperature	–33 ± 1.5°C
Acetone or petroleum naptha (see 7) with solid carbon dioxide added to give the desired temperature	–51 ± 1.5°C
Acetone or petroleum naptha (see 7) with solid carbon dioxide added to give the desired temperature	–69 ± 1. 5°C

8. Procedure

8.1 Bring the sample to be tested to a temperature at least 14°C above the expected cloud point. Remove any moisture present by a method such as filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature of at least 14°C above the approximate cloud point.

8.2 Pour the sample into the test jar to the level mark.

8.3 Close the test jar tightly by the cork carrying the test thermometer. Use the high cloud and pour thermometer if the expected cloud point is above −36°C and the low cloud and pour thermometer if the expected cloud point is below −36°C. Adjust the position of the cork and the thermometer so that the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is resting on the bottom of the jar.

NOTE 2—Liquid column separation of thermometers occasionally occurs and may escape detection. Thermometers should be checked periodically and used only if their ice points are 0 ± 1°C, when the thermometer is immersed to the immersion line in an ice bath, and when the emergent column temperature does not differ significantly from 21°C. Alternatively, immerse the thermometer to a reading and correct for the resultant cooler stem temperature.

8.4 See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. The disk and jacket shall have been placed in the cooling medium a minimum of 10 min before the test jar is inserted. The use of a jacket cover while the empty jacket is cooling is permitted. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

NOTE 3—Failure to keep the disk, gasket, and the inside of the jacket clean and dry may lead to frost formation, which may cause erroneous results.

8.5 Maintain the temperature of the cooling bath at 0 ± 1.5°C.

8.6 At each test thermometer reading that is a multiple of 1°C, remove the test jar from the jacket quickly but without disturbing the specimen, inspect for cloud, and replace in the jacket. This complete operation shall require not more than 3 s. If the oil does not show a cloud when it has been cooled to 9°C, transfer the test jar to a jacket in a second bath maintained at a temperature of −18 ± 1.5°C (see Table 2). Do not transfer the jacket. If the specimen does not show a cloud when it has been cooled to −6°C, transfer the test jar to a jacket in a third bath maintained at a temperature of −33± 1.5°C. For the determination of very low cloud points, additional baths are required, each bath to be maintained in accordance with Table 2. In each case, transfer the jar to the next bath, if the specimen does not exhibit cloud point and the temperature of the specimen reaches the lowest specimen temperature in the range identified for the current bath in use, based on the ranges stated in Table 2.

TABLE 2 Bath and Sample Temperature Ranges

Bath	Bath Temperature Setting, °C	Sample Temperature Range, °C
1	0 ± 1.5	Start to 9
2	−18 ± 1.5	9 to −6
3	−33 ± 1.5	−6 to −24
4	−51 ± 1.5	−24 to −42
5	−69 ± 1.5	−42 to −60

8.7 Report the cloud point, to the nearest 1°C, at which any cloud is observed at the bottom of the test jar, which is confirmed by continued cooling.

NOTE 4—A wax cloud or haze is always noted first at the bottom of the test jar where the temperature is lowest. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature is lowered, is usually due to traces of water in the oil. Generally this water haze will not interfere with the determination of the wax cloud point. In most cases of interference, filtration through dry lintless filter papers, such as described in 8.1, is sufficient. In the case of diesel fuels, however, if the haze is very dense, a fresh portion of the sample should be dried by shaking 100 mL with 5 g of anhydrous sodium sulfate for at least 5 min and then filtering through dry lintless filter paper. Given sufficient contact time, this procedure will remove or sufficiently reduce the water haze so that the wax cloud can be readily discerned. Drying and filtering should be done always at a temperature at least 14°C above the approximate cloud point but otherwise not in excess of 49°C.

9. Report

9.1 Report the temperature recorded in 8.7 as the cloud point, Test Method D 2500.

10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 4°C only in 1 case in 20.

10.1.3 The precision statements were derived from a 1990 interlaboratory cooperative test program.[4] Participants analyzed 13 sample sets comprised of various distillate fuels and lubricating oils with temperature range from -1 to -37°C. Eight laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

10.2 *Bias*—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

10.3 *Precision for Biodiesel Products*[5]—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.3.1 *Repeatability for Blends of Biodiesel in Diesel*—The difference between successive test results obtained by the same operator, using the same apparatus, under constant operating

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1444.

[5] Supporting data (the results of the 2001 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1524.

conditions, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.3.2 *Reproducibility for Blends of Biodiesel in Diesel*—The difference between two single and independent test results obtained by different operators, working in different laboratories, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 3°C only in 1 case in 20.

NOTE 5—The precision for blends of biodiesel in diesel samples comprised cloud points from about −2 to +10°C.

10.3.3 The precision statements were derived from a 2001 interlaboratory cooperative test program.[5] Participants analyzed eleven sample sets comprised of different blends of two petroleum distillate fuels, diesel and kerosene, with various biodiesel fuels with temperature range from +10 to −45°C. Ten laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

NOTE 6—One of the outcomes of the interlaboratory study was the selection of the sample types, since the ones used in the study contributed to a difficulty in determining the precision statement. Kerosene is a sufficiently different fuel type from biodiesel to cause some slight separation of phases upon cooling when in B20 blends. Also, the particular kerosene sample used was atypical, which complicated the study further. Therefore, data from the blends of kerosene in biodiesel were not used in the precision statement. In addition, the diesel fuel used in the research report was high cloud point material. Due to the cloud point of the base diesel material, this temperature range in the precision statement was limited.

NOTE 7—A future interlaboratory cloud study will be done to include a wider range of base biodiesel fuels with various distillate blend stocks.

10.4 *Bias for Biodiesel Products*[5]—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

11. Keywords

11.1 cloud point; petroleum products; wax crystals

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 2500–05) that may impact the use of this standard.

(*1*) Revised 6.7.
(*2*) Revised 7.
(*3*) Added Table 1.
(*4*) Deleted original Note 2.

APPENDIX 4

ASTM D 97-05

Designation: D 97 – 05

An American National Standard

Designation: 15/95

Standard Test Method for Pour Point of Petroleum Products[1]

This standard is issued under the fixed designation D 97; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method is intended for use on any petroleum product.[2] A procedure suitable for black specimens, cylinder stock, and nondistillate fuel oil is described in 8.8. A procedure for testing the fluidity of a residual fuel oil at a specified temperature is described in Appendix X1.

1.2 Several ASTM test methods offering alternative procedures for determining pour points using automatic apparatus are available. None of them share the same designation number as Test Method D 97. When an automatic instrument is used, the ASTM test method designation number specific to the technique shall be reported with the results. A procedure for testing the pour point of crude oils is described in Test Method D 5853.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [3]

- D 117 Guide for Sampling, Test Methods, and Specifications for Electrical Insulating Oils of Petroleum Origin
- D 396 Specification for Fuel Oils
- D 1659 Test Method for Maximum Fluidity Temperature of Residual Fuel Oil[4]
- D 2500 Test Method for Cloud Point of Petroleum Products
- D 3245 Test Method for Pumpability of Industrial Fuel Oils
- D 5853 Test Method for Pour Point of Crude Oils
- E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standards:*

Specifications for IP Standard Thermometers [5]

3. Terminology

3.1 *Definitions:*

3.1.1 *black oil*, *n*—lubricant containing asphaltic materials. Black oils are used in heavy-duty equipment applications, such as mining and quarrying, where extra adhesiveness is desired.

3.1.2 *cylinder stock*, *n*—lubricant for independently lubricated engine cylinders, such as those of steam engines and air compressors. Cylinder stock are also used for lubrication of valves and other elements in the cylinder area.

3.1.3 *pour point*, *n*—*in petroleum products*, the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.

3.1.4 *residual fuel*, *n*—a liquid fuel containing bottoms remaining from crude distillation or thermal cracking; sometimes referred to as heavy fuel oil.

3.1.4.1 *Discussion*—Residual fuels comprise Grades 4, 5, and 6 fuel oils, as defined in Specification D 396.

4. Summary of Test Method

4.1 After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved June 1, 2005. Published July 2005. Originally approved in 1927, replacing D 47. Last previous edition approved in 2004 as D 97–04.

In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method was adopted as a joint ASTM-IP Standard in 1965.

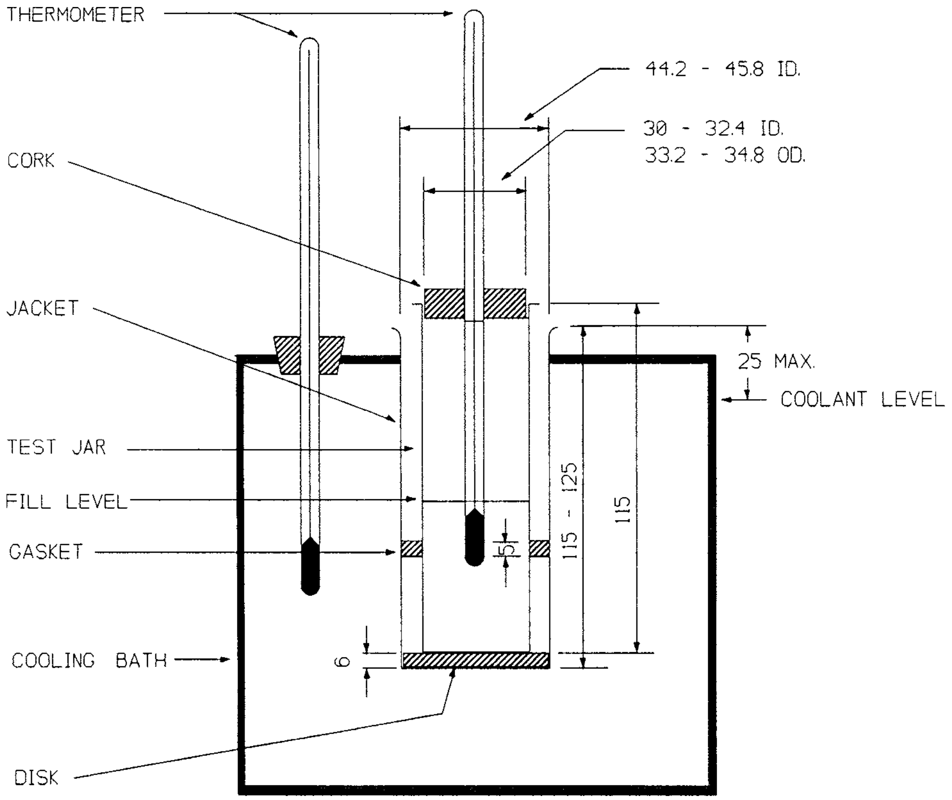
[2] Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in Guide D 117.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] Withdrawn.

[5] Methods for Analysis and Testing, *IP Standards for Petroleum and its Products*, Part I, Vol 2.

***A Summary of Changes section appears at the end of this standard.**



NOTE—Dimensions are in millimetres (not to scale).

FIG. 1 Apparatus for Pour Point Test

5. Significance and Use

5.1 The pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications.

6. Apparatus

6.1 *Test Jar*, cylindrical, of clear glass, flat bottom, 33.2 to 34.8-mm outside diameter, and 115 to 125 mm in height. The inside diameter of the jar can range from 30.0 to 32.4 mm, within the constraint that the wall thickness be no greater than 1.6 mm. The jar shall have a line to indicate a sample height 54 ± 3 mm above the inside bottom. See Fig. 1.

6.2 *Thermometers*, having the following ranges and conforming to the requirements prescribed in Specification E 1 for thermometers:

	Temperature	Thermometer Number	
Thermometer	Range	ASTM	IP
High cloud and pour	−38 to +50°C	5C	1C
Low cloud and pour	−80 to +20°C	6C	2C
Melting point	+32 to +127°C	61C	63C

6.2.1 Since separation of liquid column thermometers occasionally occurs and may escape detection, thermometers should be checked immediately prior to the test and used only if they prove accurate within ±1°C (for example ice point).

6.3 *Cork*, to fit the test jar, bored centrally for the test thermometer.

6.4 *Jacket*, watertight, cylindrical, metal, flat-bottomed, 115 ± 3-mm depth, with inside diameter of 44.2 to 45.8 mm. It shall be supported in a vertical position in the cooling bath (see 6.7) so that not more than 25 mm projects out of the cooling medium, and shall be capable of being cleaned.

6.5 *Disk*, cork or felt, 6 mm thick to fit loosely inside the jacket.

6.6 *Gasket*, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

6.7 *Bath or Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be obtained by refrigeration if available, otherwise by suitable freezing mixtures. Freezing mixtures commonly used for temperatures down to those shown are as follows:

	For Temperatures Down
Ice and water	9°C
Crushed ice and sodium chloride crystals	−12°C
Crushed ice and calcium chloride crystals	−27°C
Acetone or petroleum naphtha (see Section 6) chilled in a covered metal beaker with an ice-salt mixture to −12°C then with enough solid carbon dioxide to give the desired temperature.	−57°C

7. Reagents and Materials

7.1 The following solvents of technical grade are appropriate for low-temperature bath media.

7.1.1 *Acetone*, (**Warning**—Extremely flammable).

7.1.2 *Alcohol, Ethanol* (**Warning**—Flammable).

7.1.3 *Alcohol, Methanol* (**Warning**—Flammable. Vapor harmful).

7.1.4 *Petroleum Naphtha*, (**Warning**—Combustible. Vapor harmful).

7.1.5 *Solid Carbon Dioxide*, (**Warning**—Extremely cold −78.5°C).

8. Procedure

8.1 Pour the specimen into the test jar to the level mark. When necessary, heat the specimen in a water bath until it is just sufficiently fluid to pour into the test jar.

NOTE 1—It is known that some materials, when heated to a temperature higher than 45°C during the preceding 24 h, do not yield the same pour point results as when they are kept at room temperature for 24 h prior to testing. Examples of materials which are known to show sensitivity to thermal history are residual fuels, black oils, and cylinder stocks.

8.1.1 Samples of residual fuels, black oils, and cylinder stocks which have been heated to a temperature higher than 45°C during the preceding 24 h, or when the thermal history of these sample types is not known, shall be kept at room temperature for 24 h before testing. Samples which are known by the operator not to be sensitive to thermal history need not be kept at room temperature for 24 h before testing.

8.1.2 Experimental evidence supporting elimination of the 24-h waiting period for some sample types is contained in a research report.[6]

8.2 Close the test jar with the cork carrying the high-pour thermometer (5.2). In the case of pour points above 36°C, use a higher range thermometer such as IP 63C or ASTM 61C. Adjust the position of the cork and thermometer so the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is immersed so the beginning of the capillary is 3 mm below the surface of the specimen.

8.3 For the measurement of pour point, subject the specimen in the test jar to the following preliminary treatment:

8.3.1 *Specimens Having Pour Points Above −33°C*—Heat the specimen without stirring to 9°C above the expected pour point, but to at least 45°C, in a bath maintained at 12°C above the expected pour point, but at least 48°C. Transfer the test jar to a water bath maintained at 24°C and commence observations for pour point.

8.3.2 *Specimens Having Pour Points of −33°C and Below*—Heat the specimen without stirring to 45°C in a bath maintained at 48°C and cool to 15°C in a water bath maintained at 6°C. Remove the high cloud and pour thermometer, and place the low cloud and pour thermometer in position.

8.4 See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

8.5 After the specimen has cooled to allow the formation of paraffin wax crystals, take great care not to disturb the mass of specimen nor permit the thermometer to shift in the specimen; any disturbance of the spongy network of wax crystals will lead to low and erroneous results.

8.6 Pour points are expressed in integers that are positive or negative multiples of 3°C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the expected pour point (estimated as a multiple of 3°C). At each test thermometer reading that is a multiple of 3°C below the starting temperature remove the test jar from the jacket. To remove condensed moisture that limits visibility wipe the surface with a clean cloth moistened in alcohol (ethanol or methanol). Tilt the jar just enough to ascertain whether there is a movement of the specimen in the test jar. The complete operation of removal, wiping, and replacement shall require not more than 3 s.

8.6.1 If the specimen has not ceased to flow when its temperature has reached 27°C, transfer the test jar to the next lower temperature bath in accordance with the following schedule:

Specimen is at +27°C, move to 0°C bath
Specimen is at +9°C, move to −18°C bath
Specimen is at −6°C, move to −33°C bath
Specimen is at −24°C, move to −51°C bath
Specimen is at −42°C, move to −69°C bath

8.6.2 As soon as the specimen in the jar does not flow when tilted, hold the jar in a horizontal position for 5 s, as noted by an accurate timing device and observe carefully. If the specimen shows any movement, replace the test jar immediately in the jacket and repeat a test for flow at the next temperature, 3°C lower.

8.7 Continue in this manner until a point is reached at which the specimen shows no movement when the test jar is held in a horizontal position for 5 s. Record the observed reading of the test thermometer.

8.8 For black specimen, cylinder stock, and nondistillate fuel specimen, the result obtained by the procedure described in 8.1 through 8.7 is the upper (maximum) pour point. If required, determine the lower (minimum) pour point by heating the sample while stirring, to 105°C, pouring it into the jar, and determining the pour point as described in 8.4 through 8.7.

8.9 Some specifications allow for a pass/fail test or have pour point limits at temperatures not divisible by 3°C. In these cases, it is acceptable practice to conduct the pour point measurement according to the following schedule: Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the specification pour point. Continue observations at 3°C intervals as described in 8.6 and 8.7 until the specification temperature is reached. Report the sample as passing or failing the specification limit.

9. Calculation and Report

9.1 Add 3°C to the temperature recorded in 8.7 and report the result as the Pour Point, ASTM D 97. For black oil, and so forth, add 3°C to the temperature recorded in 8.7 and report the

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1377.

result as Upper Pour Point, ASTM D 97, or Lower Pour Point, ASTM D 97, as required.

10. Precision and Bias

10.1 *Lubricating Oil and Distillate and Residual Fuel Oil.*[7]

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 3°C only in one case in twenty. Differences greater than this should be considered suspect.

10.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 6°C only in one case in twenty. Differences greater than this should be considered suspect.

10.2 *Bias*—There being no criteria for measuring bias in these test-product combinations, no statement of bias can be made.

10.3 The precision statements were prepared with data on ten new (unused) mineral oil-based lubricants and sixteen assorted fuel oils tested by twelve cooperators. The mineral oil-based lubricants had pour points ranging from −48 to −6°C while the fuel oils had pour points ranging from −33 to +51°C. The following precision data were obtained:

	Mineral Oil Lubricants	Fuel Oils
95 % Confidence		
Repeatability, °C	2.87	2.52
Reproducibility, °C	6.43	6.59

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[7] The cloud point procedure formerly part of this test method now appears as Test Method D 2500.

APPENDIX

(Nonmandatory Information)

X1. TEST FOR FLUIDITY OF A RESIDUAL FUEL OIL AT A SPECIFIED TEMPERATURE

X1.1 General

X1.1.1 The low-temperature flow properties of a waxy fuel oil depend on handling and storage conditions. Thus, they may not be truly indicated by pour point. The pour point test does not indicate what happens when an oil has a considerable head of pressure behind it, such as when gravitating from a storage tank or being pumped along a pipeline. Failure to flow at the pour point is normally attributed to the separation of wax from the fuel; however, it can also be due to the effect of viscosity in the case of very viscous fuel oils. In addition pour points of residual fuels are influenced by the previous thermal history of the specimens. A loosely knit wax structure built up on cooling of the oil can be normally broken by the application of relatively little pressure.

X1.1.2 The usefulness of the pour point test in relation to residual fuel oils is open to question, and the tendency to regard the pour point as the limiting temperature at which a fuel will flow can be misleading. The problem of accurately specifying the handling behavior of fuel oil is important, and because of the technical limitations of the pour point test, various pumpability tests have been devised to assess the low-temperature flow characteristics of heavy residual fuel oils. Test Method D 3245 is one such method. However, most alternative methods tend to be time-consuming and as such do not find ready acceptance as routine control tests for determining low-temperature flow properties. One method which is relatively quick and easy to perform and has found limited acceptance as a "go-no-go" method is based on the appendix method to the former Test Method D 1659–65. The method is described as follows.

X1.2 Scope

X1.2.1 This method covers the determination of the fluidity of a residual fuel oil at a specified temperature in an as-received condition.

X1.3 Definition

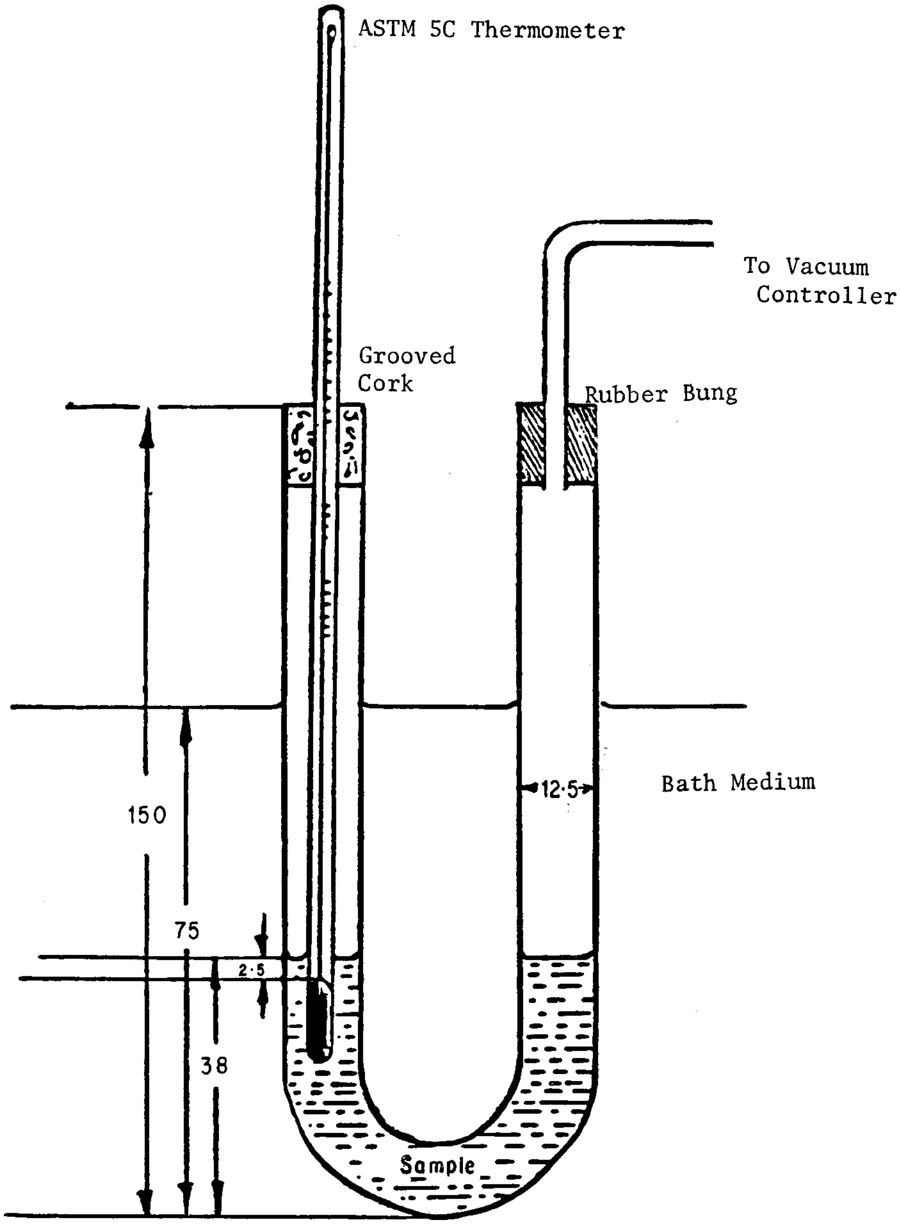
X1.3.1 *fluidity temperature*—the sample when tested in an as-received condition is considered "fluid at the temperature of the test" if it will flow 2 mm in 1 min in a 12.5 mm U-tube under a maximum pressure of 152 mm of mercury.

X1.4 Summary of Test Method

X1.4.1 A sample of fuel in its as-received condition is cooled at the specified temperature for 30 min in the standard U-tube and is tested for movement under prescribed pressure conditions.

X1.5 Significance and Use

X1.5.1 This method may be used as a "go-no-go" procedure for operational situations where it is necessary to ascertain the fluidity of a residual oil under prescribed conditions in an as-received condition. The conditions of this method simulate those of a pumping situation where the oil is expected to flow through a 12-mm pipe under slight pressure at a specified temperature. Fluidity, like Test Method D 97, is used to define cold flow properties. It differs from D 97, however, in that (*1*) it is restricted to residual fuel oil and (*2*) a prescribed pressure is applied to the sample. The latter represents an attempt to overcome the technical limitations of the Pour Point Method where gravity-induced flow is the criterion. Test Method



NOTE—All dimensions are in millimetres

FIG. X1.1 Disposition of U-tube in Fluidity Temperature Test Bath

D 3245, represents another method for predicting field performance in cold flow conditions. Test Method D 3245, however, does have limitations and may not be suitable for use with very waxy fuel oils which solidify so rapidly in the chilling bath that a reading cannot be obtained under the conditions of the test. It is also a time-consuming test and therefore not suitable for routine control testing.

X1.6 Apparatus

X1.6.1 *Glass U-Tubes*, 150 mm high, having a uniform internal diameter of 12.5 ± 1 mm and a radius of curvature, measured to the outside curve of the tube of 35 mm (Fig. X1.1).

X1.6.2 *Thermometers*—Thermometers having a range from −38 to +50°C and conforming to the requirements of Thermometer 5C as prescribed in Specification E 1, shall be used for insertion in the glass U-tubes and for measuring the temperatures of the baths.

X1.6.3 *Fluidity Temperature Test Bath,*[8]

consists of a reservoir, a stirrer, and a motor and pump to circulate coolant through the coils of the tubing placed in the bottom of the test bath and passing through the cold bath. The flow of coolant through these coils can be controlled by a thermostat and a solenoid valve. It is possible that, where justified by the quantity of work, more than one such bath could be utilized to permit concurrent testing at more than one temperature (Fig. X1.2).

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[8] A kinematic viscosity bath is usually satisfactory.

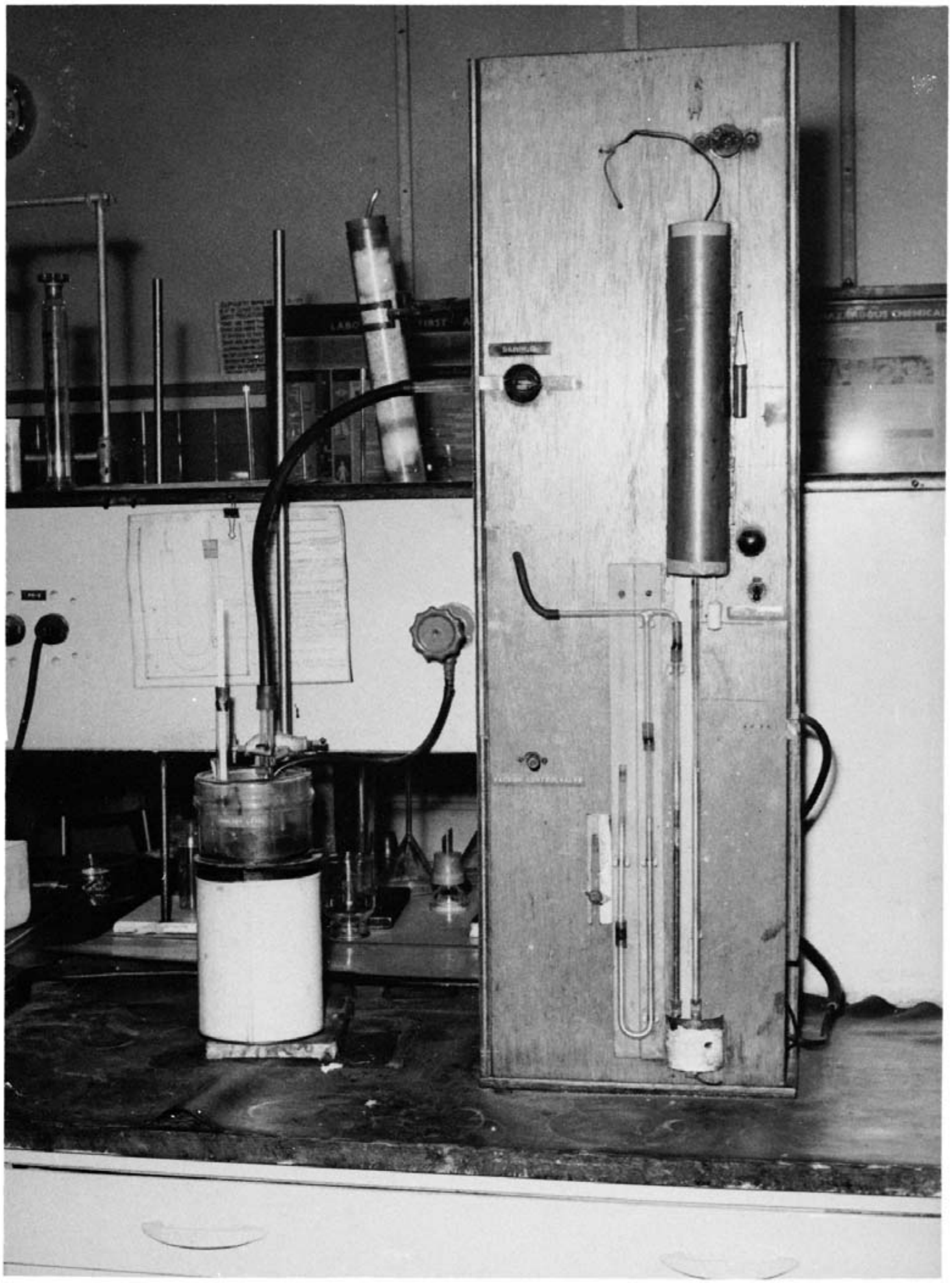

FIG. X1.2 Fluidity Temperature Apparatus

X1.6.4 *Mercury Manometer* calibrated in 10-mm divisions with a distinguishing mark at 152 mm (equivalent to 20.3 kPa).

X1.6.5 *Automatic Vacuum Controller*[9] *(as shown in Fig. X1.3 and Fig. X1.4)*—A device that gradually increased the vacuum applied to one end of the U-tube at the specified rate of 10 mm/4S.

X1.7 Preparation of Apparatus

X1.7.1 Adjust the automatic vacuum controller as follows: close the stopcock on the tube connecting the automatic vacuum controller to the fluidity tester. A pinchcock on the rubber tube will serve as well as a stopcock. Wind the thread attached to the steel rod around the pulley on the synchronous motor until the end of the rod is about 15 mm above the zero level of the mercury in the control manometer. Turn on the power switch. The thread will begin to unwind, lowering the steel rod. When the rod contacts the mercury, the relay will

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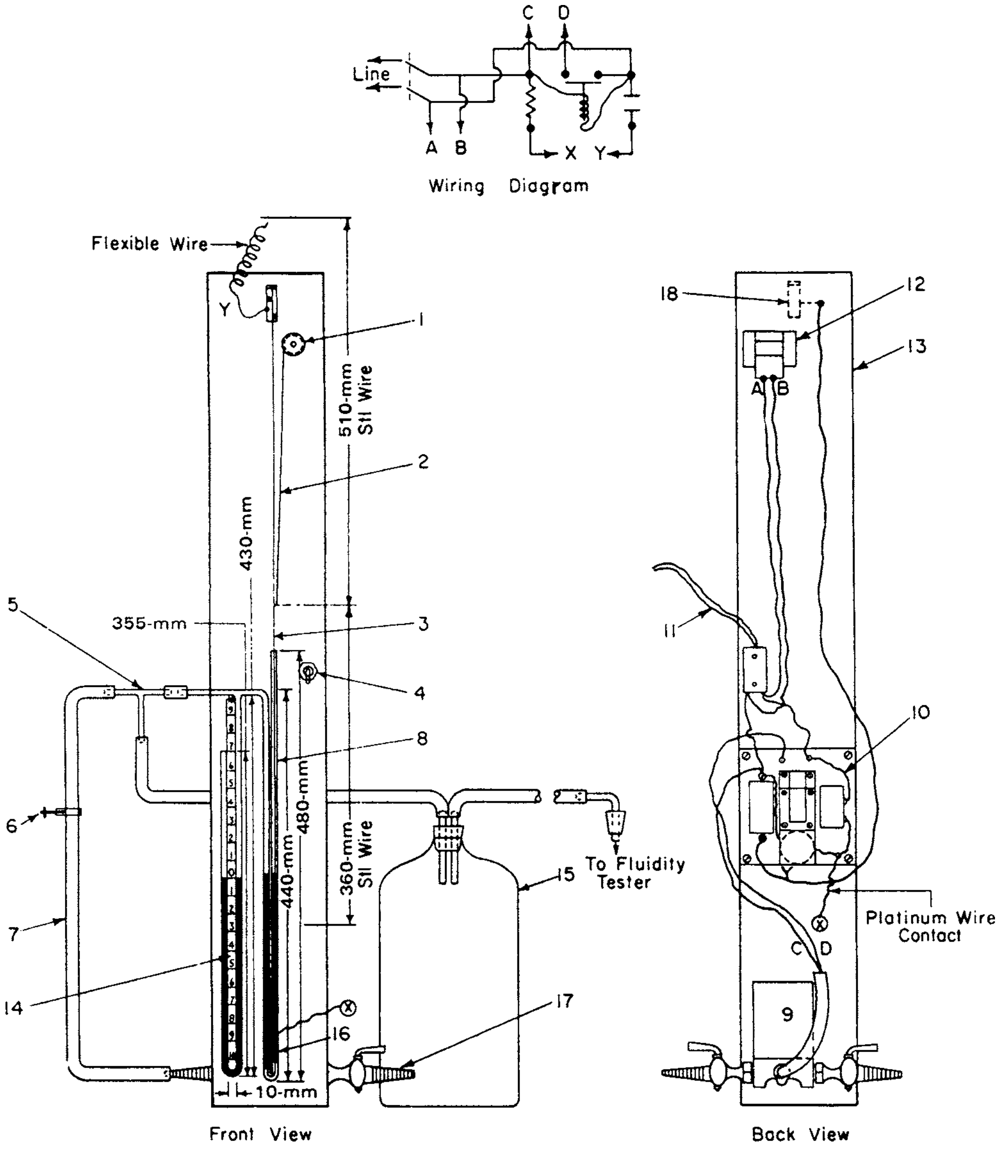
[9] This apparatus may be shop fabricated. Details of special parts are indicated in Figs. X1.3 and X1.4. Alternatively the apparatus can be purchased.



1—26-mm diameter face pulley
2—Thread
3—Steel rod
4—Switch-DPST
5—Tee, 90-mm long
6—Needle valve
7—Rubber or plastic tubing
8—6-mm heat-resistant glass tube
9—Solenoid valve
10—Electric relay
11—Electric cord to outlet
12—Synchronous motor
13—Plywood of approximately 10-mm thickness
14—Millimeter scale
15—4-L bottle
16—0.5-mm heat-resistant glass capillary
17—To vacuum line
18—Rod holder

FIG. X1.3 Assembly Automatic Vacuum Controller Apparatus

open the solenoid valve in the vacuum line and air will be pumped from the system at a rate limited by the needle valve. Adjust this needle valve until the descending mercury in the control manometer just leads the rod, reducing the relay operation to a minimum. When properly adjusted, the pulsations caused by the opening and closing of the solenoid valve should not exceed ±1 mm. In this manner the pressure in the system will be reduced gradually at a rate governed by the descent of the steel rod.

X1.8 Procedure

X1.8.1 Pour the sample as received into a thoroughly cleaned and dry standard fluidity U-tube, without contacting the upper walls of the tube, until the vertical height of the

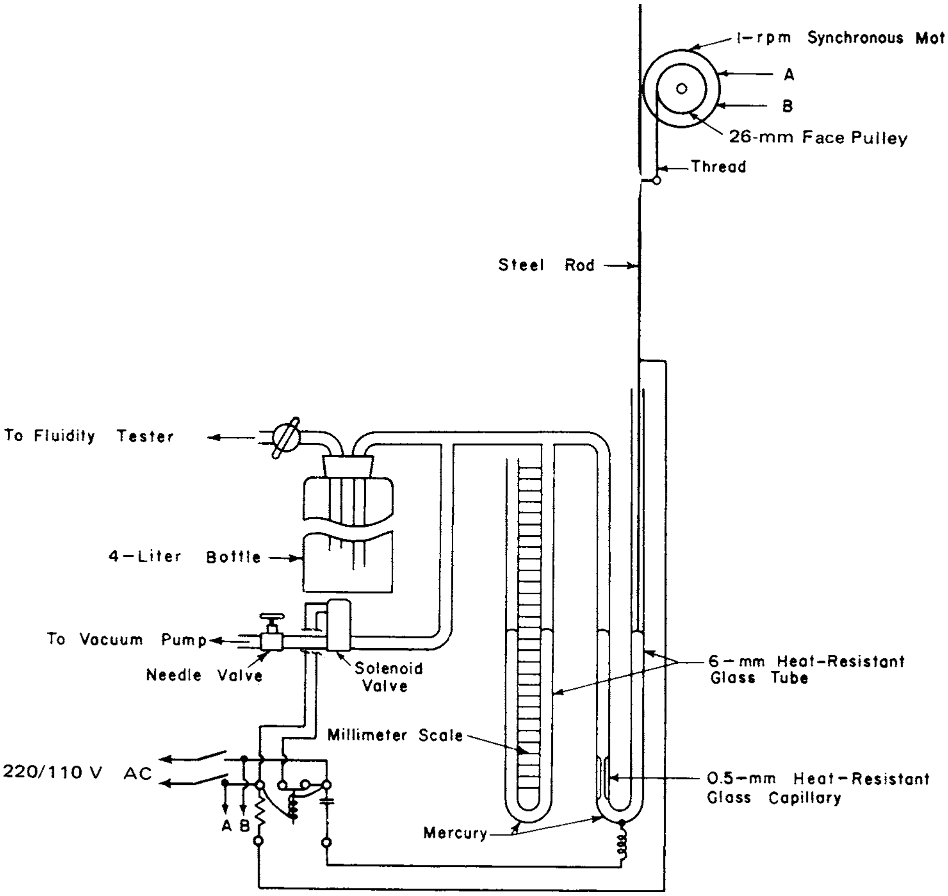


FIG. X1.4 Detail of Automatic Vacuum Controller

sample in the U-tube is 38 mm. Insert in one leg of each U-tube an ASTM Thermometer 5C in a cork that has been grooved to permit the passage of air. The thermometer must be placed in the center of the tube and its bulb immersed so that the beginning of the capillary is 3 mm below the surface of the specimen.

X1.8.2 Fix the tube in the bath set at the specific temperature, immersed to a depth of approximately 75 mm. Control the bath and sample temperatures within ±1°C and ±0.5°C, respectively, of the specified temperature of the test.

X1.8.3 Maintain the sample at the specified temperature for 30 min ± 30 s, with the U-tube connected to the automatic vacuum controller, and the stopcock or pinch-clamp open. Wind the thread on the pulley attached to the synchronous motor. Turn the power switch to the ON position. Apply suction automatically to the U-tube at the prescribed rate. Observe any movement of the specimen during a one-minute interval which is the time required to apply 152-mm Hg vacuum to the specimen in the U-tube. Immediately disconnect the U-tube from the automatic vacuum controller, turn off the power switch and rewind the thread. If the specimen has moved 2 mm or more during the time (1 min) the suction was applied, the specimen is considered fluid at the temperature of the test.

X1.9 Report

X1.9.1 Report the fluidity of the sample at a specified temperature as follows:

X1.9.1.1 If the sample fulfills the conditions of flow, as defined in X1.3.1, report fluidity: "Fluid at (temperature of test)" or fluidity at (temperature of test): "Pass."

X1.9.1.2 If the sample does not fulfill the conditions of flow, as defined in X1.3.1, report fluidity: "Not fluid at (temperature of test)" or fluidity at (temperature of test): "Fail."

X1.10 Precision and Bias

X1.10.1 As in the case of pass-fail data, no statement is made about either the precision or the bias of this method for measuring the fluidity of a residual fuel specimen since the result merely states whether there is conformance to the criteria for success specified in the procedure.

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 97–04) that may impact the use of this standard.

(*1*) Added Test Method D 5853 to the Scope and Referenced Documents sections.