Mohammed Mustafa Mohammed Ghisheer

# DETERMINATION OF KINEMATIC VISOCSITY, DENSITY AND COLD FLOW PROPERTIES OF BIODIESEL BLEND AT CONSTANT STORAGE TEMPERATURE

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

By Mohammed Mustafa Mohammed Ghisheer

In Partial Fulfillment of the Requirements for the Degree of Master in Mechanical Engineering

NICOSIA, 2017

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**Approval of Director of Graduate School of** 

**Applied Sciences** 

#### Prof. Dr. Nadire ÇAVUŞ

#### We certify this thesis is satisfactory for the award of the degree of Master in Mechanical Engineering

**Examining Committee in Charge:** 

Assist. Prof. Dr. Elbrus IMANOV

Head of Jury, Computer Engineering Department, NEU

Dr. Youssef Kassem

Mechanical Engineering Department, NEU

Assist. Prof. Dr. Hüseyin ÇAMUR

Supervisor, Mechanical Engineering Department, NEU

I hereby declare that, all the 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.

Name, Last Name :

Signature :

Date:

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To my parents ...

#### ABSTRACT

Biodiesel defined as mono-alkyl esters of vegetable oils and animal fats, has had a considerable development and great acceptance as an alternative fuel for diesel engines. The transesterified fatty acid methyl ester of waste vegetable oil collected from local restaurants and cafes was used as neat biodiesel. In this work, mixture of biodiesel and Euro diesel summer (B50) was used to study the variation of viscosity, density and cold flow properties as a function of temperature. Experimental measurements were carried out for B50 at temperatures in the range of 0- 90°C. It is found that both, density and viscosity decrease because of the increase as the temperature increase. Moreover, the present study reported the kinematic viscosity and density changes in biodiesel blends at constant storage temperature (40°C) for 5 months. The results indicated that the viscosity and density of all the blends of biodiesel and diesel increased over extended the period.

Keyword: Biodiesel; density; Euro diesel summer; viscosity; storage period

#### ÖZET

Bitkisel yağların ve hayvan yağlarının mono-alkil esterleri olarak tanımlanan biyodizel, önemli bir gelişme ve dizel motorlar için alternatif bir yakıt olarak kabul görülmüştür. Yerel restoranlar ve kafelerden toplanan atık bitkisel yağın transesterifikasyonlu yağ asidi metil esteri düzgün biyodizel olarak kullanıldı. Bu çalışmada, viskozite, yoğunluk ve soğuk akış özelliklerinin sıcaklığın bir fonksiyonu olarak değişimini incelemek için biyodizel ile Avrupa dizel "yazının" (B50) karışımı kullanılmıştır. Deneysel ölçümler 0-90°C aralığındaki sıcaklıklarda B50 için uygulandı. Sıcaklık arttığı için hem yoğunluğun hem de viskozitenin azaldığı bulunmuştur. Üstelik, bu çalışma, 5 ay boyunca sabit depolama sıcaklığında (40°C) biyodizel karışımlarında kinematik viskozite ve yoğunluk değişikliklerini bildirmiştir. Sonuçlar, biyodizel ve dizelin tüm harmanlarının viskozitesi ve yoğunluğunun, dönemi fazla uzattığını gösterdi.

Anahtar Kelimeler: Biyodizel; yoğunluk; Euro dizel yaz; viskozite; depolama dönemi

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#### LIST OF SYMBOLS USED

- *H* Height, m
- **K** Calibration constant, dimensionless
- *L* Length of vertical pipe, m
- $\frac{\partial p}{\partial p}$  Pressure gradient in z-direction
- $\frac{\partial z}{\partial z}$
- Q Volume flow rate, m<sup>3</sup>/s **R** Radius of capillary, m
- **R** Radius of capillary, in
- **R** Universal gas constant, J(mole/K)
- T Temperature, K or °C
- $\frac{\partial u}{\partial z}$  velocity gradient in z-direction
- $v_z$  Velocity of liquid in z-direction
- $v_{\rm r}$  Velocity of liquid in r-direction
- $v_{\theta}$  Velocity of liquid in  $\theta$ -direction
- *x* Input data
- $\alpha$  Learning rate
- β Momentum rate
- $\mu$  dynamic viscosity, Pa.s
- $\boldsymbol{v}$  kinematic viscosity, mm<sup>2</sup>/s
- $\rho$  density of the liquid, kg/m<sup>3</sup>
- $\tau$  shear stress, Pa

## CHAPTER 1 INTRODUCTION

#### 1.1 Background

Biodiesel is made up of monoalkylester of fatty acid derived from vegetable oil and animal fat and is used to replace fossil fuel (Hong et al., 2016; Prieto et al., 2015; Yuan et al., 2009). It is produced by transesterification of triglycerides with a short chain alcohols, such as methanol or ethanol in the presence of a catalyst, leading to fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) and glycerol (Prieto et al., 2015).

Biodiesel is a promising alternative to vegetable/waste vegetable oil-derived diesel fuels because it is renewable, significantly reduces particulate matter, hydrocarbon, carbon monoxide and life cycle net carbon dioxide emissions from combustion sources (McCormick et al., 2001; Yuan et al., 2009).

Furthermore, it improves remarkably the lubricity of diesel in blends. However, biodiesel has some disadvantages that include lower heat of combustion and in some cases higher cloud point (Benjumea et al., 2008). Biodiesel can be blended with petroleum diesel in any percentage (Ramírez-Verduzco et al., 2011).

Two important properties are density and viscosity. The viscosity is a measure of the internal friction or resistance of a substance to flow. As the temperature of the substance is increased, its viscosity decreases and it is therefore able to flow more readily. Viscosity affects the operation of fuel injection equipment, especially at low temperatures. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Demirbas, 2008). The fatty acid methyl esters of seed oils and fats have already been found suitable for use as fuel in diesel engine because transesterification provides a biodiesel viscosity that is close to that diesel (Singh & Singh, 2010).

Density is another important property of biodiesel. It is defined as its mass per unit volume, whereas the specific gravity of biodiesel is the ratio of its density and the density of water as reference compound. The increase in biodiesel density can affect the operation of the fuel injection system due to the delivery of a slightly greater mass of fuel in the volume metering equipment (Ramírez-Verduzco et al., 2011).

#### **1.2 Research Aims**

The aims of this work are

- 1. To experimentally examine the effect of temperature on kinematic viscosity and density of biodiesel blends with Euro diesel summer (B50 i.e. 50 percentage of biodiesel is mixed with 50 percentage of Euro diesel summer).
- 2. To experimentally measure the cold flow properties such as Cloud Point and Pour Point of biodiesel blend.
- 3. Investigate the influence of storage period on the properties of biodiesel in terms of viscosity, density and cold flow properties.

#### **1.3 Thesis Outlines**

Chapter 1 provides a short description of biodiesel, research motivation and the aims of this work. In chapter 2 explains the fundamental concept of some thermo-physical biodiesel properties like viscosity, density and cold flow properties (Cloud Point and Pour point). Chapter 3 is describes the experimental setup and the procedures for measuring biodiesel properties. The effects of temperature on biodiesel properties for biodiesel sample are discovered in order to know the relationship between the temperature and biodiesel properties by varying temperatures from 0°C to 90°C is discussed in chapter 4. The effectiveness of low temperature on biodiesel properties (kinematic viscosity and density) is described in chapter 4. The final conclusion on the current study is described in chapter 5.

### CHAPTER 2 BIODIESEL

#### **2.1 Biodiesel**

Biodiesel is a renewable fuel derived from vegetable oil, waste vegetable oil or animal fat via transesterification process. 'Bio' represents the renewable and biological source in contrast to petroleum-based diesel fuel and 'Diesel' refers to its use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the volume fraction of biodiesel contained in the blend (i.e. B50 is 50% biodiesel, 50% petroleum diesel, B100 is pure biodiesel). Biodiesel can be mixed at any level with petro-diesel to make biodiesel blend. Moreover, it can bused in combustion engine. Biodiesel is an alternative source to fossil fuels that can be accessed via transesterification of biologically renewable sources such as edible, non-edible and waste oils. Biodiesel is a promising unconventional to crude oil-derived diesel fuels because it has low toxicity, low particulate matter and CO exhaust emissions, high flash point which is greater than  $130^{\circ}$ C, low sulfur and aromatic content, and inherent lubricity that extends the life of diesel engines. However, it has some disadvantages such as higher nitrous oxide (NO<sub>x</sub>) emissions and freezing point than diesel fuel.

#### **2.2 Biodiesel Production**

#### 2.2.1 Feedstocks for Biodiesel Production

Biodiesel can be produced by transesterification of any triglyceride feedstock, which includes any oil-bearing crops, and animal fats. However, most current research is focusing considerably on the production of biodiesel from vegetable oil (Balat, 2011; Hoekman et al., 2012). The use of vegetable oils as an alternative fuel has been around for 100 years, ever since the invention of the compression ignition engine by Rudolph Diesel using peanut oil (Shay, 1993).

Generally, the raw material contributes the biggest portion of the overall biodiesel production cost. Nowadays, with the current economic situation, the increment of refined oil prices is unavoidable and thus contributes to an even higher fraction of the feedstock cost in the total production expenditure. The properties of feedstocks also cause a significant impact on the quality of the product.

The feedstocks employed in biodiesel production are generally classified into vegetable oil (edible oil and non-edible oil), animal oil and fats, and waste oil.

#### 2.2.1.1 Edible Oil

At present, the dominant feedstock for biodiesel production is edible vegetable oil, with different countries using different types of vegetable oils, depending upon the climate and soil conditions (Sharma et al., 2008). Table 2.1 shows the physical of biodiesel from different oil sources are compared to petroleum derived diesel (Endalew, 2010).

The increasing world population increases the demand for both food and fuels, and significantly contributes to the food versus fuel issues (Balat, 2011). Therefore, the non-edible feedstocks are found to be the most promising alternative to replace edible feedstocks.

#### 2.2.1.2 Non-edible Oil

Nowadays, the major obstacle to commercializing biodiesel from vegetable oil is the high cost of the raw feedstock. Therefore, the cheap non-edible vegetable oil, animal fats and waste oils are found to be an effective feedstocks replacement to reduce the cost of biodiesel. Examples of non-edible oils used in the production of biodiesel are rubber, Jatropha and tobacco.

Table 2.1 shows the physical of biodiesel from different oil sources are compared to petroleum derived diesel (Endalew, 2010).

	Specie	Viscosity [cSt, 40°C)	Density [g/cm <sup>3</sup> ]	Specific gravity	Pour Point [°C]	Flash Point [°C]
li	Jatropha curcas	4.8	0.92	-	2	135
ble (	Sea mango	29.57	0.92	-	-	-
Non-Edi	Palanga	72	0.9	-	-	221
	Rubber seed	5.81	-	0.874	-	130
Edible Oil	Rapeseed oil	4.5	-	0.882	-12	170
	Soybean	4.08	-	0.885	-3	69
	Palm	4.42	-	0.9	15	182
	Sunflower	32.6	0.92	-	-	274
Petrol	eum Diesel	2.6	-	0.85	-20	68

Table 2.1: Biodiesel properties form different oil sources

#### 2.2.1.3 Waste Oil

The use of cheap low quality feedstocks such as waste cooking oils, greases and soapstocks (a by-product of vegetable oil refinery) significantly helps to improve the economic feasibility of biodiesel (Ramadhas *et al.*, 2005). Used cooking oil (UCO) is generally in the liquid state at room temperature, whereas greases and soapstocks are in solid state at room temperature. UCO was found to be 2.5 - 3.5 times cheaper than virgin vegetable oils, depending on the sources and availability (Balat, 2011). The amount of UCO generated each year in every country is quite massive, depending on the use of vegetable oil.

#### **2.3 Biodiesel Production Method-Transesterification**

In order for vegetable oils and fats to be compatible with the diesel engine, it is necessary to reduce their viscosity. This can be accomplished by breaking down triglyceride bonds, with the final product being referred to as biodiesel.

Transesterification is the most commonly used method. The transesterification process is achieved by reaction of a triglyceride molecule with an excess of alcohol in the presence of a catalyst to produce glycerin and fatty esters. The chemical reaction with methanol is shown schematically in Figure 2.1.



Figure 2.1: Overall mechanism of Transesterification (Gerpen, 2005)

Direct use of vegetable oil as fuel for diesel engine can cause particle agglomeration, injector fouling due to its low volatility and high viscosity, which is about 10 to 20 times greater than petroleum diesel.

Transesterification is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that alcohol is employed instead of water (Srivastava & Prasad, 2000). The transesterification process consists of a sequence of three consecutive reversible reactions, which include conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yield one ester molecule in each step. Since this reaction is reversible, excess amount of alcohol is often used to help drive the equilibrium towards the right. In the presence of excess alcohol, the forward reaction is a pseudo-first order reaction and the reverse reaction is a second-order reaction.

#### 2.4 Kinematic Viscosity

Viscosity, a measure of resistance to flow of a liquid due to the internal fluid friction (Knothe et al., 2010; Meng et al., 2014), is an important property because of its direct relation with the fuel injection process in engines (Knothe et al., 2010; Hoekman et al., 2012).

Viscosity is one of the most important factors affecting the in-cylinder fuel atomization process in direct injection diesel engines. Previous research showed that the higher viscosity of biodiesel could increase fuel penetration in the chamber (Lee & Huh, 2013), consequently affecting combustion and emissions from the engine. An increased spray tip penetration and a decreased spray cone angle with biodiesel have been verified using in-cylinder measurement techniques (Senda et al., 2004).

Some researchers have measured viscosity experimentally for some biodiesel fuels (Kerschbaum & Rinke, 2004) and their diesel blends (Tat & Van Gerpen, 1999). These measurements, however, are for specific biodiesel fuels. Because there are numerous biodiesel source materials and the composition of each type of material may vary substantially, it is impractical to determine experimentally the viscosity of fuels produced from each material source.

biodiesel fuels can be used in high pressure combustion engines such as common rail injection engines in which high injection pressures allow rapid atomization and combustion resulting in higher efficiencies and low emissions (Chhetri & Watts, 2012). Due to the high temperature and pressure environment in compression engines, the viscosity of biodiesel fuels varies significantly (Chhetri & Watts, 2012). Hence, it is important to know the atomization properties of biodiesel such as the viscosity at elevated temperatures. As the temperature of the substance is increased, its viscosity decreases and it is therefore able to flow more readily (Ramírez-Verduzco et al., 2011). Viscosity affects the operation of fuel injection equipment, especially at low temperatures. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Ramírez-Verduzco et al., 2011).

#### 2.4.1 Concept of Viscosity

Viscosity is an important property of the liquids. Viscosity is the quantity that describes fluid resistance to flow. (Latini et al., 2006). Viscosity can be classified into two types:

- a. Dynamic viscosity
- b. Kinematic viscosity

Dynamic viscosity is referred to shear viscosity or it can be defined as the ratio of shear stress to the velocity gradient and it is can be given as:

$$\tau = \mu \frac{\partial u}{\partial z} \tag{2.1}$$

Where,  $\tau$  is the shear stress (N/m<sup>2</sup>),  $\mu$  is the dynamic viscosity (Pa.s) and  $\frac{\partial u}{\partial z}$  is the velocity gradient or better known as shear rate (1/s).

Kinematic viscosity is deified as the ratio of dynamic viscosity to the mass density of the liquid ( $\rho$ ) at specified temperature and pressure and is can be given as

$$v = \frac{\mu}{\rho} \tag{2.2}$$

Where v is the kinematic viscosity (m<sup>2</sup>/s),  $\rho$  is the mass density of the liquid (m<sup>3</sup>/kg) (Viswanath et al., 2007).

#### 2.4.2 Measurement of Viscosity

Viscometers used for measuring the viscosity of liquid. The measurement procedures of viscosity are based on the mechanical approaches, since tension and elongation are mechanical values which are determined on the basis of a defined deformation of the sample. Two main types of Viscometer are suitable for the determination of the viscosity of the liquid:

- 1. Rotational viscometer
- 2. Capillary viscometer

The following subsection illustrates and gives details about capillary viscometer, the type of viscometer chosen for this study.

The general form of capillary flow viscometers is a U- tube. The advantages of these types of viscometers can be simplified as

- 1. Simple.
- 2. Inexpensive.
- 3. Suitable for low viscosity of fluid.

Capillary viscometers are suitable devices for estimation of the viscosity of the liquid. Often the driving force has been the hydrostatic head of the test liquid itself (Viswanath et al., 2007). Generally, kinematic viscosity of the liquid is determined using capillary viscometers. They are in regular use in many countries, for standard measurements in support of industrial investigations of the viscosity of liquids at atmospheric pressure For calculating the kinematic viscosity, it is an important to measure the time of liquid needs to pass through the capillary tube. (Sahin & Sumnu, 2006).

The list and specification of different types of capillary viscometers are given in appendix 1. The Ubbelohde viscometer used in this work will be explained in details in later subsections.

#### 2.4.4 Theory of Capillary Viscometers

The principle of the capillary viscometer is based on the Hagen-Poiseuille equation of fluid dynamics. The derivation of the Hagen-Poiseuille equation for measuring the viscosity of the liquid is based on the following two assumptions;

- 1. The capillary is straight with a uniform circular cross section,
- 2. The fluid is incompressible and Newtonian fluid, and
- 3. The flow is laminar and there is no slip at capillary wall. (Viswanath et al., 2007)

The Hagen-poiseuille equation can be derived from the Navier Stokes equation and the continuity equation in cylindrical coordinates. Figure 2.2 shows a fully developed laminar flow through a straight vertical tube of circular cross section.

Continuity equation in cylindrical coordinates for incompressible unsteady flow

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (\rho r V_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho r V_\theta) + \frac{\partial}{\partial z} (\rho V_z) = 0$$
(2.3)

Navier Stokes equation in cylindrical coordinates for incompressible unsteady flow

$$\rho\left(V_{r}\frac{\partial V_{r}}{\partial r} + \frac{V_{\theta}}{r}\frac{\partial V_{r}}{\partial r} - \frac{V_{\theta}^{2}}{r} + V_{z}\frac{\partial V_{r}}{\partial r} + \frac{\partial V_{r}}{\partial t}\right)$$
$$= \rho g_{r} - \frac{\partial p}{\partial t} + \mu \left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(rV_{r}\right)\right) + \frac{1}{r^{2}}\frac{\partial^{2}V_{r}}{\partial \theta^{2}} + \frac{1}{r^{2}}\frac{\partial V_{\theta}}{\partial \theta} + \frac{\partial^{2}V_{r}}{\partial z^{2}}\right] (2.4)$$

$$\rho\left(V_{r}\frac{\partial V_{\theta}}{\partial r} + \frac{V_{\theta}}{r}\frac{\partial V_{\theta}}{\partial r} - \frac{V_{r}V_{\theta}}{r} + V_{z}\frac{\partial V_{\theta}}{\partial r} + \frac{\partial V_{\theta}}{\partial t}\right)$$

$$= \rho g_{\theta} - \frac{\partial p}{\partial t}$$

$$+ \mu \left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(rV_{\theta}\right)\right) + \frac{1}{r^{2}}\frac{\partial^{2}V_{\theta}}{\partial \theta^{2}} + \frac{1}{r^{2}}\frac{\partial V_{\theta}}{\partial \theta} + \frac{\partial^{2}V_{\theta}}{\partial z^{2}}\right]$$
(2.5)

$$\rho\left(V_{r}\frac{\partial V_{z}}{\partial r} + \frac{V_{\theta}}{r}\frac{\partial V_{z}}{\partial r} + V_{z}\frac{\partial V_{z}}{\partial r} + \frac{\partial V_{z}}{\partial t}\right)$$

$$= \rho g_{z} - \frac{\partial p}{\partial t}$$

$$+ \mu \left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rV_{z})\right) + \frac{1}{r^{2}}\frac{\partial^{2}V_{z}}{\partial \theta^{2}} + \frac{1}{r^{2}}\frac{\partial V_{z}}{\partial \theta} + \frac{\partial^{2}V_{z}}{\partial z^{2}}\right]$$
(2.6)



Figure 2.2 Hagen-Poiseuille flow through a vertical pipe

If z-axis is taken as the axis of the tube along which all the fluid particle travels and considering rotational symmetry to make the flow two dimensional axially symmetric. the solution for axially symmetric are

$$v_z \neq 0, v_r = 0, v_\theta = 0$$
 (2.7)

From continuity equation,

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0$$
(2.8)

For rotational symmetry,

$$\frac{1}{r} \cdot \frac{\partial v_{\theta}}{\partial \theta} = 0; \qquad v_z = v_z(r, t) \qquad or \qquad \frac{\partial}{\partial \theta} (any \ quantity) = 0 \ (2.9)$$

as the flow occurs only in z-direction, then Navier Stoke's Equation in cylindrical coordinates (z-direction) can be simplified as

$$\frac{\partial v_z}{\partial t} = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial z} + v \left( \frac{\partial^3 v_z}{\partial r^3} + \frac{1}{r} \cdot \frac{\partial v_z}{\partial r} \right) \text{ in z direction}$$
(2.10)

And for steady flow it becomes

$$\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial v_z}{\partial r} = \frac{1}{\mu} \frac{dp}{dz}$$
(2.11)

Solving differential equation 2.11 with boundary conditions

 $r = 0; v_z \text{ is finite}$ (2.12)

$$r = R; v_z = 0$$
 (2.13)

Yields

$$\nu_z = \frac{R^3}{4\mu} \left(-\frac{dp}{dz}\right) \left(1 - \frac{r^3}{R^3}\right) \tag{2.14}$$

While

$$-\frac{dp}{dz} = \frac{\Delta p}{L} \tag{2.15}$$

The volume flow rate discharge is given by

$$Q = \int_0^R 2\pi v_z r \, dr$$
 (2.16)

Inserting 2.14 and 2.15 into 2.16, we obtain

$$Q = \pi \frac{R^4}{8\mu} \left(\frac{\Delta p}{L}\right) \tag{2.17}$$

Also

$$Q = \frac{V}{t} \tag{2.18}$$

$$v = \frac{\mu}{\rho} \tag{2.19}$$

 $if \Delta p = \rho g H$  as in Pressure – Height relationship,

Then,

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

Declaring a calibration constant K,

$$K = \frac{\pi g H R^4}{8LV} \tag{2.21}$$

Then,

$$v = Kt \tag{2.22}$$

Equation 2.22 is similar to ASTM kinematic viscosity equation (Marchetti et al. 2007) with an exception of the correction factor.

$$\upsilon = \frac{10 \,\pi \text{g}\text{D}^4\text{Ht}}{138 \,\text{VL}} - \frac{\text{E}}{\text{t}^3} \tag{2.23}$$

where E is the correction factor.

#### 2.5 Density

Density is another important property of biodiesel. It is defined as its mass per unit volume, whereas the specific gravity of biodiesel is the ratio of its density and the density of water as reference compound. The increase in biodiesel density can affect the operation of the fuel injection system due to the delivery of a slightly greater mass of fuel in the volume metering equipment (Ramírez-Verduzco et al., 2011).

In general, density of biodiesel is higher than petro-diesel i.e. at same volume, mass of biodiesel is higher than mass of diesel. As a result, the increase in biodiesel density can affect the process of the fuel injection (Aldrich, 2016; Lalvani et al., 2015).

#### 2.6 Cold Flow Properties of Biodiesel

Although biodiesel can be used in engine with very little or no modification, improvements that prevent the fuel from plugging the engine in cold weather would be beneficial (Bessee & Fey, 1997). Cloud Point (CP), Pour Point (PP), Low Temperature Filterability Test (LTFT) and Cold Filter Plugging Point (CFPP) are considered as cold flow properties that used to classify the cold weather performance (Atabani et al., 2012; Knothe, 2010; Knothe, 2005; Boshuiet al., 2010; Demirbas, 2009). Clod flow properties measure a fuel's ability to function in cold temperature. The key temperature, flow properties for winter fuel specified, are cloud and pour points which describe the freezing range of fuel (Duffield, 1998).

#### 2.6.1 Cloud Point

Cloud point (CP) (ASTM D-2500) is the temperature at which, as the fuel is cooled, wax that may plug the fuel filter begins to form (Duffield, 1998). Another definition for cloud point is the temperature at which a cloud or haze wax crystals appear at the bottom of the test jar when the oil is cooled under prescribed conditions (Ramadhas, 2011). It is measured as the temperature of the first formation of wax as the fuel is cooled (Duffield, 1998). Cloud point is defined as the temperature at which the fuel shows visible cloudiness, which indicates that, the fuel starts to solidify. At this stage, the fuel starts to get solidified. The cloud point of biodiesel is higher than diesel, so it is more difficult to operate at lower temperatures than diesel (Ramadhas, 2011; Selvaraj, 2016).

#### 2.6.2 Pour Point

Pour Point (PP) (ASTM D-97), a measure of the fuel gelling point, is the temperature at which the fuel is no longer pumpable (Duffield, 1998). The Pour Point is the lowest temperature at which the oil is observed to flow when cooled and examined under prescribed conditions (Ramadhas, 2011).

The Pour Point is always lower than the cloud point. It shows that the pour point is the minimum temperature at which the vehicle can be operated without any heating aid of the fuel. The pour point of biodiesel is higher than diesel, so it makes less feasible to operate vehicle with biodiesel in colder region than with mineral diesel oil (Ramadhas, 2011; Selvaraj, 2016). Fuel Cloud and Pour Points are often varied by refiners to meet local climatic conditions.

#### 2.7 Parameters indicating the extent of oxidation stability of biodiesel

An understanding of selected fuel parameters is highly important in evaluating the oxidation stability of biodiesel. Most of those parameters are directly related to the fatty acid composition of the biodiesel ester molecules. The important parameters that help to predict the oxidation stability of a biodiesel sample, their determination and its effect on the oxidation of biodiesel are discussed below.

#### 2.7.1 Iodine value (IV)

The estimation of the IV for biodiesel fuel, which is the measure of the total degree of unsaturation, provides useful guidance for preventing various problems in engines. The IV is based on the reactivity of alkyl double bonds, and an increased IV of biodiesel indicates the possibility for the formation of various degradation products that can negatively affect engine operability and reduces the quality of lubrication (Bouaid et al., 2007). The IV is expressed as the gram of iodine consumed per 100 g of the substance, which is the most parameter employed for determining the magnitude of unsaturation in the esters of fatty acids, fats, oils and their derivatives (Yaakob ET AL., 2014).

#### 2.7.2 Peroxide value (PV)

The PV is generally based on the primary oxidation products, such as the hydroperoxides of the biodiesel, and is measure of the peroxide units formed during the oxidation process. The PV is measured in milli-equivalents of peroxide units per kg of the biodiesel sample. The PV influences various parameters in the fuel standard, such as the cetane number (CN), density, viscosity, etc. The increase in PV increases CN, which may reduce the ignition delay time (Clothier et al., 1993). The increase in PV as well as the acidity after the Induction period can also cause the corrosion of the fuel system components, the hardening of the rubber components, the fusion of the moving components and engine operation problems (Monyem & Van Gerpen, 2001).

#### 2.7.3 Acid value (AV)

Another parameter used to understand biodiesel degradation is the acid value (AV) because it is directly related to stability. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound and can be used to quantify the amount of acid present. The AV is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in one gram of the sample. Formally, the AV was not used for the evaluation of oxidative stability but is useful for assessing the quality of stored biodiesel and is included in the standards (Knothe, 2007). The biodiesel ester molecule has a tendency to hydrolyze to alcohol and acid in the presence of air or oxygen. The presence of acid will lead to an increase in the total acid number (Sarin et al., 2009). Thus, the presence of water in biodiesel should be minimized. The increasing peroxide formation during the oxidation of biodiesel will eventually increase the AV as the peroxides experience complex reactions, including a split into more reactive aldehydes, which further oxidise to form acids. An increase in the oxidation causes an increase in the acid number. In addition to the oxidation and hydrolysis products, the residual mineral acids from the production process are responsible for the presence of acidic compounds in biodiesel.

#### 2.7.4 Oxidisability (OX)

Another stability index used for the investigation of biodiesel stability is the oxidisability, which is a dependent variable that measures the relative rate of oxidation (Neff et al., 1992). Neff et al. (1992) expressed the OX with

$$OX = \frac{[0.02(\%0) + (\%L) + 2(\%Ln)]}{100}$$
(2.24)

where O, L, and Ln refer to the amount of oleicacid (18:1), linoleic acid (18:2) and linolenic acid (18:3) present in the test sample. The coefficients specified for oleic, linoleic, and linolenic fatty esters represent the relative rates of oxidation of these compounds. The OX applies only to the biodiesel that predominantly contains 18 carbon fatty acid units that originated from lipids, such as soy, tallow, etc. (Cormick et al., 2007). The increase in insoluble formation and the reduction in induction time is highly influenced by the oxidisability.

#### 2.8 Required Standards for Biodiesel

Biodiesel standards are in place to ensure that only high-quality biodiesel reaches the marketplace. The two most important fuel standards are ASTM D6751 (ASTM, 2008a) in the United States and EN 14214 (European Committee for Standardization (CEN) (Tomes et al., 2011) in the European Union. Table 2.1 summarizes the limit values of density and kinematic viscosity for biodiesel and biodiesel petrodiesel blend (B6–B20) fuel, ASTM D7467 (ASTM, 2008b), ASTMD975 (ASTM, 2008c), EN 590 (Can et al., 2004), ASTM D396 (ASTM, 2008d) and EN 14213 (Canakci & Van Gerpen, 2003). In the cases of ASTM D7467, D975, and D396, the biodiesel component must satisfy the requirements of ASTM D6751 before inclusion in the respective fuels. Correspondingly, in the European Union, biodiesel must satisfy EN 14214 before inclusion into petrodiesel, as mandated by EN 590.

Property	Unit	Standard method	Value according to			
			the standard method			
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	ASTM/D6751	1.9-6.0			
Α	STM D675	1 biodiesel fuel standard				
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	ASTM D445	1.9-6.0			
Cloud Point	°C	D2500	Report			
European Committe	e for Standa	ardization EN 14214 biodiese	el fuel standard			
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	EN ISO 3104, ISO 3105,	3.5-5.0			
		EN ISO 310				
Density at 15 °C	kg/m <sup>3</sup>	EN ISO 3675,	860-900			
		EN ISO 12185				
Cloud Point	°C	EN 23015	Location & season			
			dependant			
ASTM D7467 biodiesel-petrodiesel blend (B6–B20) fuel standard						
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	ASTM D445	1.9–4.1			
Physicochemical properties of waste frying oils based-biodiesel (ASTM D 6751)						
Kinematic viscosity at 40°C	$mm^2/s$	ASTM D445	4.21-6.0			
Density at 15 °C	kg/m <sup>3</sup>	ASTM D40	867			

Table 2.2: Generally applicable requirements and test methods

# CHAPTER 3 EXPERIMENTAL METHODS

#### 3.1 Material

Biodiesel and Euro diesel summer were used to study the properties of biodiesel blend. Mixture waste vegetable oils methyl ester produced by Mechanical labor (Cyprus) was used to measure the properties of biodiesel blend. Biodiesel was produced by transesterification from a mixture of waste vegetable oils. The percentage of biodiesel added in the diesel fuel was 50% by volume.

The characteristics of the diesel fuel is shown in Table 3.1. Moreover, the properties of biodiesel is tabulated in Table 3.2. Biodiesel blends were prepared by weighting with an analytic balance. The uncertainty was  $\pm 0.0001$  g. The system was mixed perfectly into a homogeneous solution by a magnetic stirrer before to the experimental measurement of biodiesel properties was done.

The methyl esters composition of the biodiesel samples was determined by gas chromatography and Fatty acid composition of the biodiesel is presented in Table 3.2.

Duon orting	T 1	Limit		Dogulta	Mathad
Properties	Unit	Low	High	Kesuits	Method
Density at 15°C	kg/m <sup>3</sup>	820	845	827.8	ASTM D 4052
Cetane number	-	51	-	55	ASTM D 613
Cetane index	-	47	-	54.8	ASTMD 4737
Kinematic viscosity at 40°C	cst	2	4.5	2.8	ASTMD 455
CFPP	°C	-	5	-6	IP 309
Sulphur content	mg/kg	-	10	5.3	ASTMD 5453
Oxidation stability	mg/l	-	25	3	ASTMD 2274
Total acid	mg KOH/gr	-	0.2	0.1	ASTMD 664
Flash point	°C	55	-	67	ASTM D 93
Lubricity at 60°C	UM	-	440	385	ISO 12158/1

 Table 3.1: Euro diesel summer properties

Dreamonting	T ] :4	Limit		Degulta	Mathad
Properties	Unit	Low	High	Results	Method
FAME content	mass%	96.5	-	>99.5	EN 14103
Density at 15°C	kg/m <sup>3</sup>	860	900	878.4	ASTM D 4052
Cetane number	-	51	-	59.7	EN 15195
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	3.5	5	4.483	EN ISO 3104
Oxidation stability (110°C)	hour	8	-	>11	EN 14112
Acid number	mg KOH/gr	-	0.5	0.31	EN 14104
Lodin value	gl2/100g	-	120	74	EN 14111
Linolenic acid methyl ester	mass%	-	12	2.6	EN 14103
Methanol	mass%	-	0.2	0.02	
Glyceride content		-	-		EN 14105
Mono-glyceride	mass%	-	-	0.7	0.21
Di- glyceride	mass%	-	-	0.2	0.02
Tri- glyceride	mass%	-	-	0.2	< 0.03
Free glycerol	mass%	-	-	0.02	< 0.01
Total glycerol	mass%	-	-	0.25	0.065
Flash point	°C	101	-	>140	ISO 3679
Sulphated ash	mass%	-	0.02	< 0.005	ISO 3987
Sulphur	mg/kg	-	10	9.8	EN ISO 20846
CFPP	°C	-	5	5	EN 116
Kinematic viscosity at 20°C	mm <sup>2</sup> /s	-	-	7.5	ASTM D 455

 Table 3.2: Properties and fatty acid compositions of biodiesel

#### **3.2 Storage test procedures**

2000 mL sample of biodiesel and its diesel blend were stored in closed glass bottles of 500mL (Figure 3.1) capacity for 6 months and were kept indoors, at a room temperature of 40  $\pm$ 1 °C (temperature controlled laboratory oven in the dark). Samples were taken out periodically every 15 days to study the storage conditions effects.



Figure 3.1: Biodiesel sample

#### 3.2.1 Laboratory Oven

The oven consists of a thermally insulated, thermostat and two lamps as shown in Figure 3.2. The heaters are driven by a two lamp source of 100W controlled by thermostat. In essence, the laboratory oven is used to store biodiesel sample over long term storage under appropriate constant temperature. The lamps are covered by Aluminum sheet to store the biodiesel samples in dark environment and to heat the air inside the oven (Figure 3.2). The thermostat is used to control the temperature inside the oven and keep it at  $40 \pm 1$ .



Figure 3.2: Laboratory oven

#### 3.3 Experimental Setup for Measuring the Viscosity and Density from 20-90°C

#### 3.3.1 Kinematic Viscosity Measurements

The kinematic viscosity ( $\nu$ ) was measured using an Ubbelohde viscometer calibrated with pure water according to ASTM D455 (Appendix 1). This viscometer is equipped with a thermostat whose accuracy is ±0.02°C. The kinematic viscosity was measured in the temperature range 20–90°C at 10 °C intervals with an accuracy of ±0.1%. Figure 3.3 shows the experimental setup used to determine the temperature dependence of kinematic viscosity of the samples analyzed. To ensure precise and stable temperature control during measurements, a two thermometer were used to control the temperature. A uniform temperature inside the heating bath was attained. In addition, the mixer enabled the regulation of the temperature of a heated bath containing the viscometer by means of an electromagnetic hot plate. Each sample was tested three times, and the average kinematic viscosity were calculated.

For absolute measurement, the corrected flow time multiplied by the viscometer constant K directly gives the kinematic viscosity  $[mm^2/s]$  as given in Equation (3.1).

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

where *v*, *K*, *t*, and *y* represent the kinematic viscosity, the calibration constant, measured time of flow and kinetic energy correction, respectively. The instrument constant, K,  $[(mm^2/s)/s]$  was determined by the manufacturer and given as in Table 3.3. Also, t<sup>he kinetic</sup> energy correction is given by the manufacturer and tabulated for each viscometer in term of flow time as shown in Table 3.4.


**Figure 3.3:** Experimental setup used to measure the kinematic viscosity of biodiesel blends in the temperature range 20-90°C

Capillary	Capillary	Constant , K,	Measuring range
No.	Dia. I ± 0.01[mm]	$(\mathbf{mm}^2/\mathbf{s})/\mathbf{s}$	[mm <sup>2</sup> /s]
0c	0.36	0.002856	0.6 to 3
1	0.58	0.009132	2 to 10
1C	0.78	0.02799	6 to 30

 Table 3.3: Ubbelohde viscometer technical specifications

Flow				Capillary	no		
time	0	0c	0a	Ι	IC	la	1
40	_ <sup>B</sup>	_B	_ <sup>B</sup>	1.03	0.45	0.15	
50	_ <sup>B</sup>	_ <sup>B</sup>	_ <sup>B</sup>	3.96	0.66	0.29	0.10
60	- <sup>B</sup>	_ <sup>B</sup>	_ <sup>B</sup>	2.75	0.46	0.20	0.07
70	- <sup>B</sup>	- <sup>B</sup>	_ <sup>B</sup>	2.02	0.34	0.15	0.05
80	- <sup>B</sup>	- <sup>B</sup>	4.78 <sup>B</sup>	1.55	0.26	0.11	0.04
90	- <sup>B</sup>	- <sup>B</sup>	3.78 <sup>B</sup>	1.22	0.20	0.09	0.03
100	- <sup>B</sup>	7.07 <sup>B</sup>	3.06 <sup>B</sup>	0.99	0.17	0.07	0.02
110	_ <sup>B</sup>	5.84 <sup>B</sup>	2.53	0.82	0.14	0.06	0.02
120	_ <sup>B</sup>	4.91 <sup>B</sup>	2.13	0.69	0.12	0.05	0.02
130	- <sup>B</sup>	4.18 <sup>B</sup>	1.81	0.59	0.10	0.04	0.01
140	_ <sup>B</sup>	3.61 <sup>b</sup>	1.56	0.51	0.08	0.04	0.01
150	- <sup>B</sup>	3.14 <sup>B</sup>	1.36	0.44	0.07	0.03	0.01
160	_ <sup>B</sup>	2.76	1.20	0.39	0.06	0.03	0.01
170	_ <sup>B</sup>	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	_ <sup>B</sup>	1.96	0.85	0.28	0.05	0.02	0.01
200	10.33 <sup>B</sup>	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	1.57	0.20	0.09	0.03	0.01		
650	0.98	0.17	0.07	0.03	<0.01		
700	0.25	0.14	0.07	0.02	< 0.01		
750	0.74	0.13	0.05	0.02	< 0.01		
100	U.7 T	0.15	0.05	0.02	10.01		

**Table 3.4:** Table of kinetic energy correction" Ubbelohde viscometer ISO 3105/DIN51 562/Part1/BS188/NFT 60-100, Ref.No.501...530...532.." Correction seconds <sup>A</sup>:

Flow				Capillary	no			
time	0	0c	0a	Ι	IC	la	1	
800	0.65	0.11	0.05	0.01				
850	0.57	0.10	0.04	0.01				
900	0.51	0.09	0.04	0.01				
950	0.46	0.08	0.03	0.01				
1000	0.42	0.07	0.03	0.01				
A						1		

Table 3.4: Continued

<sup>A</sup> The correction seconds stated are related to the respective theoretical constant
 <sup>B</sup> For precision measurement, these flow times should not be applied. Selection of a viscometer with a smaller capillary diameter is suggested

The determination of kinematic viscosity of biodiesel samples was carried out with an Ubbelohde viscometer (Figure 3.4). The procedure for measuring the kinematic viscosity of biodiesel samples (Figure 3.5) can be described as follows:

- 1. Fill the viscometer through a tube (3) with a sufficient quantity of the sample liquid that is appropriate for the viscometer being used or by following the manufacturer's instructions (15 mL).
- 2. Placed the viscometer in oil silicone bath stabilized at the temperature specified.
- 3. Maintain the viscometer in a vertical position for a time period (more than 20 minutes) to allow the sample temperature to reach equilibrium.
- 4. Close tube (2), and raise the level of the liquid in tube (1) to a level about 8 mm above mark  $(M_1)$ .
- 5. Keep the liquid at this level by closing tube (1) and opening tube (2).
- 6. Open tube (1), and measure the time required for the level of the liquid to drop from mark  $(M_1)$  to  $(M_2)$ , using an appropriate accurate timing device.
- 7. Calculate the kinematic viscosity of the sample using formula in equation 3.1.
- 8. Without recharging the viscometer, make check determinations by repeating steps 6 to 8 four times for each experiment.



Figure 3.4: Illustrated diagram of Ubbelohde viscometer



Figure 3.5: Procedures for measuring kinematic viscosity using Ubbelohde viscometer

## **3.3.2 Density Measurements**

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  $\pm$  0.1mg. The density values of the samples were measured for temperatures between 20°C to 90°C. The density of biodiesel blend was estimated according to the EN ISO 12185 (Appendix 2). The experimental setup of measuring the density of biodiesel samples from 20°C to 90 is shown in Figure 3.3.

The Pycnometer is a glass container with a close-fitting ground glass stopper with a fine hole through it (see Figure 3.3), so that a given volume can be accurately obtained. This enables the density of a fluid to be measured accurately.

Firstly, the volume of the Pycnometer is determined by filling it with water as the density of water already known temperature. Secondly, the procedure of measuring the density of biodiesel is as follows and shown in Figure 3.6:

- 1) Before use, clean the glassware with water and then rinse with a small amount of acetone.
- 2) The Pycnometer is completely filled with biodiesel, and the mass of the biodiesel in the Pycnometer measured using an electronic balance.
- 3) Then placed in silicon bath until it reaches the selecting temperature.
- 4) Weigh the full Pycnometer on an electronic balance.
- 5) Determine the density of biodiesel at selecting temperature.



Figure 3.6: Procedures for determining the density of biodiesel

#### 3.4 Electromagnetic Hot Plate and Stirrer

For the purpose safe heating and mixing, the Hiedolph MR Hei-tec electromagnetic heater and stirrer was used. It is made of aluminum, thus making it to provide fast heating times and the water-thin ceramic coating makes the heating plate both chemically and scratch resistant. Figure 3.7 gives a sample of the used plate.



Figure 3.7: Heidolph MR Hei-Tec

#### 3.5 Experimental Setup for Measuring the Viscosity and Density from 0-20°C

Figure 3.6 shows the experimental setup used to measure the kinematic viscosity and density of biodiesel and its blends with Euro diesel in the temperature range 0 to 20°C. The experimental setup consists of Ubbelohde viscometer, Pycnometer, a compressor, a mixer a thermostat. Alcohol (ethanol) is the simplest and cheapest cooling bath. To obtain a uniform temperature distribution within cooling bath, the cooling bath is equipped with a mixer to circulate the alcohol. The bath temperature was controlled using a thermostat, by automatically starting up and shutting down the compressor. A coil connected to a compressor cools down the liquid bath, and the compressor is cooled down by a radiator as shown in Figure 3.8. The cooling bath was thermally isolated from the rest of its surroundings by a 3cm thick Styrofoam layer.



**Figure 3.8:** Experimental setup used to measure the kinematic viscosity of biodiesel blends in the temperature range 0-20°C

#### **3.6 Cold Flow Properties**

In this study, cold flow properties in terms of Cloud Point and Pour Point were examined for biodiesel blend over 6 months. The assembly used for measuring the cloud point and pour point is shown in Figure 3.9 and called cloud point and pour point measurement apparatus. The cloud point is defined as the temperature at which a cloud of wax crystals first appear in a liquid when it is cooled under controlled conditions during a standard test. The pour point is defined as the temperature at which the fuel can no longer be poured due to gel formation. The cloud point and pour point measurements were done as per ASTM standards, D 2700-91 (Appendix 3) for cloud point and D 97-96a (Appendix 4) for pour point. To obtain a uniform temperature distribution within cooling bath, the cooling bath is equipped with a mixer to circulate the alcohol. The bath temperature was controlled using a thermostat, by automatically starting up and shutting down the compressor. A coil connected to a compressor cools down the liquid bath, and the compressor is cooled down by a radiator as shown in Figure 3. The glass jar (Figure 3.10) was immersed in cooling bath containing an alcohol at -20°C under prescribed conditions and inspected at intervals of 1°C. The glass test jar was thermally isolated from the polished brass cylinder by means of a cork support, stopper and ring assembly. In order to isolate it from any vibrations and heat transfer to keep the cooling bath temperature at the required temperature during the test very cold for a long period of time, the cooling bath was thermally isolated from the rest of its surroundings by 11cm thick Styrofoam layer. Three T-type thermocouples were used to measure the temperature in the cooling bath; the first one to measure CP, which was placed at the bottom of the glass test jar, the temperature of the bath, the second one is used to measure the PP, which was placed in the upper part of the sample in the glass test jar, while the last one to measure the cooling bath temperature as shown in Figure 3.9.



Figure 3.9: Cloud point and pour point measurement apparatus



Figure 3.10: Glass test jar

# 3.7 Determination of oxidation stability and Acid Value

The oxidation stability (induction period i.e. IP) of two pure biodiesel and their diesel blends were estimated according to the ASTM D664-04 (Appendix 5) "Oxidation stability of fuel". The induction time of biodiesel in presence of different storage period at two constant temperatures was investigated. Also, the acid value is a measure of the amount of acidic substances in fuel. Acid value (AV, mg KOH/g) titrations were performed as described in EN 15751 (Appendix 6).

# **CHAPTER 4**

# **RESULT AND DISCUSSION**

# 4.1 Repeatability for Kinematic Viscosity and Density of Biodiesel Blend

To ensure the accuracy of the results, an accuracy and repeatability test was carried out. For each sample type, the measurement of the flow time was repeated at each specific temperature three times, and the average flow time was recorded for the calculation of kinematic viscosity (Table 4.1). However, with accuracy and repeatability error less than 1%, it can be concluded that the results to be discussed are 99% accurate and precise.

System	Tomporature [ °C]	Kinematic vis	cosity [mm <sup>2</sup> /s]	Percentage
Bystem		Measured	Average	error [%]
		5.67		0.17
	20	5.66	5.67	0.52
		5.69		0.52
D'		3.47		0.28
bloulesei	40	3.48	3.48	0.20
blend		3.49		0.29
		1.59		0.63
	90	1.60	1.61	1.00
		1.62		1.23

**Table 4.1:** Ubbelohde viscometer repeatability results for some selecting temperature

Similarly, each sample of biodiesel was tested three times, and the average density was calculated as shown in Table 4.2.

System	Tomporatura [°C]	Density	[kg/m <sup>3</sup> ]	Percentage
System		Measured	Average	error [%]
		859.87		0.0012
	15	859.88	859.87	0.0035
		859.85		0.0055
Diadiasal		833.25		0.0012
blond	40	833.24	833.25	0.0012
bienu		833.23		0.0012
		795.65		0.0025
	90	795.63	795.63	0.0012
		795.62		0.0012

**Table 4.2:** Pycnometer repeatability results for some selecting temperature

# 4.2 Effect of Temperature on Kinematic Viscosity and Density of Biodiesel Blend

Figures 4.1 and 4.2 show the kinematic viscosity and density of biodiesel blend from 0°C to 90°C at atmospheric pressure. In addition, the experimental data of kinematic viscosity and density of biodiesel blend is summarized in Table 4.3. It is observed that the viscosity and density of biodiesel blend decreased as the test temperature increased.



Figure 4.1: Kinematic viscosity vs. temperature



Figure 4.2: Density vs. temperature

T 19C1	Kinematic viscosity	Density
I['U]	$[\mathrm{mm}^2/\mathrm{s}]$	$[kg/m^3]$
0	10.110	901.848
2	9.788	893.436
5	8.743	885.024
8	7.798	876.613
10	7.536	868.201
15	6.489	859.870
20	5.670	851.539
30	4.566	843.208
40	3.481	833.245
50	3.048	831.335
60	2.473	822.179
70	2.168	815.364
80	1.923	801.908
90	1.607	795.631

**Table 4.3:** Experimental data of kinematic viscosity and density

# 4.3 Effect of Storage Period on Kinematic Viscosity and Density of Biodiesel Blend

Figure 4.3 and Table 4.4 shows the variation of kinematic viscosity at 40°C with various storage periods. It is observed that, the kinematic viscosity of biodiesel blend over storage period is ranged from 3.48 to 4.26 mm<sup>2</sup>/s. Over storage periods, the viscosities of the biodiesel blend were observed within the limit as mentioned in ASTMD 445. It is noticed that as the storage period increases, the kinematic viscosity of biodiesel increases also as shown in Figure 4.3 and Table 4.2.



Figure 4.3: Kinematic viscosity vs. period (time)

Days	0	10	20	30	40	50	60	70	80	90
Kinematic viscosity	3.481	3.509	3.537	3.740	3.770	3.800	3.920	3.928	3.936	4.171

In diesel biodiesel blend, the density of fuel increases with the increase of amount of biodiesel in the mixture. The experimental results of density at testing temperature of 15°C for waste cooking oil methyl ester biodiesel -Euro diesel summer at different storage period has been depicted in Figure 4.4 and Table 4.5. It is noticed that the density of the blend was observed within the limit as mentioned in ASTM D 4052 standard at various storage period. Moreover, the increase in storage period leads to increase the density of biodiesel sample.



Figure 4.4: Density vs. period (time)

**Table 4.5:** Effect of storage period on density in kg/m<sup>3</sup> at 15°C

Days	0	10	20	30	40	50	60	70	80	90
Density	859.8	860.9	862.1	864.7	865.8	866.9	871.5	872.6	873.7	875.0

# 4.4 Effect of Storage Period and Temperature on Kinematic Viscosity and Density of Biodiesel Blend

The effect of testing temperature on kinematic viscosity for different storage period has been plotted in Figure 4.5 and summarized in Table 4.6 for some selected storage periods. It is observed that the samples demonstrate temperature-dependent behavior; their kinematic viscosities decrease nonlinearly with temperature. And, increasing the storage period leads to increase the kinematic viscosity of biodiesel blends.



Figure 4.5: Kinematic viscosity vs. temperature at different storage period

TIOCI		We	eks	
I[ C]	0	4	8	12
0	10.110	10.152	10.256	10.392
2	9.788	9.908	10.005	9.990
5	8.743	8.850	8.926	8.920
8	7.798	8.106	8.113	8.086
10	7.536	7.628	7.621	7.635
15	6.489	6.568	6.576	6.564
20	5.670	5.739	5.748	5.759
30	4.566	4.621	4.781	4.807
40	3.481	3.744	3.918	4.171
50	3.048	3.085	3.132	3.158
60	2.473	2.503	2.730	2.756
70	2.168	2.195	2.335	2.427
80	1.923	1.947	2.044	2.090
90	1.607	1.627	1.782	1.843

Table 4.6: Kinematic viscosity in mm<sup>2</sup>/s as function of storage periods and temperatures

Figure 4.6 and Table 4.7 show the effect of the testing temperature on the density of blend over some selected storage period for biodiesel blend. It is noticed that as the temperature increases, the density decreases. Also, storage over an extended period (12 weeks) resulted in higher density for fuel.



Figure 4.6: Density vs. temperature at different storage period

TIOCI	Weeks							
I[ C]	0	4	8	12				
0	901.848	906.965	914.016	917.731				
2	893.436	898.506	905.491	909.171				
5	885.024	890.046	896.966	900.612				
8	876.613	881.587	888.441	892.052				
10	868.201	873.128	879.916	883.492				
15	859.870	864.745	871.495	875.014				
20	851.539	856.371	863.029	866.536				
30	843.208	847.993	854.585	858.059				
40	833.245	837.973	844.488	847.920				
50	831.335	836.053	842.552	845.977				
60	822.179	826.844	833.272	836.659				
70	815.364	819.991	826.366	829.725				
80	801.908	806.458	812.728	816.031				
90	795.631	800.146	806.366	809.644				

**Table 4.7:** Effect of storage period on density in kg/m<sup>3</sup> for different storage period

# 4.4 Effect of Storage Period and Temperature on Dynamic Viscosity of Biodiesel Blend

Figure 4.6 and Table 4.8 show the effect of the testing temperature on the density of blend over some selected storage period for biodiesel blend. It is noticed that as the temperature increases, the density decreases. Also, storage over an extended period (12 weeks) resulted in higher density for fuel.



Figure 4.6: Dynamic viscosity vs. temperature at different storage period

TIOCI		Weeks							
I[ C]	0	4	8	12					
0	9.12E-03	9.21E-03	9.37E-03	9.54E-03					
2	8.75E-03	8.90E-03	9.06E-03	9.08E-03					
5	7.74E-03	7.88E-03	8.01E-03	8.03E-03					
8	6.84E-03	7.15E-03	7.21E-03	7.21E-03					
10	6.54E-03	6.66E-03	6.71E-03	6.75E-03					
15	5.58E-03	5.68E-03	5.73E-03	5.74E-03					
20	4.83E-03	4.92E-03	4.96E-03	4.99E-03					
30	3.85E-03	3.92E-03	4.09E-03	4.12E-03					
40	2.90E-03	3.14E-03	3.31E-03	3.54E-03					
50	2.53E-03	2.58E-03	2.64E-03	2.67E-03					
60	2.03E-03	2.07E-03	2.27E-03	2.31E-03					
70	1.77E-03	1.80E-03	1.93E-03	2.01E-03					
80	1.54E-03	1.57E-03	1.66E-03	1.71E-03					
90	1.28E-03	1.30E-03	1.44E-03	1.49E-03					

**Table 4.8:** Effect of storage period on density in kg/m<sup>3</sup> for different storage period

#### 4.6 Oxidation Stability and Acid Value of Biodiesel Blend

The determination of oxidation stability and acid value of biodiesel were carried out at Petrochemical Laboratory in Cyprus. Table 4.9 shows the results of oxidation stability and acid value of waste cooking biodiesel blends with Euro diesel summer.

 Days
 Acid Number
 Oxidation stability

 03.11.2017
 0.21
 8.8

 16.12.2017
 0.23
 3.25

Table 4.9: Oxidation stability in Hours and acid value in mgKOH/gr of biodiesel blend

#### 4.7 Cold Flow Properties of Biodiesel Blend

Pour Points (PP) and Cloud Points (CP) of biodiesel blend are shown in Table 4.10. Low temperature properties of the biodiesel were also investigated using DSC. Figure 4.7 shows the cooling curve and bath temperature during both the cooling and heating cycle scans. In order to know the values of cold flow properties, the second derivative of temperature (as function of time) has been calculated and plotted as shown in Figure4.7. It is observed that, the value of CP, CFPP and PP from cooling curve and observation data (Table 4.10) are almost equals which are 11, 7 and 6°C, respectively.

Table 4.10: Cold flow properties

СР	PP	CFPP
3°C	-2°C	0°C



Figure 4.7: Cooling curve of biodiesel blend

# CHAPTER 5 CONCLUSION AND FUTURE WORK

# **5.1** Conclusion

Waste cooking vegetable oil is used as a biodiesel in a mixture with Euro diesel summer. Ubbelohde viscometer and Pycnometer were used to measure the kinematic viscosity and density of biodiesel blend, respectively at elevated temperatures. The present study reported the viscosity and density of biodiesel blended with Euro diesel summer (50% volume/volume), at constant storage temperature with for 6 months. Also, determination of oxidation stability and acid value of biodiesel blend at various storage period were reported. The following conclusions can be drawn from the results of the present study.

- The experimental data showed that the kinematic viscosity of biodiesel blend decreased with an increase in temperature up to 90°C. However, the rate of decrease was more significant at lower temperatures than at higher temperatures. It was found that the viscosity of biodiesel blend depends on temperature.
- In all cases, the density and dynamic viscosity of blend decreases as temperature increases.
- It was observed that the biodiesel properties such as viscosity and density increases with increasing the storage period.

#### 5.2 Future Work

An interesting future study might involve studying other physical properties of biodiesel such cold flow properties (CFPP), peroxide value. In addition, the effect of long term storage on properties of biodiesel blends with different diesel fuels by varying the volume fraction of biodiesel from 0 to 100% in step of 5%.

## REFERENCES

- Aldrich, S. (2016). Silicone oil for oil baths. Retrieved November 7, 2017, from http://www.sigmaaldrich.com/catalog/product/sial/85409?lang=en®ion=TR
- ASTM Standard specification for biodiesel fuel (B100) blend stock for distillate fuels. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D6751-08; 2008a.
- ASTM Standard specification for diesel fuel oil, biodiesel blend (B6 to B20). In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D7467-08a; 2008b.
- ASTM Standard specification for diesel fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D975-08a; 2008c.
- ASTM Standard specification for fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D396-08b; 2008d.
- Benjumea, P., Agudelo, J., & Agudelo, A. (2008). Basic properties of palm oil biodiesel– diesel blends. *Fuel*, 87(10-11), 2069-2075.
- Bessee, G. B., & Fey, J. P. (1997). Compatibility of Elastomers and Metals in Biodiesel Fuel Blends. *SAE Technical Paper Series*.
- Bouaid, A., Martinez, M., & Aracil, J. (2007). Long storage stability of biodiesel from vegetable and used frying oils. *Fuel*, 86(16), 2596-2602.
- Canakci, M., & Van Gerpen, J. H. (2003). Comparison Of Engine Performance And Emissions For Petroleum Diesel Fuel, Yellow Grease Biodiesel, And Soybean Oil Biodiesel. *Transactions of the ASAE*, 46(4).
- Chhetri, A., & Watts, K. (2012). Viscosities of canola, jatropha and soapnut biodiesel at elevated temperatures and pressures. *Fuel*, *102*, 789-794.
- Clothier, P. Q., Aguda, B. D., Moise, A., & Pritchard, H. O. (1993). How do diesel-fuel ignition improvers work? *Chemical Society Reviews*, 22(2), 101.

- Cormick, R., Ratcliff, M., Moens, L., & Lawrence, R. (2007). Several factors affecting the stability of biodiesel in standard accelerated tests. *Fuel Processing Technology*, 88(7), 651-657. doi:10.1016/j.fuproc.2007.01.006
- Demirbas, A. (2008). Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel*, 87(8-9), 1743-1748.
- Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50(1), 14-34.
- Duffield, J. A., & United States. (1998). Biodiesel development: New markets for conventional and genetically modified agricultural products. Washington, DC: U.S. Dept. of Agriculture, ERS.
- Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. (2012). Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews*, 16(1), 143-169.
- Hong, I. K., Jeon, H., Kim, H., & Lee, S. B. (2016). Preparation of waste cooking oil based biodiesel using microwave irradiation energy. *Journal of Industrial and Engineering Chemistry*, 42, 107-112.
- Kerschbaum, S., & Rinke, G. (2004). Measurement of the temperature dependent viscosity of biodiesel fuels. *Fuel*, 83(3), 287-291.
- Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology*, 86(10), 1059-1070.
- Knothe, G. (2007). Some aspects of biodiesel oxidative stability. *Fuel Processing Technology*, 88(7), 669-677.
- Knothe, G. (2010). Biodiesel: Current Trends and Properties. *Topics in Catalysis*, 53(11-12), 714-720.
- Knothe, G., Krahl, J., & Van, G. J. (2010). *The biodiesel handbook*. Urbana, IL: AOCS Press.
- Lalvani, J. I., Parthasarathy, M., Dhinesh, B., & Annamalai, K. (2015). Experimental investigation of combustion, performance and emission characteristics of a modified piston. *Journal of Mechanical Science and Technology*, 29(10), 4519-4525.
- Latini, G., Cocci, G. R., & Passerini, G. (2006). *Transport properties of organic liquids*. Southampton: WIT Press.

- Lee, Y., & Huh, K. Y. (2013). Numerical study on spray and combustion characteristics of diesel and soy-based biodiesel in a CI engine. *Fuel*, 113, 537-545.
- McCormick, R. L., Graboski, M. S., Alleman, T. L., Herring, A. M., & Tyson, K. S. (2001). Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environmental Science & Technology*, 35(9), 1742-1747.
- McCormick, R. L., Graboski, M. S., Alleman, T. L., Herring, A. M., & Tyson, K. S. (2001). Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environmental Science & Technology*, 35(9), 1742-1747.
- Meng, X., Jia, M., & Wang, T. (2014). Neural network prediction of biodiesel kinematic viscosity at 313K. *Fuel*, 121, 133-140.
- Monyem, A., & H. Van Gerpen, J. (2001). The effect of biodiesel oxidation on engine performance and emissions. *Biomass and Bioenergy*, 20(4), 317-325.
- Neff, W. E., Selke, E., Mounts, T. L., Rinsch, W., Frankel, E. N., & Zeitoun, M. A. (1992). Effect of triacylglycerol composition and structures on oxidative stability of oils from selected soybean germplasm. *Journal of the American Oil Chemists' Society*, 69(2), 111-118.
- Prieto, N. M., Ferreira, A. G., Portugal, A. T., Moreira, R. J., & Santos, J. B. (2015). Correlation and prediction of biodiesel density for extended ranges of temperature and pressure. *Fuel*, 141, 23-38.
- Ramadhas, A. S. (2011). Alternative fuels for transportation. Boca Raton, FL: CRC Press.
- Ramírez-Verduzco, L. F., García-Flores, B. E., Rodríguez-Rodríguez, J. E., & Del Rayo Jaramillo-Jacob, A. (2011). Prediction of the density and viscosity in biodiesel blends at various temperatures. *Fuel*, 90(5), 1751-1761.
- Ramírez-Verduzco, L. F., García-Flores, B. E., Rodríguez-Rodríguez, J. E., & Del Rayo Jaramillo-Jacob, A. (2011). Prediction of the density and viscosity in biodiesel blends at various temperatures. *Fuel*, 90(5), 1751-1761.
- Sahin, S., & Sumnu, S. G. (2006). *Physical properties of foods*. New York: Springer
- Sarin, A., Arora, R., Singh, N., Sharma, M., & Malhotra, R. (2009). Influence of metal contaminants on oxidation stability of Jatropha biodiesel. *Energy*, 34(9), 1271-1275.

- Selvaraj, R. A. (2016). *Green fuel technology. Microbial oil production from oleaginous yeast (cryptococcus curvatus).* S.l.: anchor academic publishin.
- Senda, J., Okui, N., Suzuki, T., & Fujimoto, H. (2004). Flame Structure and Combustion Characteristics in Diesel Combustion Fueled with Bio-diesel. SAE Technical Paper Series.
- Singh, S., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, 14(1), 200-216.
- Tat, M., & Van Gerpen, H. (1999). The kinematic viscosity of biodiesel and its blends with diesel fuel. *J Am Oil Chem*, *76*(12), 1511–1514.
- Tomes, D. T., Lakshmanan, P., & Songstad, D. (2011). *Biofuels: Global impact on renewable energy, production agriculture, and technological advancements.* New York: Springer. LLC.
- 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.
- Yaakob, Z., Narayanan, B., Padikkaparambil, S., & Akbar, M. (2014). A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews*, 35, 136-153.
- Yuan, W., Hansen, A., & Zhang, Q. (2009). Predicting the temperature dependent viscosity of biodiesel fuels. *Fuel*, 88(6), 1120-1126.

APPENDICES

# **APPENDIX 1**

# STANDARD TEST METHOD FOR KINEMATIC VISCOSITY OF TRANSPARENT AND OPAQUE LIQUIDS (AND CALCULATION OF DYNAMIC VISCOSITY)

Designation: D 445 – 09



Designation: 71/1/97

# Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)<sup>1</sup>

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 ( $\varepsilon$ ) 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,  $\nu$ , 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,  $\eta$ , can be obtained by multiplying the kinematic viscosity,  $\nu$ , by the density,  $\rho$ , 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  $300\ 000\ \text{mm}^2/\text{s}$  (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 appro-

<sup>1</sup> 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.

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 2. Referenced Documents

- 2.1 ASTM Standards:<sup>2</sup>
- 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:<sup>3</sup>

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

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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.

<sup>&</sup>lt;sup>2</sup> 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.

<sup>&</sup>lt;sup>3</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

- 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:<sup>4</sup>

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,  $\rho$ . For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity,  $\nu$ , where  $\nu = \eta/\rho$ , and  $\eta$  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  $1^{\circ}$  in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within  $0.3^{\circ}$  in all directions (see Specifications D 446 and ISO 3105).

<sup>&</sup>lt;sup>4</sup> 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  $\pm 0.02$ °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  $\pm 0.05$ °C.

6.4 Temperature Measuring Device in the Range from 0 to  $100^{\circ}C$ —Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of  $\pm 0.02^{\circ}C$  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  $0.04^{\circ}$ 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  $\pm 0.05$ °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  $\pm 0.1$ °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  $\frac{1}{5}$  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  $\pm 0.07$  % (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 nonchromiumcontaining, 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. Nonchromiumcontaining, 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  $\pm 0.35\%$  of the certified value have been used. The data to support the limit of  $\pm 0.35\%$  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.

Licensee=Bogazici University/5964815002 Not for Resale, 04/08/2010 05:34:03 MDT 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:

$$C_2 = (g_2/g_1) \times C_1 \tag{1}$$

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

#### **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.<sup>A</sup>

Viscosity of Reference Material, mm <sup>2</sup> /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%	

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

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.

#### 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  $\mu$ m 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  $\pm$  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,  $\nu$ , in mm<sup>2</sup>/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.)

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#### 14. Calculation

14.1 Calculate each of the determined kinematic viscosity values,  $v_1$  and  $v_2$ , 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:

 $\nu_{I,2}$  = determined kinematic viscosity values for  $\nu_1$  and  $\nu_2$ , respectively, mm<sup>2</sup>/s,

C = calibration constant of the viscometer, mm<sup>2</sup>/s<sup>2</sup>, and

 $t_{1,2}$  = measured flow times for  $t_1$  and  $t_2$ , respectively, s.

Calculate the kinematic viscosity result,  $\nu$ , as an average of  $\nu_1$  and  $\nu_2$  (see 11.2.3 and 12.5.1).

14.2 Calculate the dynamic viscosity,  $\eta$ , from the calculated kinematic viscosity,  $\nu$ , and the density,  $\rho$ , by means of the following equation:

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

where:

 $\eta$  = dynamic viscosity, mPa·s,

 $\rho$  = density, kg/m<sup>3</sup>, at the same temperature used for the determination of the kinematic viscosity, and

 $\nu$  = kinematic viscosity, mm<sup>2</sup>/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 <sup>5</sup>	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C <sup>6</sup>	0.0013 y	(0.13 %)
Formulated oils at 150°C7	0.015 y	(1.5 %)
Petroleum wax at 100°C <sup>8</sup>	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C9	0.011 (y + 8)	
Residual fuel oils at 50°C9	0.017 y	(1.7 %)
Additives at 100°C <sup>10</sup>	0.00106 y <sup>1.1</sup>	

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Gas oils at 40°C<sup>11</sup>
Jet fuels at –20°C<sup>12</sup>
```

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

0.0013 (y+1)

(0.18 %)

0.0018 y

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°C⁵	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C <sup>6</sup>	0.0026 x	(0.26 %)
Formulated oils at 150°C7	0.0056 x	(0.56 %)
Petroleum wax at 100°C <sup>8</sup>	0.0141 x <sup>1.2</sup>	
Residual fuel oils at 80 and 100°C9	0.013 (x + 8)	
Residual oils at 50°C <sup>9</sup>	0.015 x	(1.5 %)
Additives at 100°C <sup>10</sup>	0.00192 x <sup>1.1</sup>	
Gas oils at 40°C <sup>11</sup>	0.0043 (x+1)	
Jet fuels at -20°C <sup>12</sup>	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.

<sup>7</sup> 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 mm<sup>2</sup>/s at 150°C, and first published in 1991. See Guide D 6074.

<sup>8</sup> 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 mm<sup>2</sup>/s at 100°C, and were first published in 1988.

<sup>9</sup> 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 mm<sup>2</sup>/s at 50°C and from 5 to 170 mm<sup>2</sup>/s at 80 and 100°C, and were first published in 1984.

<sup>10</sup> 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 mm<sup>2</sup>/s at 100°C and were first available in 1997.

<sup>11</sup> 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 mm<sup>2</sup>/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 mm<sup>2</sup>/s at– 20°C and were first available in 1997.

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<sup>&</sup>lt;sup>5</sup> 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 mm<sup>2</sup>/s at 40°C and from 2 to 43 mm<sup>2</sup>/s at 100°C, and were first published in 1989. Request See Guide D 6074.

<sup>&</sup>lt;sup>6</sup> 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 <sup>2</sup>/s at 40°C and from 6 to 25 mm<sup>2</sup>/s at 100°C, and were first published in 1991. See Guide D 6071.


Base oils at 40 and 100°C <sup>5</sup>	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C <sup>6</sup>	0.0076 x	(0.76 %)
Formulated oils at 150°C7	0.018 x	(1.8 %)
Petroleum wax at 100°C <sup>8</sup>	0.0366 x <sup>1.2</sup>	
Residual fuel oils at 80 and 100°C <sup>9</sup>	0.04 (x + 8)	
Residual oils at 50°C9	0.074 x	(7.4 %)
Additives at 100°C <sup>10</sup>	0.00862 x <sup>1.1</sup>	
Gas oils at 40°C <sup>11</sup>	0.0082 (x+1)	
Jet fuels at -20°C <sup>12</sup>	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.<sup>13</sup>

#### 18. Keywords

18.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

<sup>13</sup> 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 Ki	nematic Viscosity Range, <sup>A</sup> mm <sup>2</sup> /s			
A. Ostwald Types for	Transparent Liquids			
Cannon-Fenske routine <sup>B</sup>	0.5 to 20 000			
Zeitfuchs	0.6 to 3 000			
BS/U-tube <sup>B</sup>	0.9 to 10 000			
BS/U/M miniature	0.2 to 100			
SIL <sup>B</sup>	0.6 to 10 000			
Cannon-Manning semi-micro	0.4 to 20 000			
Pinkevitch <sup>B</sup>	0.6 to 17 000			
B. Suspended-level Types	for Transparent Liquids			
BS/IP/SL <sup>B</sup>	3.5 to 100 000			
BS/IP/SL(S) <sup>B</sup>	1.05 to 10 000			
BS/IP/MSL	0.6 to 3 000			
Ubbelohde <sup>B</sup>	0.3 to 100 000			
FitzSimons	0.6 to 1 200			
Atlantic <sup>B</sup>	0.75 to 5 000			
Cannon-Ubbelohde(A), Cannon	0.5 to 100 000			
Ubbelohde dilution <sup>B</sup> (B)				
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			

<sup>A</sup> 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.

<sup>B</sup> In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

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TABLE A1.2 Certified Viscosity Reference Standards

Designation	Approximate Kinematic Viscosity, mm <sup>2</sup> /s					
Designation	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** 

	lest			le	lest	
Thermometer No.	Tempe	rature	Thermometer No.	Tempe	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-inglass 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)







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  $0.005^{\circ}$ 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

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

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

A4.1.1 If the standard deviation for site uncertainty,  $\sigma_{site}$ , 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.

 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.

A4.3 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.

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# **APPENDIX 2**

# STANDARD TEST METHOD FOR DENSITY AND RELATIVE DENSITY (SPECIFIC GRAVITY) OF LIQUIDS BY LIPKIN BICAPILLARY PYCNOMETER

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An American National Standard

H-26-30

# Standard Test Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer<sup>1</sup>

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 ( $\epsilon$ ) 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<sup>2</sup>/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<sup>2</sup>

E 1 Specification for ASTM Thermometers<sup>3</sup>

#### 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<sup>4</sup>

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  $15^{\circ}$ C or  $60^{\circ}$ F.

#### 6. Apparatus

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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  $20 \pm 0.02^{\circ}$ C or  $25 \pm 0.02^{\circ}$ 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  $\frac{1}{8}$  in. (3.2 mm) in thickness by 1 in. (25 mm) in width, of a length suitable for

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<sup>&</sup>lt;sup>1</sup> 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.

<sup>&</sup>lt;sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>&</sup>lt;sup>3</sup> Annual Book of ASTM Standards, Vois 05.03 and 14.01.

<sup>&</sup>lt;sup>4</sup> 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.

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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

the bath used, and with seven  $\frac{9}{32}$ -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



Metric Equivalents

in.	mm	in.	mm
5/16	7.94	3⁄4	19
9/16	14.3	11/2	38
1/8	3.2	1%	41.3
3/8	9.53	23/16	55.6
1/4	6.4	51⁄4	133.4
1⁄2	12.7	71/4	184.2

#### FIG. 2 Pycnometer Holder

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  $25^{\circ}$ 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.

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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.

TABLE 1 Air Buoyancy Corrections

W/V	Correction, <sup>A</sup> plus	W/V	Correction, <sup>A</sup> 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

<sup>A</sup> 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.

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  $\frac{1}{2}$  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  $\pm 0.02$ °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.

#### 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----

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TABLE 2 Density of Water Temperature, Density, Temperature, Density, Temperature, Density, °C g/mL °C g/mL °C g/mL 0.99224 0 0.99987 0.99802 40 21 3 0.99999 22 0.99780 45 0.99025 23 0.98807 4 1.00000 0.99756 50 5 0.99999 24 0.99732 55 0.98573 60 0,98324 0.99973 0.99707 10 25 0.98059 15 0.99913 26 0.99681 65 15.56 0.99904 27 0.99654 70 0.97781 28 75 0.97489 16 0.99897 0.99626 29 0.99597 80 0.97183 0.99880 17 85 0 96865 0.99862 30 0.99567 18 0.96534 19 0.99843 35 0.99406 90 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  $20^{\circ}C = x.xxxx \text{ g/mL}$ ). In reporting relative density, give both the test temperature and the reference temperature, but no units (For example: relative density,  $15.56/15.56^{\circ}C = x.xxxx$ ). 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**

4

#### 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**

# STANDARD TEST METHOD FOR CLOUD POINT OF PETROLEUM PRODUCTS





# Standard Test Method for Cloud Point of Petroleum Products<sup>1</sup>

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 ( $\epsilon$ ) 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:<sup>2</sup>

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:<sup>3</sup>

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

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

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<sup>&</sup>lt;sup>1</sup> 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.

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<sup>&</sup>lt;sup>2</sup> 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.

<sup>&</sup>lt;sup>3</sup> Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

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



Note—All dimensions are in millimetres. FIG. 1 Apparatus for Cloud Point Test

mm. The jar should be marked with a line to indicate sample height  $54 \pm 3$  mm above the inside bottom.

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

		Thermo	meter
		Num	ber
Thermometer	Temperature Range	ASTM	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
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	Bath Temperature
Ice and water	0 ± 1.5°C
Crushed ice and sodium chloride crystals, or acetone or petroleum	$-18 \pm 1.5^{\circ}C$
naptha (see 7) with solid carbon dioxide added to give the desired	
temperature	
Acetone or petroleum naptha (see 7) with solid carbon dioxide	$-33 \pm 1.5^{\circ}C$
added to give the desired temperature	
Acetone or petroleum naptha (see 7) with solid carbon dioxide	–51 ± 1.5°C
added to give the desired temperature	
Acetone or petroleum naptha (see 7) with solid carbon dioxide	$-69 \pm 1.5^{\circ}C$
added to give the desired temperature	

#### 8. Procedure

8.1 Bring the sample to be tested to a temperature at least  $14^{\circ}$ 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  $14^{\circ}$ 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  $-36^{\circ}$ C and the low cloud and pour thermometer if the expected cloud point is below  $-36^{\circ}$ 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  $0 \pm 1$ °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  $\pm$  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  $-18 \pm 1.5$ °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  $-33 \pm 1.5$ °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

TABLE 2 Bath and Sample Temperature Ranges

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

reaches the lowest specimen temperature in the range identified for the current bath in use, based on the ranges stated in Table 2.

8.7 Report the cloud point, to the nearest  $1^{\circ}$ 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  $2^{\circ}$ 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  $4^{\circ}$ C only in 1 case in 20.

10.1.3 The precision statements were derived from a 1990 interlaboratory cooperative test program.<sup>4</sup> 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*<sup>5</sup>—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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<sup>&</sup>lt;sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1444.

<sup>&</sup>lt;sup>5</sup> 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  $2^{\circ}$ 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  $+10^{\circ}$ C.

10.3.3 The precision statements were derived from a 2001 interlaboratory cooperative test program.<sup>5</sup> 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  $-45^{\circ}$ 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*<sup>5</sup>—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.

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# **APPENDIX 4**

# PETROLEUM PRODUCTS - DETERMINATION OF POUR POINT

# INTERNATIONAL STANDARD



Second edition 1994-08-01

Corrected and reprinted 1995-03-15

# Petroleum products — Determination of pour point

Produits pétroliers — Détermination du point d'écoulement



Reference number ISO 3016:1994(E)

# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 3016 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 3016:1974), which has been technically revised.

Annex A forms an integral part of this International Standard.

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# **Petroleum products — Determination of pour point**

WARNING — The use of this International 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.

## 1 Scope

This International Standard specifies a method for the determination of the pour point of petroleum products. A separate procedure suitable for the determination of the lower pour point of fuel oils, heavy lubricant base stock, and products containing residual fuel components is also described.

NOTE 1 A method for the pour point of crude oils is under development. The pour point of crude oils may be determined by the general procedure described in this International Standard, but some crude oils may need a modified pretreatment to avoid the loss of volatile material. The precision in this International Standard was derived on a sample matrix that did not include crude oils (see note 5).

# 2 Definition

For the purposes of this International Standard, the following definition applies.

**2.1 pour point:** Lowest temperature at which a sample of petroleum product will continue to flow when it is cooled under specified standard conditions.

# 3 Principle

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 sample is observed is recorded as the pour point.

# 4 Reagents and materials

- 4.1 Sodium chloride (NaCl), crystals.
- **4.2 Calcium chloride (CaCl<sub>2</sub>)**, crystals.
- **4.3 Carbon dioxide (CO<sub>2</sub>)**, solid.

**4.4 Coolant liquid**: acetone, methanol or petroleum naphtha.

4.5 Wiping fluid: acetone, methanol or ethanol.

# **5 Apparatus** (see figure 1)

**5.1 Test jar**, cylindrical, of clear glass, flat-bottomed, 33,2 mm to 34,8 mm outside diameter and 115 mm to 125 mm in height. The test jar shall have an inside diameter of 30,0 mm to 32,4 mm, with the constraint that the wall thickness be no greater than 1,6 mm. The jar shall be marked with a line to indicate a contents level 54 mm  $\pm$  3 mm above the inside bottom.

**5.2 Thermometers**, partial immersion type conforming to the specifications given in annex A.

**5.3 Cork**, to fit the test jar, bored centrally to take the test thermometer.

**5.4 Jacket**, watertight, cylindrical, metal, flatbottomed, 115 mm  $\pm$  3 mm in depth with inside diameter 44,2 mm to 45,8 mm, and a wall thickness of approximately 1 mm. It shall be supported in a vertical

position in the cooling bath (5.7) so that no more than 25 mm projects out of the cooling medium, and shall be capable of being cleaned.



Figure 1 — Apparatus for pour point test

**5.5 Disc**, of cork or felt approximately 6 mm in thickness, to fit inside the jacket.

**5.6 Gasket**, ring form, approximately 5 mm in thickness, to fit snugly on the outside of the test jar and loosely inside the jacket. This gasket shall be made of rubber, leather or other suitable material, elastic enough to cling to the test jar and hard enough to hold its shape.

NOTE 2 The purpose of the ring gasket is to prevent the test jar from touching the jacket.

**5.7 Cooling bath**, of a type suitable for obtaining the required temperatures. The size and shape of the bath are optional, but a support to hold the jacket firmly in a vertical position is essential. The bath temperature shall be monitored by means of the appropriate thermometer (specified in annex A) immersed to the correct immersion depth. For the determination of pour points below 9 °C, two or more baths are required. The required bath temperatures shall be obtained either by refrigeration or by suitable freezing mixtures, and shall be maintained at the desired temperatures  $\pm 1,5$  °C.

NOTE 3 The freezing mixtures commonly used are as follows:

For pour-point temperatures down to:

- a) 9 °C: ice and water (can be used to prepare the 0 °C bath in 6.8);
- b) -12 °C: crushed ice and sodium chloride (4.1) (can be used to prepare the -18 °C bath in 6.8);
- c) -27 °C: crushed ice and calcium chloride (4.2) (can be used to prepare the -33 °C bath in 6.8);
- d) -57 °C: carbon dioxide (4.3) and coolant liquid (4.4)<sup>1)</sup> (can be used to prepare the -51 °C and -69 °C baths in 6.8).

**5.8 Timing device**, capable of measuring up to 30 s with an accuracy of 0,2 s.

# 6 Procedure

**6.1** Pour the sample into the test jar to the level mark. If necessary, heat the sample in a water bath until it is just sufficiently fluid to pour into the test jar.

If it is necessary to heat the sample to a temperature greater than 45 °C to effect the transfer to the test jar, or when it is known that a sample has been heated to a temperature higher than 45 °C during the preceding 24 h, or when the thermal history of the sample is not known, keep the sample at room temperature for 24 h before testing it.

**6.2** Close the test jar (5.1) with the cork (5.3) carrying the high-cloud-and-pour thermometer or, if the expected pour point is above 36 °C, the melting point thermometer (annex A). Adjust the position of the cork and thermometer so that the cork fits tightly, the thermometer and the test jar are coaxial, and the thermometer bulb is immersed to a depth which places the beginning of the capillary 3 mm below the surface of the sample.

**6.3** Subject the sample in the test jar to a preliminary treatment, appropriate to its pour point, in accordance with 6.4 or 6.5.

**6.4** Samples having pour points above – 33 °C shall be treated as follows.

**6.4.1** Heat the sample without stirring to 9 °C above the expected pour point, or to 45 °C, whichever is greater, in a bath maintained at 12 °C above the expected pour point, but at least 48 °C.

**6.4.2** Transfer the test jar to a bath maintained at 24 °C  $\pm$  1,5 °C.

**6.4.3** When the sample temperature reaches  $9 \degree C$  above the expected pour point (estimated as a multiple of  $3 \degree C$ ), commence observations for flow in accordance with 6.7.

**6.4.4** If the sample has not ceased to flow when the temperature has reached 27 °C, carefully remove the test jar from the bath, wipe the outside surface with a clean cloth moistened with wiping fluid (4.5), and place it in the 0 °C bath (5.7) in accordance with 6.6. Make observations for flow in accordance with 6.7 and cool as specified in the schedule given in 6.8.

**6.5** Samples having pour points of -33 °C and below shall be treated as follows.

**6.5.1** Heat the sample without stirring to 45 °C in a bath maintained at 48 °C, and cool to 15 °C in a bath maintained at 6 °C  $\pm$  1,5 °C.

<sup>1)</sup> This mixture may be made as follows: in a covered metal beaker chill a suitable amount of coolant liquid (4.4) to -12 °C, or lower, by means of an ice-salt mixture. Then add enough carbon dioxide (4.3) to the chilled coolant liquid to give the desired temperature. Solid carbon dioxide is commercially available in many areas.

**6.5.2** When the temperature has reached 15 °C, carefully remove the test jar from the water bath, wipe the outside surface with a clean cloth moistened with wiping fluid (4.5), remove the high-cloud-and-pour thermometer and replace it with the low-cloud-and-pour thermometer (annex A). Place the test jar in the 0 °C bath (6.7) in accordance with 6.6. Successively place the test jar into lower-temperature baths in accordance with the schedule specified in 6.8.

**6.5.3** When the temperature reaches 9 °C above the expected pour point, commence observations for flow in accordance with 6.7.

**6.6** Ensure that the disc (5.5), gasket (5.6) and the inside of the jacket (5.4) are clean and dry, and place the disc in the bottom of the jacket. The disc and jacket shall have been placed in the cooling medium (see 5.7) a minimum of 10 min before the test jar is inserted. Place the gasket around the test jar approximately 25 mm from the bottom, and insert the test jar into the jacket. With the exception of the baths at 24 °C and 6 °C, never place a test jar directly into the cooling medium.

6.7 Carry out observations for flow.

**6.7.1** At each thermometer reading that is a multiple of 3 °C below the temperature of the first observation, remove the test jar from the bath or jacket, as applicable, and tilt it just sufficiently to ascertain whether there is movement in the sample in the test jar. The complete operation of test jar removal, observation of the sample for flow, and return of the test jar to the bath shall not exceed 3 s.

**6.7.2** Continue observations at each thermometer reading that is a multiple of 3 °C below the temperature of the first observation.

Take great care not to disturb the mass of sample or to permit the thermometer to shift in the sample after the sample has cooled sufficiently to allow for the formation of wax crystals, as any disturbance of the spongy network of wax crystals will lead to low and erroneous results.

NOTE 4 At low temperatures, condensed moisture may limit visibility. This can be removed by wiping the outside surface of the test jar with a clean cloth moistened with wiping fluid (4.5) close to the bath temperature.

**6.7.3** As soon as the sample does not flow when tilted, hold the test jar in a horizontal position for 5 s, as measured by the timing device (5.8), and observe carefully. If the sample shows any movement, replace

the test jar immediately in the bath or jacket, as applicable, and repeat the observation at the next temperature, 3 °C lower.

**6.7.4** Continue in this manner until a temperature is reached when the sample shows no movement when the test jar is held in a horizontal position for 5 s. Record the observed reading of the thermometer.

**6.8** If the sample has not ceased to flow when its temperature has reached 9 °C, transfer it to the next lower temperature bath, and similarly at -6 °C, -24 °C and -42 °C in accordance with the following schedule:

- a) sample is at +9 °C, move to 18 °C bath;
- b) sample is at -6 °C, move to -33 °C bath;
- c) sample is at 24 °C, move to 51 °C bath;
- d) sample is at -42 °C, move to -69 °C bath.

**6.9** To determine compliance with existing obsolescent specifications having pour-point limits at temperatures not divisible by 3 °C, it is acceptable practice to conduct the pour-point measurement according to the following schedule.

Begin to examine the appearance of the sample when the temperature of the sample is 9 °C above the specification pour point. Continue observations at 3 °C intervals in accordance with 6.7 and 6.8 until the specification temperature is reached. Report the sample as passing or failing the specification limit.

**6.10** For fuel oils, heavy lubricant base stock and products containing residual fuel components, the result obtained by the procedure given in 6.1 to 6.8 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 given in 6.2 to 6.8.

**6.11** If automatic testing instruments are used, the user shall ensure that all of the manufacturer's instructions for calibration, adjustment and operation of the instrument are followed. As the precision of automatic pour-point testers has not been determined, in any case of dispute, the pour point shall be determined by the manual method described herein and shall be considered as the reference test.

# 7 Expression of results

Add 3  $^{\circ}$ C to the temperature recorded in 6.7.4 or 6.10 and report this as the pour point, or lower pour point, as applicable.

# 8 Precision

## 8.1 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 3 °C only in one case in 20. Differences greater than this should be considered suspect.

# 8.2 Reproducibility

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 the test method, exceed 6 °C only in one case in 20. Differences greater than this should be considered suspect.

NOTE 5 The precision statements were prepared with data on ten new (unused) mineral oil-based lubricants and

16 assorted fuel oils tested by 12 co-operators. The mineral oil-based lubricants had pour points ranging from -48 °C to -6 °C, while the fuel oils had pour points ranging from -33 °C to +51 °C. The following precision data was obtained:

	Mineral oils, lubricants	Fuel oils
95 % confidence:		
Repeatability, °C	2,87	2,52
Reproducibility, °C	6,43	6,59

# 9 Test report

The test report shall contain at least the following information:

- a) sufficient details for complete identification of the product tested;
- b) a reference to this International Standard;
- c) the result of the test (see clause 7);
- d) any deviation, by agreement or otherwise, from the procedures specified (see clause 6);
- e) the date of the test;
- f) whether the test was determined by an automatic instrument.

# Annex A

(normative)

# **Thermometer specifications**

Table A.1 gives the specifications for the partial immersion liquid-in-glass thermometers required for this International Standard. Thermometers ASTM 6C/IP 2C (low cloud and pour), ASTM 5C/IP 1C (high cloud and pour), and ASTM 61C/IP 63C (melting point) meet these requirements.

		Low cloud and pour	High cloud and pour	Melting point
Range	°C	- 80 to + 20	– 38 to + 50	32 to 127
Immersion	mm	76	108	79
Graduation at each	°C	1	1	0,2
Longer lines at each	°C	5	5	1
Figured at each	°C	10	10	2
Scale error, max	°C	1 down to – 33 2 below – 33	0,5	0,2
Expansion chamber to permit heating to	°C	60	100	150
Overall length	mm	230 ± 5	230 ± 5	380 ± 5
Stem diameter	mm	6 to 8	6 to 8	6 to 8
Bulb length	mm	7,0 to 10	7,0 to 10	18 to 28
Bulb diameter	mm	5,0 to stem	5,5 to stem	5,0 to 6,0
Distance from bottom of bulb to				
line at	°C	- 70	- 38	32
	mm	100 to 120	120 to 130	105 to 115
Length of scale/range	mm	70 to 100	65 to 85	200 to 240

# Table A.1 — Thermometer specifications

#### NOTES

6 The emergent stem temperature is 21 °C throughout the scale range.

7 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  $\pm$  1 °C (for example ice point).

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