AN EXPERIIMENTAL AND NUMERICAL INVESTIGATION OF SOME THERMO-PHYSICAL PROPERTIES OF WASTE VEGETABLE OIL BIODIESEL AT VARIOUS TEMPERATURES

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

By YOUSSEF KASSEM

In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Mechanical Engineering

YOUSSEF KASSEM

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 Doctor of Philosophy in Mechanical Engineering

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To my parents ...

ABSTRACT

Biodiesel is considered as an alternative source of energy obtained from renewable materials. The purpose of this study was to investigate the effect of the temperature on the kinematic, dynamic viscosity and density of transesterified methyl ester using waste frying oil biodiesel (WFME) and waste canola oil biodiesel (WCME) and their blends (25-WFME, 50 WFME and 75-WFME). Also, this survey has examined the cold flow properties (Cloud Point (CP) and Pour Point (PP)) of the produced biodiesel. The kinematic viscosity, density, CP and PP measurements were made according to ASTM standards. The properties of the biodiesel produced such as viscosity and density were measured within temperature ranges -10°C to 270°C. CP and PP were measured within temperature range -10°C to 20°C. In this study, five general correlations were presented for estimating the density and kinematic viscosity of the two biodiesel and their blends at several temperatures. Furthermore, the viscosity and density of biodiesel samples were predicted at a temperature between 20°C and 270°C using adaptive Neuro-fuzzy inference system (ANFIS), and artificial neural networks (ANN) approaches. An experimental database was used for the developing of models, where the input variables in the network were the temperature and volume fraction of WFME. The learning task was done through hybrid and back-propagation methods, while, Sugeno-type fuzzy inference system Levenberg-Marquardt algorithm were used for the optimization process of ANFIS and ANN, respectively. In order to show the best-fitted algorithm, an extensive comparison test was applied on the ANFIS and ANN. The experimental investigation showed that CP and PP of WCME were increased with an increase in the concentration of WFME. Furthermore, empirical equations for predicting the thermo-physical properties (viscosity, density, CP and PP) of biodiesel samples resulted in values in good agreement with experiments. The results obtained showed that with the increase of the temperature, kinematic viscosity, dynamic viscosity and density decreased. Moreover, the test revealed that the ANFIS procedure yielded very accurate results in comparison with ANN procedures. Moreover, the mathematical models can be used for predicting the viscosity and density of biodiesel without needing experimental measurements

Keyword: ANFIS; ANN; densities; mathematical equations; viscosities

ÖZET

Biyodizel, bir katalizör varlığında transesterifikasyon ile bitkisel yağlardan veya hayvansal yağlardan üretilen, özellikle dizel motorlar için cazip bir alternatif yakıttır. Bu deneyde biyodizel üretimi için hammadde olarak atık kızartma yağı ve atık kanola yağı kullanılmıştır. Farklı yüzdeliklerde, 25-atık yağ bazlı, 50-atık yağ bazlı ve 75 atık yağ bazlı biyodizel üretilmiştir. Bu çalışmanın amacı, sıcaklığın biyodizel numunelerinin kinematik, dinamik viskozitesi ve yoğunluğu üzerindeki etkisini araştırmaktır. Bu çalışma ayrıca üretilen biyodizelin akışkanlık özelliklerinin yanı sıra kinematik viskozite, Bulutlanma Noktasını (BN) ve Akma Noktasını (AN) incelemektedir. Yoğunluk, kinematik viskozite, BN ve AN ölçümleri ASTM standartlarına göre yapılmıştır. Üretilen biyodizelin viskozite ve yoğunluk gibi özellikleri -10 °C ila 270 °C arasındaki sıcaklık aralıklarında ölçülmüştür. BN ve AN, -10°C ile 20 °C sıcaklık aralığında ölçülmüştür. Bu çalışmada, iki biyodizelin ve karışımlarının yoğunluğunu ve kinematik viskozitesini çeşitli sıcaklıklarda tahmin etmek için beş genel korelasyon sunulmuştur. Buna ek olarak, biyodizel örneklerinin viskozitesi ve yoğunluğu, uyarlanabilir Nöro-bulanık çıkarım sistemi (ANFIS) ve yapay sinir ağları (YSA) yaklaşımları kullanılarak 20°C ile 270 °C arasındaki bir sıcaklıkta öngörülmüştür. Ağdaki girdi değişkenlerinin atık yağ bazlı biyodizelin sıcaklık ve hacim fraksiyonu olduğu modellerin geliştirilmesi için deneysel bir veri tabanı kullanılmıştır. En uygun algoritmayı göstermek için, ANFIS ve ANN'de kapsamlı bir karşılaştırma testi uygulanmıştır. Deneysel araştırmalar, atık kanola bazlı biyodizelin, BN ve AN'sının, atık yağ bazlı biyodizelin konsantrasyonunda bir artış göstermiştir. Ayrıca, biyodizel numunelerinin termo-fiziksel özelliklerini (viskozite, yoğunluk, BN ve AN) tahmin etmede ampirik denklemler kullanılmış ve iyi sonuçlar vermiştir. Elde edilen sonuçlar, sıcaklığın artmasıyla kinematik viskozite, dinamik viskozite ve yoğunluğun azaldığını göstermektedir. Ayrıca, test ANFIS prosedürünün ANN prosedürlerine göre yapılan kıyasla çok doğru sonuçlar verdiğini ortaya koymuştur.

Anahtar Kelimeler: ANFIS; ANN; matematiksel denklemler; yoğunluk; viskozite

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LIST OF SYMBOLS USED

- A₁ Specific constant, dimensionless
- *a* Intercept, dimensionless
- a_i Activation of the unit
- **B** Specific constant, dimensionless
- **b** Negative slope, dimensionless
- *E* Backward propagation of errors
- *E* Correction factor, dimensionless
- *E* Constant, dimensionless
- E_a Activation energy for flow, J/mole
- g Acceleration gravity, m/s²
- *H* Height, m
- *h* Hidden layer
- *i* Input layer
- **K** Calibration constant, dimensionless
- *L* Length of vertical pipe, m
- *M_i* Molecular weight, g/mole
- *N_i* Number of double bond
- *n* Node number
- *o* Output layer
- p_j Potential of unit j
- P_i Potential of unit *i*
- $\frac{\partial p}{\partial z}$ Pressure gradient in z-direction
- Q Volume flow rate, m³/s
- \tilde{R} Radius of capillary, m
- **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_{θ} Velocity of liquid in θ -direction
- w_i Mass fraction
- w_{ii} Weight of the connection from unit *i* to unit *j*
- *x* Input data
- α Learning rate
- β Momentum rate
- μ dynamic viscosity, Pa.s
- \boldsymbol{v} kinematic viscosity, mm²/s
- ρ density of the liquid, kg/m³
- σ Sigmoid function
- τ shear stress, Pa

CHAPTER 1 INTRODUCTION

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. Moreover, it is obtained from vegetable oil, animal fats, or waste vegetables. Biodiesel is a promising unconventional to crude oil-derived diesel fuels because it has low toxicity (Zhang et al., 1998; Sendzikiene et al., 2007), low particulate matter and CO exhaust emissions (Krahl et al., 2009), high flash point which is greater than 130°C (Guo et al., 2009), low sulfur and aromatic content (Knothe et al., 2006), and inherent lubricity that extends the life of diesel engines (Munoz et al., 2011). However, it has some disadvantages such as the higher nitrous oxide (NO_x) emissions and freezing point than diesel fuel. It must be noted that these drawbacks are reduced when biodiesel is used in blends with diesel fuel (Knothe et al., 2006).

1.2 Biodiesel Definition

Biodiesel is a fuel composed ofmono-alkyl esters of long chain fatty acids derived from renewable sources via transesterification process (Demirbas, 2008). '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. B30 is 30% biodiesel, 70% petroleum diesel, B100 is pure biodiesel) (Coronado et al. 2009).

Biodiesel can be mixed at any level with petrodiesel to make biodiesel blend. Moreover, it can be used in a combustion engine. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics (Patel, 2013).

1.3 Biodiesel as a Fuel

Biodiesel is registered as a fuel and fuel additive with the Environmental Protection Agency (EPA) and meets clean diesel standards established by the California Air Resources Board (CARB). Neat (B100) biodiesel has been designated as an alternative fuel by the Department of Energy (DOE) and the U.S. Department of Transportation (DOT) (Ramadhas, 2011).

In petrodiesel the energy content may vary up to 15%, but in biodiesel the variation is lower. Pure biodiesel contains up to 10-12% oxygen by weight, while in diesel oxygen content is almost negligible. The presence of oxygen allows more complete combustion, which reduces hydrocarbons, carbon monoxide, and particulate matter emission. However, higher oxygen content increases nitrogen oxides emissions (Lal & Reddy, 2005).

Biodiesel is suitable fuel because it has higher cetane number than petro-diesel. The cetane number indicates the ignition quality of a diesel fuel. It is a measure of fuel's ignition delay, which is the period between the start of injection and start of combustion (ignition) of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed (Dahlquist, 2013).

1.4 Research Aims

The aims of this work are

- 1. To experimentally examine the effect of temperature on the thermo-physical properties of two biodiesel with their blends including kinematic viscosity, density, dynamic viscosity.
- 2. Investigate the influence of biodiesel blends on temperature and volume fraction of waste frying methyl ester.
- 3. To experimentally investigate the variation of Cloud Point and Pour Point with changing the percentage of blends of two biodiesel samples CP and PP of two biodiesel and their blends.
- 4. Correlate or predict biodiesel properties and cold flow properties by using simple empirical equations.
- 5. Improve the accuracy in the prediction of biodiesel properties for wind range of temperature (20°C to 270°C) by using ANFIS approach.

- 6. Represent biodiesel properties as simultaneous function of temperature and volume fraction of biodiesel in three dimensional plots (3D-plots).
- 7. Develop a mathematical model using ANN to estimate the biodiesel properties in temperature range 20°C to 270°C.
- 8. Compare and evaluated the efficiency of ANFIS and ANN in accurately predicting the biodiesel properties of biodiesel samples.

1.5 Thesis Outline

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). The empirical models were used to predict the thermo-physical properties of biodiesel are described in chapter 3. Chapter 4 is describes the experimental setup and the procedures for measuring biodiesel properties. The effects of temperature on biodiesel properties for five biodiesel samples are discovered in order to know the relationship between the temperature and biodiesel properties by varying temperatures from 20°C to 270°C. The effectiveness of low temperature on biodiesel properties (kinematic viscosity) is described in chapter 5. In the last section, comparison between the empirical models and experimental data of biodiesel properties are discussed chapter 5. The thesis ends with conclusions and suggestions for future work in chapter 6.

CHAPTER 2

THERMOPHYSICAL BIODIESEL PROPERTIES

2.1 Reviews on Biodiesel Properties

The properties investigated in this work are; biodiesel properties including kinematic viscosity, dynamic viscosity, density and cold flow properties including of Cloud Point (CP) and Pour Point (PP) for waste vegetable oil biodiesel.

The behavior kinematic viscosity of biodiesel blends with diesel at different percentages of biodiesel in the temperature range of -20°C and 100°C depends on the type of petrodiesel (Tat & Gerpen, 1999).

Knothe and Steidley (2007) measured the kinematic viscosity of biodiesel blends in the temperature range -10°C to 40°C and these data compared with diesel fuel.

Esteban et al. (2012) measured the density and viscosity of several vegetable oils within a wide variety of temperatures. The authors concluded that the density and viscosity of several commonly used vegetable oils depend on the temperature.

According to Chhetri, et al. (2008) the biodiesel properties of waste cooking oil including density, density, viscosity, acid value, flash point, cloud point, pour point, cetane index, water and sediment content, total and free glycerin content phosphorus content and sulfur content are in ASTM Standard range. Therefore, producing biodiesel from waste cooking oil reduces trend of economical extracted oil reserves and the environmental problems caused due to the use of fossil fuel.

Moradi et al. (2013) examined experimentally the relationship between temperature, volume fraction of biodiesel and biodiesel properties. Results concluded that the density and kinematic viscosity of biodiesel blends increased with decreasing the temperature.

Ustra et al. (2013) concluded that the viscosity, density and thermal conductivity of biodiesel decreased as the temperature increase.

Verma et al. (2016) studied the effect of higher alcohols on biodiesel production. Additionally, they studied the effect of fatty acid composition of biodiesel on oxidation stability and cold flow properties. The results showed that cold flow properties depended on fatty acid of biodiesel.

Rasimoglu and Temur (2014) studied the effects of parameters of transesterification on the cold flow properties of corn oil based biodiesel. The results showed that when the

transesterification reaction period is kept longer than 10 min, there were no changes in cold flow properties of the biodiesel produced from corn oil. Moreover, better cold flow properties were monitored when alcohol-to-oil ratio was kept between 3.15:1 and 4.15:1. In addition, no effect of reaction temperature on cold flow properties was observed above 20 °C.

Nainwal et al. (2015) examined the cold flow properties of Jatropha curcas and waste cooking oil biodiesel. They concluded that winterization is giving noble improvement in the cold flow properties of both biodiesel without any blending but at the same time reducing the yield and oxidation stability of biodiesel. In addition, the blending of biodiesel with kerosene is giving very decent improvements in cold flow properties.

Park et al. (2008) studied the effect of temperature and volume fraction of biodiesel on biodiesel properties. They concluded that CP of biodiesel-ethanol blending fuels decreased with an increase of ethanol contents mixture fuels and dynamic viscosity is inversely proportion to the fuel temperature.

Kim et al. (2012) studied the cold performance of six different types of biodiesel blends in a passenger car and a light duty truck comparing the suitability and drivability of a passenger car and a light duty truck at -16°C and -20 °C. The results showed that the cold flow properties of biodiesel dictate that the length of the hydrocarbon chains and the presence of unsaturated structures significantly affect the low temperature properties of biodiesel.

Mushtaq et al. (2013) measured kinematic viscosity, CP and PP of modified biodiesel and studied the effects of cold properties on the attachment of alkoxy side chains to biodiesel. He obtained the lowest CP as -11°C and PP as-14°C with n-decoxybiodiesel.

2.2 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, τ is the shear stress (N/m²), μ is the dynamic viscosity (Pa.s) and $\frac{\partial u}{\partial z}$ is the velocity gradient or better known as shear rate (1/s) (Giap et al., 2009).

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

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

Where v is the kinematic viscosity (m²/s), ρ is the mass density of the liquid (m³/kg) (Viswanath et al., 2007).

2.2.1 Viscosity of Biodiesel

The viscosity of fuel is an important property of fuel that affects the performance of engine. Viscosity affects the operation of fuel injection equipment. The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets (Demirbas, 2008). The effect of viscosity on the engine performance can classified as follow:

- Too low viscosity can lead to excessive internal pump leakage whereas system pressure reaches an unacceptable level and will affect injection during the spray atomization. The effect of viscosity is at critical low speed or light load conditions (Suresh & Mamilla, 2012).
- High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Demirbas, 2008). Vegetable oils are extremely viscous with viscosities 10 to 20 times greater than that of petroleum diesel fuel (Demirbas, 2008).

Biodiesel viscosity is higher than the viscosity of perodiesel, as the percentage of concentration of biodiesel blend with diesel increases, the viscosity of biodiesel blend increases. Additionally, viscosity is greatly affected by temperature; many of the problems resulting from high viscosity are most noticeable under low ambient temperature and cold start engine condition (Sarin, 2012).

As a result, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of biodiesel can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as that of the diesel fuel.

2.2.2 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.

2.3 Capillary Viscometers

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 (Sahin & Sumnu, 2006)..

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). In commercial capillary viscometers for non-gaseous material, the liquids usually flow through the capillaries under gravity (Boyes, 2003). 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 (Tropea et al., 2007). 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).

2.3.1 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 2.1 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

$$\rho \left(v_r \frac{\partial v_r}{\partial r} + \frac{v_{\theta}}{r} \frac{\partial v_r}{\partial r} - \frac{v_{\theta}^2}{r} + v_z \frac{\partial v_r}{\partial r} + \frac{\partial v_r}{\partial t} \right)$$

$$= \rho g_r - \frac{\partial p}{\partial t} + \mu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (rv_r) \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} + \frac{1}{r^2} \frac{\partial v_{\theta}}{\partial \theta} + \frac{\partial^2 v_r}{\partial z^2} \right] (2.4)$$

$$\rho \left(v_r \frac{\partial v_{\theta}}{\partial r} + \frac{v_{\theta}}{r} \frac{\partial v_{\theta}}{\partial r} - \frac{v_r v_{\theta}}{r} + v_z \frac{\partial v_{\theta}}{\partial r} + \frac{\partial v_{\theta}}{\partial t} \right)$$

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

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

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

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

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



Figure 2.1: 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)

$$r = R ; v_z = 0 \tag{2.13}$$

Yields

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

While

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

The volume flow rate discharge is given by

$$Q = \int_{0}^{R} 2\pi v_{z} r \, dr \tag{2.16}$$

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.

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

where E is the correction factor.

2.3.2 Types of Capillary Viscometers

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 Density of Fuel

Density is another important property of biodiesel. It is defined as its mass per unit volume. In diesel engines, the injection is one of the most important parameters for high performance. Therefore, density of fuel is an important parameter that affects the injection properties. 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. (Atabani et al., 2013; Heywood, 1988; Lalvani et al., 2015).

2.5 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 and 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; Extension, 2012). 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).

2.5.1 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).

2.5.2 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.

2.6. 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 ² /s	ASTM D6751	1.9-6.0	
AST	M D6751	biodiesel fuel standard		
Kinematic viscosity at 40°C	mm ² /s	ASTM D445	1.9-6.0	
Cloud Point	°C	D2500	Report	
European Committee fo	European Committee for Standardization EN 14214 biodiesel fuel standard			
Kinematic viscosity at 40°C	mm ² /s	EN ISO 3104, ISO 3105,	3.5-5.0	
Density at 15 °C	kg/m ³	EN ISO 310 EN ISO 3675, EN ISO 12185	860–900	
Cloud Point	°C	EN 23015	Location &	
			season	
			dependant	
ASTM D7467 biodiesel-petrodiesel blend (B6–B20) fuel standard				
Kinematic viscosity at 40°C	mm ² /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 ³	ASTM D40	867	

Table 2.1: Generally applicable requirements and test methods

CHAPTER 3 EMPIRICAL MODELS

3.1 Reviews on empirical model of biodiesel

Numerous studies of the predicting the thermo-physical properties of biodiesel such as kinematic viscosity, density, dynamic viscosity and cold flow can be found in were the literature.

Ramírez-Verduzco et al. (2011) examined the relationship between the temperature (20°C to 100°C) on the density and viscosity of six biodiesel blends. The experimental results showed that as temperature increases, the density and viscosity of biodiesel blends decrease. Moreover, the predicted data of density and viscosity of biodiesel were much closed to the experimental data.

Meng et al. (2014) calculated numerically the kinematic viscosity of 105 biodiesel samples at 313K using artificial neural network (ANN) approach. The results showed that ANN presented the highest accuracy comparing to other empirical models.

Chavarria-Hernandez & Pacheco-Catalán (2014) estimated numerically the kinematic viscosity and density of 31 pure which collected from the literature biodiesel over a wind range temperature. Comparison results showed that the predicted data using correlation of this work had the lowest average absolute deviation error compared to another correlation.

Geacai et al. (2015), studied the effect of temperature on the kinematic viscosity of biodiesel blends with petro-diesel, benzene and toluene. Additionally, the experimental data were used to predict the kinematic viscosity using various mathematical models.

Ebna Alam et al. (2014), examined the density, dynamic viscosity and higher heating value of biodiesel blends under a wind range of temperature and. In addition, they compared the predicted data with experimental data. They concluded that the biodiesel properties are closed to the experimental data with lowest average error.

Al-Shanableh et al. (2016) obtained an empirical model using ANN for predicting the cold flow properties of biodiesel. The result showed that ANN presented of cold flow properties with highest correlation coefficient.

Eryilmaz et al. (2015), produced biodiesel as alternative fuels for internal combustion engines from edible oil and non-edible oil. In addition, they measured kinematic viscosity

at the range from 298.15 to 373.15K. Furthermore, they used ANN to predict the kinematic viscosity of biodiesel. The results showed that maximum error was 0.34 using ANN approach. Moreover, it found that ANNs appear to be a promising technique for predicting viscosity of biodiesel.

3.2 Mathematical models of biodiesel samples

A mathematical model is a simple description of physical, chemical or biological processes. The biodiesel properties obtained from different sources such as such as viscosity, density, CP and PP can be predicted using various methods Saxena et al. (2013). Sivaramakrishnan and Ravikumar (2012) predicted the viscosity, density, flash point, higher calorific value and cetane number of biodiesel using mathematical equation. They concluded that the mathematical equating presented the best accuracy within 90%.

For vegetable oils, it has been shown that increasing the temperature lead to decrease the density linearly and it correlation can be expressed mathematically as in (Rodenbush et al. 1999),

$$\rho = a + bT \tag{3.1}$$

where

 ρ : the density [g/cm³],

T: the temperature [°C],

a : the intercept and

b: a negative slope.

The visocisty of the liquid can be considered as integral of the interacton force of molecules. This force depends on the temperature of fluid. Therfore, visocisty of specified lquid can be wrriten interm of temperature and other items as follow (Krisnangkura et al., 2014)

$$\nu = A_1 exp\left(\frac{E_a}{RT}\right) \tag{3.2}$$

where

v : the kinematic viscosity $[mm^2/s]$,

E_a: the activation energy for flow[J/mole],

R: the universal gas constant[J/(mol.K)] and

T : the temperature [K].

Additionally, $A_1 = \frac{N_A h}{V}$ where N_A, V and h are the Avogadro's number, the molecular volume and the Plank's constants, respectively. In the case of vegetable oils, Equation (3.2) can be rewritten as in Equation (3.3), which is known as the Andrade equation (Rodenbush et al. 1999; Krisnangkura et al., 2014)

$$\nu = A_1 exp\left(\frac{B}{T}\right) \tag{3.3}$$

where

T : the temperature,

A1: specific constant, and

B : specific constant.

By applying logarithms to both sides of Equation (3.3) we get:

$$ln(v) = A + \frac{B}{T} \tag{3.4}$$

Equation (3.3) allows us to linearize Equation (3.4) by applying the least-squares method and making 1/T the independent variable.

Additionally, Azian et al. (2002) suggested modifying Equation (3.4), which is especially useful when dealing with wide temperature ranges,

$$ln(\nu) = A + \frac{B}{T} + \frac{C}{T^2}$$
(3.5)

Sometimes, the dynamic or absolute viscosity μ is applied, which can be calculated from the kinematic viscosity ν and the density ρ as,

$$\mu = \nu \rho \tag{3.6}$$

According Ramirez-Verduzco (2013), the density and dynamic viscosity of biodiesel (fatty acid methyl ester) as a function of mass fraction and molecular weight can be expressed as follow

$$\rho = \sum_{i=1}^{n} w_i \left(1.069 + \frac{3.575}{M_i} + 0.0113N_i - 7.41 \times 10^{-4}T \right)$$
(3.7)

$$ln\mu = \sum_{i=1}^{n} w_i \left(-18.354 + 2.362 lnM_i - 0.127N_i + \frac{2009}{T} \right)$$
(3.8)

where,

 w_i : molecular weight [g/mol],

 N_i : number of double bond in the fatty acid chain

 M_i : number of double bond in the fatty acid chain

T: temperature [K]

 ρ : density of biodiesel [kg/m³]

 μ : Dynamic viscosity of biodiesel [Pa.s]

The kinematic viscosity is estimated from Equations (3.7) and (3.8) as

$$v = \frac{\mu}{\rho} \tag{3.9}$$

Cloud Point and Pour Point of biodiesel blends were predicted as function of volume fraction of composition by empirical second order polynomial equations. According to Joshi & Pegg, 2007; Enweremadu et al. 2011, the polynomial equation has a best accuracy to predict CP and PP of biodiesel blends than linear equation.

Since the density and viscosity depend on the temperature. Therefore, The relationship between density and viscosity can be shown in Eq. 3.10 according to Rodenbush et al. 1999.

$$\rho = D + \frac{E}{\nu^{1/2}}$$
(3.10)

where, D and E are a constants.

3.3 Artificial Neural Networks

ANNs is a numerical approach which is based on processing units of artificial neurons that connected together to form a direct graph (Haykin, 2009). Graph nodes is represented the biological neurons while the connections between the neurons is represented synapses.

Whereas, in biological neural networks, connections between artificial neurons aren't usually added or removed after the network was created. As an alternative, the weighted which considered as the connection between the neurons are adapted by ANN approach. Input signal propagates through the network in the direction of connections until it reaches output of the network. In supervised learning, learning algorithm adapts the weights in order to minimize the difference between the output of the network and the predicted output.

3.3.1 Artificial Neuron (AN)

The complex behaviour of biological neurons was clarified to create a empirical model of the units. Unit receives its inputs via input connections from other units' outputs, called activations. Then it calculates a weighted sum of the inputs, called potential. Finally, unit's activation is computed from the potential and sent to other units. Weights of connections between units are stored in a matrix w, where w_{ij} denotes weight of the connection from unit i to unit j. Every unit j has a potential p_{j} , which is calculated as weighted sum of all of its N input units and bias.

$$P_j = \sum_{i=1}^{N+1} w_{ij} a_i$$
(3.11)

Bias term, also known as threshold unit, is usually represented as an extra input unit whose activation always equals one, therefore $a_{N+1} = 1$. Presence of bias term enables shifting the activation function along x-axis by changing the weight of the connection from threshold unit.

Activation of the unit a_j is then computed by transforming its potential p_j by a non-linear activation function act.

$$a_j = act(P_j) \tag{3.12}$$

Commonly used nonlinear activation function ranging from 0 to 1 is sigmoid function thanks to its easily computable derivative which is used by learning algorithms.

$$\sigma(x) = \frac{1}{1 + e^{-x}}$$
(3.13)

$$\frac{d\sigma(x)}{dx} = \sigma(x)(-\sigma(x))$$
(3.14)

where $\sigma(x)$ is sigmoid function, and x is the input data

3.3.2 Feedforward Neural Networks

Feedforward neural networks are a subset of ANNs whose nodes form an acyclic graph where information moves only in one direction, from input to output as shown in Figure 3.1.

As shown in Figure 3.1, on the left, Multilayer perception (MLP) consisting of the two inputs, four and three hidden layer and two output layers.

Multilayer perception (MLP) is a class of feedforward networks consisting of three or more layers of units. Layer is a group of units receiving connections from the same units. Units inside a layer are not connected to each other.

MLP consists of three types of layers: input layer (i), one or more hidden layers (h) and the output layer (o). Input layer is the first layer of networks and it receives no connections from other units, but instead holds network's input vector as activation of its units. Input layer is fully connected to the first hidden layer. Hidden layer i is then fully connected to

hidden layer i + 1. The last hidden layer is fully connected to the output layer. Activation of output units is considered to be output of the network.

The output of the network is calculated in a process called forward propagation in three steps:

- Network's input is copied to activations of input units
- Hidden layers compute their activations in topological order
- Output layer computes its activation and copies it to network's output

MLPs are often used to approximate unknown functions from their inputs to outputs. MLP's capability of approximating any continuous function with support in the unit hypercube with only single hidden layer and the sigmoid activation function was first proved by George Cybenko (Cybenko, 1989).



Figure 3.1: Feedforward neural networks

3.3.3 Back-propagation

Back-propagation, or backward propagation of errors, is the most used supervised learning algorithms for adapting connection weights of feedforward ANNs. The weights of the network are tuned so as to minimize square error

$$E = \frac{1}{2} \sum_{i=1}^{N} (target_i - output_i)^2$$
(3.15)

where target denotes desired the output and output are network's predictions of the output from the corresponding input, both of size N.

Considering error E as a function of network's weights w, backpropogation can be seen as an optimization problem and a standard gradient descent method can be applied. A local minimum is approached by changing weights along the direction of the negative error gradient

$$-\frac{\partial E}{\partial w}$$
(3.16)

by weight change Δw_{ij} proportionally to α , which is a constant positive value called the learning rate (α). Fraction of previous weight change called momentum rate (β) can be added to the current weight change, which often speeds up learning process.

new
$$\Delta w_{ij} = \beta \Delta w_{ij} - \alpha \frac{\partial E}{\partial w_{ij}}$$
 (3.17)

$$new w_{ij} = w_{ij} + \Delta w_{ij} \tag{3.18}$$

The central part of the algorithm is finding the error gradient. Let there be an MLP with L layers in topological order, first being input and last being output layer. Layer k has U_k units and holds a weight matrix w_{ij}^k representing weights of connections from unit *i* in layer k - 1 to unit j in layer k. The input layer has no incoming connections. The computation can be then divided into three steps:

- Forward propagation: Input vector is copied to activations a_i¹ of input layer units
 i. For every hidden or output layer k in topological order, compute for every unit i its potential (weighted input) P_i^k and activation a_i^k
- Backward propagation: Compute Δ^L_i i.e. the derivative of error E w.r.t. activation a^L_i of output layer unit *i* as

$$\Delta_i^L = (target_i - a_i^L) \frac{\partial act(P_i^L)}{\partial P_i^L}$$
(3.19)
For hidden layer h in reverse topological order starting from last hidden layer h = L-1 down to first input layer h = 2 and its units *i* compute error term as

$$\Delta_i^h = \sum_{j=1}^{U_{h+1}} \Delta_i^{h+1} w_{ij}^{h+1} \frac{\partial act(P_i^h)}{\partial P_i^h}$$
(3.20)

• Weights update: Change weights in layer k according to

$$\operatorname{new} \Delta w_{ij}^{k} = \beta \Delta w_{ij}^{k} - \alpha \Delta_{i}^{k+1} a_{j}^{k}$$
(3.21)

$$\operatorname{new} \Delta w_{ij}^k = w_{ij}^k + \Delta w_{ij}^k \tag{3.22}$$

3.4 Fuzzy Logic Based Algorithms

Fuzzy logic system (FIS) is a technique of rule-based decision making used for expert system and process control. Fuzzy logic is a structure of many-valued logic in which the truth values of variables may be any real number between 0 and 1. Values of one and zero represent the membership of a member to the set with one representing absolute membership and zero representing no membership.

Fuzzy logic allows partial membership, or a degree of membership, which might be any value along the continuum of zero to one. The idea of fuzzy theory is that an is that an element has a degree of membership to a fuzzy set.

As a particular field of application, in system modeling and control. there are many difficulties which are commonly experienced by practicing engineers FIS can be used in different branches such as engineering filed .etc.

In general, FIS consists of three main parts

- Fuzzy rules
- Membership function of fuzzy rule, and
- Mechanism of Fuzzy interface.

3.4.1 Analysis with Fuzzy Inference System

The following steps are described the procedure for analyzing fuzzy system (Nelles, 2001):

- **Fuzzification:** Fuzzy logic uses input variables as a substitute of numerical variables. The process of converting a numerical variable (real number or crisp variable) into a linguistic variable (fuzzy number) is called fuzzification.
- **Knowledge Base:** This module consists of a data base and a rule base. The data base provides the necessary information for the proper functioning of the

fuzzification module, the rule base, and the defuzzification module. This information includes; Fuzzy sets (membership functions) representing the meaning of the linguistic values of the system state and control input variables. Physical domains and their nomalized counterparts together with the normalizationl denormalization (scaling) factors. The basic function of the mle base is to represent the control policy in the form of a set of IF-THEN rules.

- **Inference Mechanism:** This module determined the overall value of the control input based on the individual contributions of each rule in the rule base.
- **Defuzzification:** The reverse of fuzzification is called defuzzification.

3.4.2 Types of Fuzzy System

Fuzzy inference system is based on fuzzy set theory. The two main types of fuzzy system can classified as:

- Mamdani fuzzy system: The Mamdani-style fuzzy inference method is carried out in four steps: fuzzification of the input variables, rule evaluation, output of the rule outputs, and finally defuzzification (Castillo & Melin, 2008; Zha & Howlett, 2006).
- Singleton Fuzzy system: A singleton is a fuzzy set with a membership function that is unity at a single particular point on the universe of discourse and zero everywhere else. Sugeno-style fuzzy inference is very similar to the Mamdani method. Sugeno changed only a rule consequent (Castillo & Melin, 2008; Zha & Howlett, 2006).

3.4.4 Adaptive Network based Fuzzy Inference System

Adaptive network based fuzzy inference system (ANFIS) is neuron fuzzy technique (Jang, 1993). It has been used as a prime tool in the present work. It is a combination between neural network and fuzzy logic system. The parameters of ANFIS which can be estimated using to models, Sugeno or Tsukamoto, (Tsukamot, 1979) can be presented in architecture of ANFIS.

Again with minor constraints the ANFIS model resembles the Radial basis function network (RBFN) functionally (Jang & Sun, 1993). The methodology of ANFIS includes two techniques

- Hybrid system of fuzzy logic
- Neural network system

The adaptive network's applications are immediate and immense in various areas. In this proposed work ANFIS was used to predict the thermo-physical properties of biodiesel including kinematic viscosity and density of five biodiesel blends.

CHAPTER 4 EXPERIMENTAL METHOD

4.1 Biodiesel Samples

Two biodiesel samples, i.e. WFME and WCME, were produced from waste frying oil and waste canola oil in the Mechanical Engineering Laboratory of Near East University. The WFME signifies methyl esters of waste frying oil, WCME represents methyl esters of waste canola oil and their different mixing percentages are referred to as 25-WFME, 50-WFME, and 75-WFME, where the number in the prefix indicates the percentage of WFME present in the mixture. The fatty acid methyl ester of biodiesel produced from the waste frying oil and waste canola oil is shown in (appendix 2). The fatty acid methyl ester of biodiesel samples produced from the waste frying oil and canola oil were compared to most common fatty acid components of biodiesel feedstock in the literature, namely, C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3, C20:0 and C20:1. It can be noted that all fatty acid components are within the limits obtained from the literature

4.2 Experimental Setups

The biodiesel samples were analyzed to determine their viscosity, density and two cold flow properties (CP and PP). The effect of temperature on the biodiesel properties including kinematic viscosity, dynamic viscosity, and density was tested within the temperature range of -10° C to 270° C.

The experimental setup for measuring the biodiesel properties and cold flow properties can be divided into two parts as follows;

- a) From 20°C to 270°C (for measuring kinematic viscosity, density and dynamic viscosity).
- b) From -10 °C to 20 °C (for measuring kinematic viscosity, density, dynamic viscosity, CP and PP).

4.2.1 Kinematic Viscosity Setup

a. From 20 to 270°C

Ubbelohde viscometer (ASTM) was used to measure the kinematic viscosity because of its well-known application and accuracy (Appendix 1). It enables transparent and high temperature measurements. Figure 4.1 shows the experimental setup used to determine the temperature dependence of density and viscosity of the samples analyzed. To ensure precise and stable temperature control during measurements, a digital temperature controller resistance was used to monitor the temperature. A uniform temperature inside the silicone oil bath was attained. In addition, the mixer enabled the regulation of the temperature of a heated oil bath containing the viscometer by means of an electric heater. The temperature of the oil bath was varied from 20 °C to 270 °C. Each sample was tested four times, and then average viscosity was calculated. In order to precisely determine the relationship between the time of flow and the kinematic viscosity for the three viscometers used, calibration of the instrument was necessary. The calibration was done by the manufacturer, SI Analytics GmbH, Mainz according to ASTM D 2525/ D 446 and ISO/DIS 3105. The instrument constant, K, [(mm²/s)/s] was determined and given as in Table 4.1. The calibration constant can be used up to the temperature of 270°C, and the influence of the temperature on the capillary constant due to thermal expansion of the Duran glass was negligible. For absolute measurement, the corrected flow time multiplied by the viscometer constant K directly gives the kinematic viscosity [mm²/s] as given in Equation (4.1).

$$v = K(t - y) \tag{4.1}$$

where v, K, t, and y represent the kinematic viscosity, the calibration constant, measured time of flow and kinetic energy correction, respectively. The kinetic energy correction is given by the manufacturer and tabulated for each viscometer in term of flow time as shown in Table 4.2.



Figure 4.1: Schematic of the experimental setup used to measure the viscosity of a biodiesel samples in the temperature range 20°C - 270°C

Capillary	Capillary	Constant, K,	Measuring range
No.	Dia. I ± 0.01[mm]	$(\mathbf{mm}^2/\mathbf{s})/\mathbf{s}$	[mm ² /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 4.1: Ubbelohde viscometer technical specifications (Viswanath et al., 2007)

Flow				Capillary	no		
time	0	0c	0a	Ι	IC	la	1
40	_ ^B	_ ^B	- ^B	1.03	0.45	0.15	
50	_ ^B	- ^B	- ^B	3.96	0.66	0.29	0.10
60	_ ^B	_ ^B	_ ^B	2.75	0.46	0.20	0.07
70	_B	_ ^B	_ ^B	2.02	0.34	0.15	0.05
80	_B	_ ^B	4.78 ^B	1.55	0.26	0.11	0.04
90	_B	_ ^B	3.78 ^b	1.22	0.20	0.09	0.03
100	_ ^B	7.07 ^B	3.06 ^B	0.99	0.17	0.07	0.02
110	_ ^B	5.84 ^B	2.53	0.82	0.14	0.06	0.02
120	B	4.91 ^B	2.13	0.69	0.12	0.05	0.02
130	_ ^B	4.18 ^B	1.81	0.59	0.10	0.04	0.01
140	_ ^B	3.61 ^B	1.56	0.51	0.08	0.04	0.01
150	_ ^B	3.14 ^B	1.36	0.44	0.07	0.03	0.01
160	B	2.76	1.20	0.39	0.06	0.03	0.01
170	_B	2.45	1.06	0.34	0.06	0.02	0.01
180	_B	2.18	0.94	0.30	0.05	0.02	0.01
190	B	1.96	0.85	0.28	0.05	0.02	0.01
200	10.33 ^B	1.77	0.77	0.25	0.04	0.02	0.01
		1 10	0.50	0.00	0.02	0.01	0.01
225	8.20	1.40	0.60	0.20	0.03	0.01	0.01
250	6.64	1.13	0.49	0.16	0.03	0.01	< 0.01
275	5.47	0.93	0.40	0.13	0.02	0.01	<0.01
300	4.61	0.79	0.34	0.11	0.02	0.01	<0.01
325	3.90	0.66	0.29	0.09	0.02	0.01	
350	3.39	0.58	0.25	0.08	0.01	0.01	
375	2.95	0.50	0.22	0.07	0.01	0.01	
400	2.59	0.44	0.19	0.06	0.01	< 0.01	
425	2.30	0.66	0.29	0.09	0.01	< 0.01	
450	2.05	0.58	0.25	0.08	0.01	< 0.01	
475	1.84	0.50	0.22	0.07	0.01		
500	1.66	0.44	0.19	0.06	0.01		
550	1.37	0.23	0.1	0.03	0.01		
600	1.15	0.20	0.09	0.03	0.01		
650	0.98	0.17	0.07	0.03	< 0.01		
700	0.85	0.14	0.06	0.02	< 0.01		
750	0.74	0.13	0.05	0.02	< 0.01		
	÷						

Table 4.2: Table of kinetic energy correction" Ubbelohde Viscometer ISO 3105/DIN51 562/Part1/BS188/NFT 60-100, Ref.No.501...530...532.." Correction seconds ^A:

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							

Table 4.2: Continued

^A The correction seconds stated are related to the respective theoretical constant
 ^B For precision measurement, these flow times should not be applied. Selection of a viscometer

with a smaller capillary diameter is suggested

b. From -10 °C to 20 °C

Figure 4.2 shows the experimental setup used to measure the kinematic viscosity of biodiesel samples in the temperature range -10°C to 20°C. The experimental setup consists of a cooling bath (glass aquarium), a compressor, a mixer, and 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 4.2. The cooling bath was thermally isolated from the rest of its surroundings by a 3cm thick Styrofoam layer.



Figure 4.2: Schematic of the cooling bath system for measuring kinematic viscosity in temperature range -10°C to 20°C

4.2.1.2 Silicone Oil

Due to the selected temperature range, it was impossible to use water as an appropriate temperature bath. Wacker silicone fluid AK oil was used. Wacker silicone fluid AK is dimethyl polyslloxane whose un-branched chains are made up of alternate silicon and oxygen atoms, the free valencies of the silicon being saturated by methyl group. While the carbon chains of organic compounds show little resistance to certain external influences, the stability of inorganic Si-O linkage is, in many ways, like the chemical inertness of silicate minerals (Aldrich, 2016). The selected silicone oil was AK 350 with the following properties listed in Table 4.3.

	T T •/	
Test	Unit	Result
Specific Gravity at 25°C	-	0.96
Refractive Index at 25°C	-	1.4022
Flash Point, Open Cup	[°C]	318
Melt Point	[°C]	-41
Pour Point	[°C]	-70
Surface Tension at 25°C	[dynes/cm]	20.8
Viscosity Temperature	-	0.59
Coefficient		
Coefficient of Expansion	[cc/cc/°C]	0.00104
Thermal Conductivity at 50°C	[g cal/cm·sec·°C]	-

Table 4.3: Properties of silicone oil (Aldrich, 2016)

4.2.1.3 Procedure of Measuring the Kinematic Viscosity Using Ubbelohde Viscometer

The determination of kinematic viscosity of biodiesel samples was carried out with an Ubbelohde viscometer (Figure 4.3). The procedure for measuring the kinematic viscosity of biodiesel samples illustrated in Figure 4.5. The details 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. Carry out the experiment with the tube in a vertical position. Fill bulb (3) with the biodiesel sample, and also ensures that the level of liquid in the bulb (B) is below the exit to the ventilation tube (2).
- 3. Immerse the viscometer in oil silicone bath stabilized at the temperature specified.

- 4. Maintain the viscometer in a vertical position for a time period (more than 20 minutes) to allow the sample temperature to reach equilibrium.
- 5. Close tube (2), and raise the level of the liquid in tube (1) to a level about 8 mm above mark (M_1) .
- 6. Keep the liquid at this level by closing tube (1) and opening tube (2).
- 7. 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.
- 8. Calculate the kinematic viscosity of the sample using formula in equation 4.1.
- 9. Without recharging the viscometer, make check determinations by repeating steps 6 to 8 four times for each experiment.



Figure 4.3: Illustrated diagram of Ubbelohde viscometer (Viswanath et al., 2007)



Figure 4.4: Procedures for measuring kinematic viscosity using Ubbelohde viscometer

4.2.2 Density Setup

The density measurement was made according to ASTM Standard D854 (appendix 3). The density of the biodiesel was measured using a Pycnometer with a bulb capacity of 25ml. All density measurements were performed in triplicate with the Pycnometer. A Pycnometer is a glass or metal container with a precisely determined volume, used for determining both the density of liquids and dispersion by simply weighing the defined volume. The weighing was done by using a high precision electronic balance with a precision of ± 0.1 mg. The density values of the samples were measured for temperatures between 20°C to 270°C. The experimental setups of measuring the density of biodiesel samples from 20°C to 270 and -10°C to 20°C are shown in Figure 4.1 and 4.2, respectively.

4.2.2.1 Procedure of Measuring the Biodiesel Density Using Pycnometer

The Pycnometer is a flask with a close-fitting ground glass stopper with a fine hole through it (see Figure 4.5), 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:

- 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 4.5: Pycnometer

Figure 4.6 shows the methodology flow chart for determination of density of biodiesel samples using Pycnometer with a bulb capacity of 25ml.



Figure 4.6: Procedures for determining the density of biodiesel

4.2.3 Cloud Point and Pour Point Setup

The biodiesel samples were tested as following the American Standard test method for Cloud Point (CP) and Pour Point (PP), ASTMD2500 (appendix 4) and ASTMD97 (appendix 5), respectively. Figure 4.7 shows the setup for measuring CP and PP which basically consisted of a cooling bath, glass test jar, thermocouples, multi-thermometer, and a regulator as depicted. A glass test jar was placed in an aluminum cylinder inside the cooling bath liquid. The glass test jar was isolated from the aluminum cylinder by means of a cork support, stopper and ring assembly. Also, the cylinder has been immersed into an 8liter stainless steel cooling bath containing alcohol at -25 °C. The cooling bath was put inside an 11cm thick Styrofoam block 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 entire system was covered by a 3cm thick wooden box. Three T-type thermocouples were used to measure the temperature in the cooling bath; the first one to measure the temperature of the bath, the second one is used to measure Cloud Point, which was placed at the bottom of the glass test jar, while the last one to measure the Pour Point, which was placed in the upper part of the sample in the glass test jar.





Figure 4.7: The schematic of the cloud point and pour point measurement apparatus

The process for measuring the cloud point and pour point of biodiesel samples is given as follow:

- 1. Transfer the required amount of biodiesel sample into the glass test jar (45ml).
- 2. Place the glass test jar into Aluminum cylinder which was immersed in the cooling bath.
- 3. Place the T-three thermocouples in the apparatus as mentioned before.
- 4. Record the temperature, this temperature is recorded as cloud point, at which the cloud (fog) appeared inspected at stepwise of 1 °C.
- 5. Repeat the procedure of measuring cloud point three times then take the average.
- 6. Heat the same sample up to 9°C above the expected pour point.
- 7. Immerse the sample into the Aluminum cylinder then into the cooling bath.
- 8. Record the temperature, this temperature is recorded as pour point, at which the biodiesel samples is totally ceased to flow inspected at stepwise of 1 °C.
- 9. Repeat the procedure of measuring pour point three times then take the average.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Accuracy and Repeatability for Kinematic Viscosity

To ensure the accuracy of the results, an accuracy and repeatability test was carried out. The kinematic viscosity of pure water at 30°C was found to be $0.803 \text{ mm}^2/\text{s}$. The value is given as $0.80908 \text{ mm}^2/\text{s}$ (Fox et al., 2012). The percent error of the measured value was calculated to be less than 1%. Table 5.1 shows the repeatability test results for some samples at specific temperatures. For each sample type, the measurement of the flow time was repeated at each specific temperature four times, and the average flow time was recorded for the calculation of kinematic viscosity. However, with accuracy and repeatability error less than 1%, it can be concluded that the results to be discussed are 99% accurate and precise. These measurements were carried out at atmospheric pressure and at different temperatures (see Table 5.1).

Samples	Tomporaturo [°C]	Kinematic vis	cosity [mm ² /s]	Percentage
Samples		Measured	Average	error [%]
		7.355		0.04
WEME	20	7.358	7 355	0.013
VV I TVILL	20	7.357	1.333	0.005
		7.350		0.095
25-WFME	120	1.625		0.12
		1.627	1.000	0.06
	120	1.628	1.020	0.07
		1.627		0.06
		0.556		0.18
75-WFME	270	0.557	0.554	0.36
	270	0.555	0.556	
		0.557		0.36

Table 5.1: Ubbelohde viscometer repeatability results for some of the biodiesel samples

5.2 Kinematic Viscosity

a) From 20°C to 270°C

Figure 5.1 shows the relationship between the kinematic viscosity and temperature of WCME, 25- WFME, 50-WFME, 75-WFME and WFME respectively. It can be seen that viscosity decreases as the temperature increases and this behavior can be explained by the kinetic molecular theory for liquid state (Brown et al. 2014). With an increase in temperature, there is typically an increase in the molecular interchange as molecules move faster in higher temperatures (Daugherty & Franzini, 1977). In a liquid state, there are additional substantial attractive, cohesive forces between the molecules of a liquid. Both cohesion and molecular interchange contribute to liquid viscosity. The impact of increasing the temperature of a liquid is to reduce the cohesive forces while simultaneously increasing the rate of molecular interchange (Daugherty & Franzini, 1977). The former effect causes a decrease in the shear stress while the latter causes it to increase. The result is that liquids show a reduction in viscosity with increasing temperature (Daugherty & Franzini, 1977).



Figure 5.1: Kinematic viscosity – Temperature relationship for all samples

Figure 5.2 shows the change of the kinematic viscosity with the increase of the percentage of WFME to WCME. The abscissa represents the fraction of WCME or WFME, whereas the kinematic viscosity values are provided on the ordinate as shown in Figure 5.2. In general, the properties of waste oils can be changed depending on the fatty acid composition methyl ester and on using or frying conditions, such as temperature, cooking time and cooking process. Therefore, it can be observed from the figure that the kinematic viscosity decreased as the percentage of WFME increased for each temperature considered. This can be due to the cooking process which causes the vegetable oil, Triglyceride to break-down to form, Diglycerides, Monoglycerides, and free fatty acids (FFAs) (Haigh et al., 2014). The amount of heat and water in the frying increases the hydrolysis of Triglycerides; therefore it causes a growth of the Free Fatty Acids (FFAs) in the waste frying oil (Kawentar et al., 2013; Carlini et al., 2014). FFA content in oil samples is a critical factor to influence biodiesel production process. Cooking process increases the FFA content in the oil. The more times the oil used for cooking, the higher the FFA content is. It also depends on the nature of the oil.



Figure 5.2: Kinematic viscosity and percentage composition relationship

b) From -10°C to 20°C

Table 5.2 shows the repeatability test results for WCME and 25-WFME at -8°C and 5°C, respectively. For each sample type, the measurements of the flow time were repeated at each specific temperature four times, and the average flow time was recorded for the calculation of kinematic viscosity. However, with accuracy and repeatability error less than 1%, it can be concluded that the results to be discussed were 99% accurate and precise. Figure 5.3 and Table 5.3 provide the kinematic viscosity of biodiesel samples. The tests were initially conducted by 5°C increments. Toward the end of the tests 1°C or 2°C increments were taken to determine the highest kinematic viscosity of the samples. It can be seen from Figure 5.3 that decreasing the temperature leads to a rapid increase in the kinematic viscosity of biodiesel samples. It is also clear that the kinematic viscosity of the WCME dramatically increased with a decreasing temperature below 0°C. As a result of the variation in fatty acid composition of two biodiesel, the amount of crystals produced by biodiesel samples at different temperatures was depended on the percentage of WFME concentrations. Moreover, variations in the fatty acid composition of two biodiesel may cause a change of temperature that the formation of the crystal can appear. As a result of the variation in composition, different behaviors may be observed in the cold flow properties. Therefore, the formation of crystals of biodiesel samples was dependent on the characteristics of the base WCME and WFME and their methyl ester. It can therefore be inferred from the results that the rapid growth of wax crystals of WFME might be another attribute for biodiesel blends to lose their fluidity at low temperatures.

Samplag	Tomporatura [°C]	Kinematic vis	Percentage	
Samples		Measured	Average	error [%]
		23.861		0.012
WCME	-8	23.864	22 862	0.004
WCME		23.863	23.803	0.0084
		23.865		
		17.58		0.114
25 WEME	5	17.56	17 57	0.06
23-WFINE	3	17.57	17.37	0
		17.57		0

Table 5.2: Ubbelohde viscometer repeatability results for some of the biodiesel samples at low temperature



Figure 5.3: Kinematic viscosity- Temperature relationships of the biodiesel samples

Temperature [°C]	Kinematic Viscosity (mm ² /s)							
	WCME	25-WFME	50-WFME	75-WFME	WFME			
20	7.351	10.4399	9.637	9.637	7.415			
15	8.612	12.315	11.472	11.426	8.711			
10	9.788	14.519	13.42	13.42922	nd ^a			
8	10.414	15.557	14.351	nd ^a	-			
5	11.834	17.57	nd ^a	-	-			
2	13.143	20.284	-	-	-			
0	14.03	nd ^a	-	-	-			
-3	15.59	-	-	-	-			
-5	18.282	-	-	-	-			
-7	21.516	-	-	-	-			
-8	23.863	-	-	-	-			
-10	nd ^a	-	-	-	-			
	^a : Not dete T <cp< th=""><th>rmine, Format</th><th>ion of crystal a</th><th>at this temperat</th><th>ture since</th></cp<>	rmine, Format	ion of crystal a	at this temperat	ture since			

 Table 5.3:
 Kinematic viscosities of five biodiesel fuel samples in the temperature range

 -10°C to 20°C

The kinematic viscosities of five biodiesel fuels were measured from -10°C to 270°C are shown in Figure 5.4 and Table 5.4. It can be seen that, WCME has the lowest viscosity than other biodiesel samples in the temperature range from 20°C to 270°C. And it has the maximum kinematic viscosity in a temperature range from -10°C to 20°C compared to other biodiesel samples. Moreover, the kinematic viscosities for all of WCME, WFME and their blends decreased as the temperature increased as shown in Figure 5.4 and Table 5.4. It is also clear that kinematic viscosity of WCME dramatically increased with a decreasing temperature below 0°C. The sharp increase in viscosity at temperatures might be an attribute to poor cold flow properties of biodiesel blends, although the viscosity increase identified below cloud point temperature somewhat differed among blends with different contents of biodiesel.



Figure 5.4: Measured kinematic viscosities of five biodiesel samples from -10°C to 270°C

W	'CME	25-	WFME	50-	WFME	75-W	FME	W	FME
Т	V	Т	ν	Т	V	Т	V 2/17	Т	ν
[°C]	[mm ² /s]	[°C]	[mm ² /s]	[°C]	[mm ² /s]	[°C]	[mm ² /s]	[°C]	[mm ² /s]
-0 7	25.005								
-/	21.510								
-5	18.282								
-3	15.590								
0	14.030	2	20.204						
2	13.143	2	20.284						
5	11.834	2	17.570	0	14.051				
8	10.414	8	15.557	8	14.351	10	10, 100		
10	9.788	10	14.519	10	13.42	10	13.429		
15	8.612	15	12.315	15	11.472	15	11.426	15	8.711
20	7.351	20	9.750	20	8.82	20	8.495	20	7.355
30	5.787	30	7.259	30	6.933	30	6.405	30	5.758
40	4.678	40	5.749	40	5.421	40	4.979	40	4.666
50	3.801	50	4.647	50	4.183	50	4.028	50	3.811
60	3.079	60	3.800	60	3.433	60	3.395	60	3.161
70	2.673	70	3.166	70	2.857	70	2.917	70	2.705
80	2.333	80	2.705	80	2.614	80	2.554	80	2.353
90	2.023	90	2.322	90	2.26	90	2.227	90	2.033
100	1.807	100	2.046	100	1.977	100	1.955	100	1.814
110	1.626	110	1.824	110	1.756	110	1.745	110	1.637
120	1.473	120	1.626	120	1.61	120	1.572	120	1.482
130	1.305	130	1.527	130	1.489	130	1.481	130	1.323
140	1.178	140	1.363	140	1.347	140	1.33	140	1.19
150	1.061	150	1.171	150	1.241	150	1.211	150	1.123
160	1.010	160	1.089	160	1.153	160	1.122	160	1.038
170	0.944	170	0.999	170	1.079	170	1.087	170	0.965
180	0.833	180	0.928	180	1.003	180	1.024	180	0.885
190	0.797	190	0.868	190	0.921	190	0.926	190	0.826
200	0.744	200	0.806	200	0.861	200	0.858	200	0.777
210	0.688	210	0.760	210	0.802	210	0.785	210	0.73
220	0.649	220	0.707	220	0.751	220	0.744	220	0.685
230	0.609	230	0.680	230	0.714	230	0.693	230	0.65
240	0.579	240	0.646	240	0.665	240	0.659	240	0.609
250	0.542	250	0.616	250	0.633	250	0.642	250	0.573
260	0.516	260	0.570	260	0.599	260	0.587	260	0.547
270	0.488	270	0.546	270	0.562	270	0.556	270	0.521

Table 5.4: Measured kinematic viscosities of five biodiesel samples

5.3 Density

a) From 20°C to 270°C

Each sample of biodiesel was tested four times, and the average density was calculated as shown in Table 5.5. The density of five samples of biodiesel was measured at a range of temperature, and the results are shown in Figure 5.5. It was observed that the density of the blends increased with percentage of WFME in the blend at all temperatures and decreased with increase in temperature for all the tested fuels. The standard for biodiesel states that the fuel should have a density between 860 kg/m³ and 900 kg/m³. Hence, the results obtained showed that for all the five biodiesel samples had a density in the range of 860-900 kg/m³.

Fluid type	Tomporatura [°C]	Density	Percentage	
		Measured	Average	error [%]
50-WFME		873.84		0.001
	40	873.85	972 95	0.001
	40	873.86	075.05	0.001
		873.85		0.001

Table 5.5: Pycnometer repeatability results for some of the biodiesel samples



Figure 5.5: Density – Temperature relationship for all samples

The relationship between the density of the sample and their relative composition percentage at some chosen temperature is shown in Figure 5.6. Similarly, feedstock, storage temperature, storage time, and biodiesel blend level are the factors may affect the biodiesel properties. Consequently, the density of the biodiesel blends increased or decreased according to WFME concentration in the blend. Different density values for biodiesel samples may be due to their different fatty acids composition as well as their purity. Density increases with decreasing chain length and increasing number of double bonds (Worgetter et al., 1998).



Figure 5.6: Density and percentage composition relationship

b) From -10°C to 20°C

The experimental results of density are presented in Figure 5.7 and Table 5.6 for all biodiesel samples. Since each type of biodiesel has different fatty acid composition methyl ester, it is found that the WCME offers the highest density while the WFME has the lowest density at a given temperature. The results from each of Figure 5.7 and Table 5.6 showed that for each of the two biodiesel and their blends, the densities were high at low temperature and decreases as the temperature increased. That is, density decreases non-linearly with temperature. Also at a fixed temperature, there was a decrease in densities of WCME as the percent volume of WFME in the mixtures increased. Comparing WCME and WFME, it was observed that WCME crystallized at higher temperatures compared to WFME as shown in Table 5.7. As a result, the formation of crystals of the blends showed at a different temperature, according to the concentration of WFME in the blend.



Figure 5.7: Density- Low temperature relationships of the biodiesel samples

Temperature			Density [kg/m	3]	
[°C]	WCME	25-WFME	50-WFME	75-WFME	WFME
20	887.20	886.925	880.19	887.48	867.82
15	895.88	895.535	888.80	896.09	876.43
10	904.56	904.145	897.41	904.70	nd ^a
8	913.24	912.755	906.02	nd ^a	
5	921.92	921.365	nd ^a		
2	930.60	929.975			
0	939.28	nd ^a			
-3	947.96				
-5	956.64				
-7	965.32				
-8	974.00				
-10	nd ^a				
	^a : Not det	termine, Forma	ation of crystal	at this tempera	ature since
	T <cp< td=""><td></td><td>-</td><td>•</td><td></td></cp<>		-	•	

Table 5.6: Density of five biodiesel fuel samples in the temperature range -10°C to 20°C

Experimental results of the density for waste frying oil and waste canola oil based biodiesel and their blends are seen in Figure 5.8 and summarized in Table 5.7 for varying temperature (-10°C to 270°C). It is found that density of biodiesel samples depends on the

temperature, i.e. as the temperature increase the density of biodiesel decreased as shown in Figure 5.8. Consequently, the behavior of the density of two biodiesel and their blends depends on the temperature and fatty acid composition. Hence, the densities of biodiesel blends (25-WFME, 50-WFME and 75-WFME) within range limits for international standard of biodiesel.



Figure 5.8: Measured density of five biodiesel samples from -10°C to 270°C

W	VCME	25-	WFME	50-	WFME	75-W	FME	W	/FME
Т	ρ	Т	ρ	Т	ρ	Т	ρ	Т	ρ
[°C]	$\frac{[kg/m^{\circ}]}{074.01}$	[°C]	[kg/m']	[°C]	[kg/m ³]	[°C]	[kg/m³]	[°C]	[kg/m³]
-8	9/4.01								
-7	965.33								
-5	956.65								
-3	947.97								
0	939.29								
2	930.61	2	929.98						
5	921.93	5	921.37	_					
8	913.25	8	912.76	8	906.02				
10	904.57	10	904.15	10	897.41	10	904.700		
15	895.89	15	895.54	15	888.8	15	896.09	15	876.44
20	887.21	20	886.93	20	880.19	20	887.48	20	867.83
30	878.53	30	878.01	30	870.88	30	881.02	30	862.76
40	868.15	40	872.23	40	867.08	40	873.85	40	851.35
50	866.16	50	861.89	50	858.56	50	864.62	50	841.48
60	856.62	60	857.96	60	849.52	60	858.9	60	837.12
70	849.52	70	845.76	70	842.71	70	850.48	70	834.67
80	835.50	80	835.66	80	834.15	80	847.6	80	822.27
90	828.96	90	823.45	90	824.48	90	840.97	90	814.06
100	820.43	100	811.16	100	816.09	100	830.06	100	800.91
110	805.05	110	802.17	110	804.93	110	820.24	110	793.89
120	794.00	120	792.33	120	795.92	120	810.15	120	786.00
130	783.23	130	784.48	130	787.14	130	800.25	130	779.45
140	769.37	140	776.67	140	777.12	140	780.09	140	770.37
150	757.93	150	763.41	150	766.62	150	775.98	150	768.12
160	742.84	160	750.43	160	752.41	160	764.61	160	749.47
170	730.94	170	740.37	170	739.99	170	753.15	170	734.66
180	722.95	180	732.39	180	729.17	180	741.38	180	726.79
190	712.41	190	724.20	190	720.43	190	732.39	190	718.77
200	704.39	200	716.90	200	712	200	723.05	200	712.02
210	696.96	210	708.63	210	705.82	210	715.39	210	703.12
220	690.86	220	701.64	220	698.23	220	705.05	220	695.45
230	682.47	230	692.82	230	694.24	230	697.22	230	686.51
240	676.12	240	686.59	240	688.69	240	687.6	240	679.65
250	668.90	250	679.29	250	682.22	250	681.61	250	672.06
260	665.50	260	673.98	260	679.67	260	675.1	260	665.31
270	662.11	270	671.46	270	675.27	270	670.19	270	657.69

 Table 5.7: Measured density of five biodiesel samples

5.4 Dynamic Viscosity

a) From 20°C to 270°C

Dynamic viscosity values were calculated from the density and kinematic viscosity by multiplying the measured density and the kinematic viscosity values as in equation 5.1. The variations in the dynamic viscosity of different blends of WFME and WCME with temperature are shown in Figure 5.9. The results showed that, for each of the blends with different percent mixture composition, the dynamic viscosity decreased exponentially with increasing temperature.



Figure 5.9: Dynamic viscosity–Temperature relationship for all biodiesel samples

The change of the dynamic viscosity with the increasing of the percentage of WFME to WCME at chosen temperatures is shown Figure 5.10. The figure shows that the increase in the percentage of WFME leads to a decrease in the dynamic viscosity of the biodiesel. The dynamic viscosities of biodiesel blends increased as the percentage of WFME in the blends increased and decreased with an increase of temperature. The Influence of compound structure on dynamic viscosity of biodiesel fuel components and related compounds as compared to petrodiesel fuel components was investigated by Knothe and Steidley (Knothe & Steidley, 2005; Knothe, 2005). Influencing factors were found to be the length of chain, position/number, and type of bonds, as well as nature of oxygenated moieties. This work

verified that the dynamic viscosity increases with the length of the chain of either the fatty acid or alcohol moiety in a hydrocarbon and that the increase in dynamic viscosity over a certain number of carbons is smaller in straight chain hydrocarbons. To this end, the dynamic viscosity of biodiesel samples strongly depends on the type of fatty acid and number of bonds.



Figure 5.10: Dynamic viscosity and percentage composition relationship

b) From -10°C to 20°C

The dynamic viscosities of five biodiesel samples at temperature range -10 °C to 20°C are shown in Figure 5.11 and Table 5.8. It can be observed from Figure 5.11 that all the dynamic viscosities of the samples decreased when the temperature increased. As the temperature decreased to below 20°C, the formation of crystals of biodiesel samples occurred at various temperatures (below cloud point temperature) depending on concentration of WFME as shown in Table 5.8.



Figure 5.11: Dynamic viscosity - Low temperature relationships of the biodiesel samples

Temperature			Density [kg/m	1 ³]	
[°C]	WCME	25-WFME	50-WFME	75-WFME	WFME
20	6.52E-03	8.65E-03	7.76E-03	7.54E-03	6.38E-03
15	7.72E-03	1.10E-02	1.02E-02	1.02E-02	7.63E-03
10	8.85E-03	1.31E-02	1.20E-02	1.21E-02	nd ^a
8	9.51E-03	1.42E-02	1.30E-02	nd ^a	
5	1.09E-02	1.62E-02	nd ^a		
2	1.22E-02	1.89E-02			
0	1.32E-02	nd ^a			
-3	1.48E-02				
-5	1.75E-02				
-7	2.08E-02				
-8	2.32E-02				
-10	nd ^a				
	^a : Not dete	ermine, Forma	tion of crystal a	t this temperatu	re since
	T <cp< td=""><td></td><td></td><td></td><td></td></cp<>				

 Table 5.8: Dynamic viscosity of five biodiesel fuel samples in the temperature range

 -10°C to 20°C

The experimental results of dynamic viscosity for waste frying and canola oil methyl ester biodiesel and their blends have been depicted in Figure 5.12 and Table 5.9. As the temperature increased, the dynamic viscosity of biodiesel samples decreased exponentially. As can be seen from Figure 5.12 and Table 5.9, WCME demonstrates higher dynamic viscosity as compared to another biodiesel samples, especially in the low temperature

range. The dynamic viscosity for each of the different blend was very high at low temperature and decreased as the temperature increased. Also at a constant temperature, there was a decrease in dynamic viscosities of WCME as percent volume of WFME in the mixture increased.



Figure 5.12: Calculated dynamic viscosity of five biodiesel samples from -10°C to 270°C

WCME		25-	25-WFME		50-WFME		-WFME	W	WFME		
Т	μ	Т	μ	Т	μ	Т	μ	Т	μ		
[°C]	[Pa.s]	[°C]	[Pa.s]	[°C]	[Pa.s]	[°C]	[Pa.s]	[°C]	[Pa.s]		
-8	2.3E-02										
-7	2.1E-02										
-5	1.7E-02										
-3	1.5E-02										
0	1.3E-02										
2	1.2E-02	2	1.89E-02								
5	1.1E-02	5	1.62E-02								
8	9.5E-03	8	1.42E-02	8	1.30E-02						
10	8.9E-03	10	1.31E-02	10	1.20E-02	10	1.21E-02				
15	7.7E-03	15	1.10E-02	15	1.02E-02	15	1.02E-02	15	7.6E-03		
20	6.5E-03	20	8.65E-03	20	7.76E-03	20	7.54E-03	20	6.3E-03		
30	5.1E-03	30	6.37E-03	30	6.04E-03	30	5.64E-03	30	4.9E-03		
40	4.1E-03	40	5.01E-03	40	4.70E-03	40	4.35E-03	40	3.9E-03		
50	3.3E-03	50	4.01E-03	50	3.59E-03	50	3.48E-03	50	3.1E-03		
60	2.6E-03	60	3.26E-03	60	2.92E-03	60	2.92E-03	60	2.6E-03		
70	2.3E-03	70	2.68E-03	70	2.41E-03	70	2.48E-03	70	2.2E-03		
80	1.9E-03	80	2.26E-03	80	2.18E-03	80	2.16E-03	80	1.9E-03		
90	1.7E-03	90	1.91E-03	90	1.86E-03	90	1.87E-03	90	1.6E-03		
100	1.5E-03	100	1.66E-03	100	1.61E-03	100	1.62E-03	100	1.4E-03		
110	1.3E-03	110	1.46E-03	110	1.41E-03	110	1.43E-03	110	1.3E-03		
120	1.2E-03	120	1.29E-03	120	1.28E-03	120	1.27E-03	120	1.1E-03		
130	1.0E-03	130	1.20E-03	130	1.17E-03	130	1.19E-03	130	1.0E-03		
140	9.1E-04	140	1.06E-03	140	1.05E-03	140	1.04E-03	140	9.1E-04		
150	8.0E-04	150	8.94E-04	150	9.51E-04	150	9.40E-04	150	8.6E-04		
160	7.5E-04	160	8.17E-04	160	8.68E-04	160	8.58E-04	160	7.7E-04		
170	6.9E-04	170	7.40E-04	170	7.98E-04	170	8.19E-04	170	7.0E-04		
180	6.0E-04	180	6.80E-04	180	7.31E-04	180	7.59E-04	180	6.4E-04		
190	5.7E-04	190	6.29E-04	190	6.64E-04	190	6.78E-04	190	5.9E-04		
200	5.2E-04	200	5.78E-04	200	6.13E-04	200	6.20E-04	200	5.5E-04		
210	4.8E-04	210	5.39E-04	210	5.66E-04	210	5.62E-04	210	5.1E-04		
220	4.5E-04	220	4.96E-04	220	5.24E-04	220	5.25E-04	220	4.7E-04		
230	4.2E-04	230	4.71E-04	230	4.96E-04	230	4.83E-04	230	4.4E-04		
240	3.9E-04	240	4.44E-04	240	4.58E-04	240	4.53E-04	240	4.1E-04		
250	3.6E-04	250	4.18E-04	250	4.32E-04	250	4.38E-04	250	3.8E-04		
260	3.4E-04	260	3.84E-04	260	4.07E-04	260	3.96E-04	260	3.6E-04		
270	3.2E-04	270	3.67E-04	270	3.80E-04	270	3.73E-04	270	3.4E-04		
270	5.22 07	210	5.57 0 0 1	210	5.00L 0T	270	5.750 04	270	5.12.01		

Table 5.9: Calculated dynamic viscosity of five biodiesel samples

5.5 Cloud Point and Pour Point

Pour Points and Cloud Points of biodiesel samples are shown in Table 5.10. It can be seen from Table 5.10 and Figure 5.13 that increasing the percentage of WFME lead to an increase of the Pour Point and Cloud Point of the biodiesel samples. This difference may be due to origin of oil and quality also. It is here to be noted that both these properties are dependent on fatty acid composition of oil that is saturated and unsaturated fatty acids present in oil. Therefore, the length of the fatty acid chain as well as its composition plays a substantial role in the cold flow properties of biodiesel.

D' . 1'11	WCME	WFME	Cloud Point	Pour Point [°C]	
Biodiesel samples	[%]	[%]	[°C]		
WCME	100	0	-1	-10.5	
25-WFME	75	25	5.7	-1	
50-WFME	50	50	11.5	3.5	
75-WFME	25	75	14	7.7	
WFME	0	100	17.8	11.3	

Table 5.10: Cloud point and pour point of the five biodiesel samples



Figure 5.13: The cloud and Pour Points of biodiesel samples

5.6 Empirical Equations

To predict the viscosities and densities of biodiesel samples at different temperature the correlation between viscosity and temperature and density and temperature, a statistical software package (Minitab 17) was used to analyze the data. The best correlation between viscosity and temperature as well as between density and temperature for each of biodiesel samples can generally be written as shown in Table 5.11. Overall, the empirical equations realize the best accuracy for the prediction of kinematic viscosity, dynamic viscosity, and density of five samples with the highest correlation coefficient of 0.99. Furthermore, this shows that the empirical equations can be used confidently to predict the biodiesel properties (kinematic and dynamic viscosity and also density). The proposed equations for calculating cloud point and pour point as a function of composition respectively, are also shown in Table 5.11.

	From 20°Cto	o 270°C			From -10 °C to 20°C					
Kine	ematic viscos	sity [mm²/s]]	Kinematic viscosity [mm ² /s]					
	v = exp(A -	+ B/T)			$\nu = exp(A + B/T)$					
	A	В	R^2		А	В		R^2		
WCME	-3.856	1677.753	0.996	WCME	-8.704	3114.84		0.970		
25-WFME	-3.953	1770.771	0.993	25-WFME	25-WFME -7.635 2921.147		147	0.996		
50-WFME	-3.678	1659.55	0.992	50-WFME	WFME -6.998 2715.690		690	0.999		
75-WFME	-3.626	1631.429	0.993	75-WFME	-7.120	2750.748		0.999		
WFME	-3.709	1629.546	0.995	WFME	-7.275	2718.542		1.000		
From 20°C to 270°C					From -10 °C to 20°C					
Density [kg/m ³]					Density [kg/m ³]					
$\rho = A - BT$					$\rho = A - BT + CT^2$					
	Α	В	R^2		А	В	С	R^2		
WCME	1176.388	0.979	0.989	WCME	6368.987	36.000	0.059	0.99		
25-WFME	1156.379	0.92	0.994	25-WFME	1591.06	2.415	0	0.98		
50-WFME	1144.683	0.893	0.991	50-WFME	1477.52	2.041	0	0.97		
75-WFME	1170.283	0.935	0.994	75-WFME	1392.027	1.722	0	1.00		
WFME	1127.348	0.872	0.997	WFME	1372.374	1.722	0	1.00		
				WFME						
Cloud Point [°C]					Pour Point [°C]					
(CP = A + By	$A + By + Cy^2 \qquad \qquad PP = A + By + Cy^2$								
Α	В	С	R^2	Α	В	С		R^2		
-0.88	0.288	-0.001	0.995	-9.989	0.347	-0.001		0.992		
WCME										
Cloud Point [°C]				Pour Point [°C]						
$CP = A + Bz + Cz^2$				$PP = A + Bz + Cz^2$						
Α	В	С	R^2	Α	В	С		R^2		
17.48	-0.084	-0.001	0.995	10.931	-0.09	-0.001		0.992		
T: the temperature of biodiesel [K] y: the pe				ercentage of WFM	centage of WFME z: the percentage of WCME					

Table 5.11: General mathematical-physical model of the biodiesel samples based on the temperature

5.6.1 Comparison between Models with Experiment data from 20°C to 270°C

The accuracy of the models obtained from the statistical software package was examined by evaluating the values of *R*-squared (R^2). The results (Figures 5.14 and 5.15) showed that the empirical equations of kinematic viscosity and density of five biodiesel samples gave good predictions due to the values of R^2 . The R^2 value of 0.98 or 0.99 indicated a very good fit of the measured data with the model equations, i.e. the experimental data correlate well with the model equations. R-squared value is a measure of goodness-of-fit, which means how close the data points are to the fitted regression line. These values are close to unity, as shown in Figures 5.14 and 5.15, highlighting proper fitting of the predicted values by empirical equations.


Figure 5.14: Comparison between predicted data with experimental data of kinematic viscosity in temperature range 20°C to 270°C



Figure 5.15: Comparison between predicted data with experimental data of density in temperature range 20°C to 270°C

5.6.2 Comparison between Models with Experiment Data from -10°C to 20°C

A. Kinematic viscosity and density

The proposed equations (Table 5.11) for calculating kinematic viscosity and density of five biodiesel samples as a function of temperature of ranging from -10°C to 20°C are shown in Figures 5.16 and 5.17. It can be observed from these figures that the kinematic viscosities and density decreased with increase in temperature. The regression coefficients R^2 for kinematic viscosity and density of five biodiesel samples are shown Figures 5.16 and 5.17. The R^2 values showed that the experimental data for kinematic viscosity and density have a very good correlation with the models for all biodiesel. Therefore, *R*-squared values are close to unity highlighting proper fitting of the predicted values.



Figure 5.16: Comparison between predicted data with experimental data of kinematic viscosity in the temperature range -10°C to 20°C



Figure 5.17: Comparison between predicted data with experimental data of density in the temperature range -10°C to 20°C

B. Cloud Point and Pour Point

The measurements of the cloud point and pour point have been correlated as a function of percentage composition by empirical second order polynomial equations. From the regression coefficient, it was observed that the regression analysis of the data shows that the polynomial equation is better fitted for the measured values than a linear equation. Figure 5.18 shows the comparison graph between experimental data (ED) and predicted data (PD) of CP and PP. These clearly show the fit values, and variance of the results predicted by the mathematical models has been expressed in terms of *R-squared* (R^2) values, which are quite encouraging. R-squared value is a measure of goodness-of-fit, which means how close the data points are to the fitted regression line. These values are close to unity, as shown in Figure 5.18, highlighting proper fitting of the predicted values by the empirical equations.



Figure 5.18: Observed and empirical values of cloud and pour points of biodiesel samples

5.7 ANFIS and ANN Models

Thermo-physical properties including kinematic viscosity, density and dynamic viscosity data of the two biodiesel and their blends at different temperatures were gathered from experimental work (from 20°C to 270°C). A total of 130 experimental data was used to predict the kinematic viscosity, density and dynamic viscosity of two biodiesel with their blends. The development of the proposed approaches was performed as follows. In the first step, the experimental data was separated into input data (independent variables, including temperature and volume fraction of WFME and output data (dependent variables in term of kinematic viscosity, density and dynamic viscosity). Subsequently, different approaches (ANFIS and ANN) were proposed to describe the behavior of the thermo-physical properties, as a function of temperature and volume fraction of WFME. In this case, the database was randomly divided into three groups with 60% to training, 20% to testing and 20% for checking or validation. The temperature and volume fraction WFME were considered as input variables for ANFIS and ANN. As the input variables and output variables for the ANFIS and ANN have different magnitude, a normalization of them is required. A range between 0 and 1 was used as follows

$$\phi_n = \frac{\phi - \min(\phi)}{\max(\phi) - \min(\phi)}$$
(5.2)

where ϕ_n is the normalized input or output variable, the minimum (min) and maximum (max) values are shown in Table 5.12.

	Limit values	Units					
Input Values							
Temperature	20 - 270	°C					
Volume fraction of WFME	0 -1	-					
Output							
Kinematic viscosity	9.75 - 0.49	mm ² /s					
Density	887.48 - 657.69	kg/m ³					
Dynamic viscosity	8.65×10 ⁻³ - 3.23×10 ⁻⁴	Pa.s					

Table 5.12: Limit values for the input and output variables for ANFIS or ANN models

5.7.1 Biodiesel Properties Modeled Using ANFIS

The ANFIS modeling investigation was implemented using the fuzzy logic toolbox in MATLAB R2013b (Mathworks Inc., Natick, MA, USA). 60% of the total data (78 samples) have been used in the training the network, 20% of the total data (26 samples) have been used in the checking while the remaining 20% (26 samples) have been used in testing the performance of the network. The use of checking sets in ANFIS learning beside the training set is a recommended technique to guarantee model generalization and to avoid over-fitting the model of the training data set. In this work, two methods, hybrid and back propagation tested for generation ANFIS. And, the results show the training error in the hybrid method is lower than back-propagation method. Therefore, the data are trained to identify the parameters of Sugeno-type fuzzy inference system based on the hybrid algorithm with Gaussian membership function has used for simulations. The training has been repeated many times until the predicted output and actual values have the acceptable accuracy. In this study, by trial and error, the best number of membership functions for each input was determined as 2, the membership grades takes the Gaussian membership function and the output part of each rule uses a constant defuzzifier formula. The numbers of the system parameters of the developed ANFIS model are given in Table 5.13. In addition, the ANFIS network was able to achieve training and checking the lowest root mean squared error (RMSE) for biodiesel properties as shown in Table 5.13. As can be seen in this table, the number of rules was significantly reduced. The developed ANFIS model's architecture with two input variables (temperature and volume fraction of WFME) and three outputs (kinematic viscosity, density and dynamic viscosity) is illustrated in Figure 5.19. The plot of the observed and predicted values of kinematic viscosity, density and dynamic viscosity of biodiesel fuels against the index is displayed in Figure 5.20, 5.21 and 5.22, respectively.



Figure 5.19: ANFIS architecture of two input–three outputs with four rules in biodiesel system



Figure 5.20: Surface plots of kinematic viscosity by ANFIS



Figure 5.21: Surface plots of density by ANFIS



Figure 5.22: Surface plots of dynamic viscosity by ANFIS

Two input - One output									
	Training error	Testing error							
	RMSE		RMSE						
v	ρ	μ	νρ						
0.0053	0.011	0.011	0.0071	0.0129	0.12				
	Checking error								
	RMSE								
	v	ρ		μ	μ				
0.0	0069	0.012	24	0.018					
Number of n	odes		21						
Number of lin	near parameters		4						
Number of n	onlinear parameter	S	8						
Number of fu	izzy rules		4						
Epoch			1000						

 Table 5.13: The ANFIS information used in this study

5.7.2 Effects of Variable Interactions on Biodiesel Properties by ANFIS

The influence of interactions of the two process input variables on the kinematic viscosity, density and dynamic viscosity of two biodiesel and their blends were graphically investigated using three dimensional surface plots (Figure 5.20, 5.21 and 5.22). It was observed that there was a relative significant interaction between every two independent variables. There is a relationship between the two independent variables (Temperature and volume fraction of WFME biodiesel) and their effects on the response variable (kinematic viscosity and density). Figure 5.20 shows that %WFME, %WCME and temperature are very significant in kinematic viscosity of biodiesel samples. It found that as WFME concentration increased, the kinematic viscosity will decrease, whereas, increasing in the amount of WCME leads to increase in the kinematic viscosity of biodiesel as shown in Figure 5.20. Additionally, it can be noticed that the increasing in the temperature leads to decrease the viscosity of biodiesel exponentially. Similarly, it can be concluded from Figure 5.21 that as the percentage of WFME concentration increases, the density of biodiesel decreases while decreasing in percentage of WCME concentration leads to increase the density of biodiesel. And, the similar effect between kinematic viscosity and temperature is observed between density and temperature. The curvatures nature of the surfaces suggested significant interactions of kinematic viscosity and density with %WFME and WCME, kinematic viscosity and density with temperature. Moreover, it can be observed from Figure 5.22 that the dynamic viscosity decreased when the percentage of WFME increased. And as the temperature increase the dynamic viscosity of biodiesel samples decreased.

The predicted results of kinematic viscosity (v), density (ρ) and dynamic viscosity (μ) obtained by ANFIS of biodiesel samples are compared with experimental results as Figures 5.23, 5.24 and 5.25, respectively and tabulated in Table 5.14. The abscissa represents the fraction of WCME, whereas the kinematic viscosity or density or dynamic viscosity values are provided on the ordinate as shown in Figures 5.23, 5.24 and 5.25, respectively. It can be observed from these figures, the predicted values by ANFIS are very close to the experimental data for each temperature considered. These results indicate that density, kinematic viscosity and dynamic viscosity prediction of five biodiesel samples can be performed with good accuracy from the ANFIS proposed in this work. Table 5.14 shows a comparison for the experimental and predicted viscosities and density data using ANFIS expressed by their absolute relative error (% ϵ) in percentage. The variations are in the range of 0.01% to 7%, which indicates an excellent agreement between the experimental and predicted values.



Figure 5.23: A comparison between experimental and ANFIS data of kinematic viscosity vs percentage composition



Figure 5.24: A comparison between experimental and ANFIS data of density vs percentage composition



Figure 5.25: A comparison between experimental and ANFIS data of dynamic viscosity vs percentage composition

WCME										
	Experiment				ANFIS			%ε		
Т [℃]	v [mm²/s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]		v [mm²/s]	ρ [kg/m ³]	μ [Pa.s]
20	7.49	879.20	6.58E-03	7.45	881.37	6.57E-03		0.47	0.25	0.22
40	4.68	868.15	4.06E-03	4.63	871.38	4.03E-03		1.02	0.37	0.65
90	2.02	828.96	1.68E-03	2.01	829.92	1.67E-03		0.82	0.12	0.71
140	1.18	769.37	9.06E-04	1.21	768.92	9.29E-04		2.60	0.06	2.54
270	0.49	662.11	3.23E-04	0.50	662.18	3.32E-04		2.78	0.01	2.79
				25-V	VFME					
		Experime	nt		ANFIS			% ε		
	v	ρ.		v	ρ.			v	ρ.	μ
Т	[mm ² /s	[kg/m ³	μ	[mm ² /s	[kg/m ³	μ		[mm ² /s	[kg/m ³	[Pa.s
[°C]]]	[Pa.s]]]	[Pa.s]	_]]]
20	9.75	886.93	8.65E-03	9.69	886.28	8.58E-03		0.66	0.07	0.73
40	5.75	872.23	5.01E-03	5.73	871.84	4.99E-03		0.37	0.04	0.41
90	2.32	823.45	1.91E-03	2.34	825.30	1.93E-03		0.81	0.22	1.04
140	1.36	776.67	1.06E-03	1.44	772.08	1.11E-03		5.43	0.59	4.80
270	0.55	671.46	3.67E-04	0.56	671.89	3.78E-04		2.98	0.06	3.04
				50-V	VFME					
		Experime	nt		ANFIS			% ε		
Т	v	ρ	μ	v	ρ	μ		v	ρ	μ
[°C]	[mm ² /s]	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	_	[mm ² /s]	[kg/m ³]	[Pa.s]
20	8.82	880.19	7.76E-03	8.80	879.58	7.74E-03		0.19	0.07	0.26
40	5.42	867.08	4.70E-03	5.44	865.85	4.71E-03		0.40	0.14	0.25
90	2.26	824.48	1.86E-03	2.16	824.66	1.78E-03		4.61	0.02	4.59
140	1.35	777.12	1.05E-03	1.41	776.09	1.09E-03		4.58	0.13	4.44
270	0.56	675.27	3.80E-04	0.54	677.73	3.65E-04		4.07	0.36	3.72
				75-V	VFME					
	Experiment			ANFIS			% ε			
т [°С]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]		v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]
20	8.50	887.48	7.54E-03	8.45	880.96	7.44E-03	_	0.56	0.73	1.29
40	4.98	873.85	4.35E-03	5.18	874.23	4.53E-03		3.97	0.04	4.01
90	2.23	840.97	1.87E-03	2.18	839.24	1.83E-03		2.10	0.20	2.30
140	1.33	780.09	1.04E-03	1.42	784.92	1.12E-03		6.87	0.62	7.53
270	0.56	670.19	3.73E-04	0.55	672.58	3.69E-04		1.29	0.36	0.93
				W	FME					
Experiment ANFIS								% ғ		
Т [℃]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	_	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]
20	7.36	867.83	6.38E-03	7.27	866.99	6.31E-03	_	1.11	0.10	1.21
40	4.67	851.35	3.97E-03	4.72	852.91	4.03E-03		1.24	0.18	1.43
90	2.03	814.06	1.65E-03	1.96	812.56	1.59E-03		3.78	0.18	3.96
140	1.19	770.37	9.17E-04	1.22	769.06	9.37E-04		2.35	0.17	2.17
270	0.52	657.69	3.43E-04	0.50	658.64	3.29E-04		4.15	0.15	4.02

Table 5.14: Comparison of density and viscosity obtained from experimental data and ANFIS of the two biodiesel and their blends

5.7.3 Biodiesel Properties Modeled Using ANN

The development and the training of the network model in this study were carried out using the MATLAB Neural Network Toolbox. In this research, the experimental data of 130 biodiesel samples were randomly split into three data set, 60% in the training set (78 samples), 20% in the validation set (26 samples) and 20% in the test set (26 samples). The inputs and targets are normalized into the range [-1, 1] to make the training procedure more efficient (Kalogirou, 2001). Training of the network was performed by using the Levenberg-Marquardt, backpropagation algorithms. There is no general rule for the determination of the optimum number of hidden layers and usually it is determined through trial and error method (Moradi et al., 2013). Therefore, the number of neurons in the hidden layer was determined by trial and error test, where a mean squared error greater than 1×10^{-5} and a correlation coefficient higher than 0.99 was obtained. In addition, with the trial and error method, training results showed that the ANN with two hidden layers has the best performance. Consequently, the developed ANN model for predicting thermophysical properties of two biodiesel and their blends is shown in Figure 5.26 and the training parameters can be found in Table 5.15. The developed network architecture has a 2-2-3 configuration with two neurons in the input layer indicating temperature and volume fraction of WFME. Two hidden layers with varying neurons and three neurons in the output layer representing kinematic viscosity, density and dynamic viscosity are used.



Figure 5.26: Neural network architecture for two inputs and three outputs

Parameter	Specification
Training Function	Levenberg-Marquardt
Performance function	Mean square error (MSE)
Activation function	Log-Sigmoid
Number of layers	2
Number of neurons	8
Normalized range	-1 to 1

Table 5.15: Neural network configuration for the training

Figure 5.27 and Figure 5.28 show a linear relation for the training, validation, testing and performance of the network with high correlation coefficients (R) of kinematic viscosity and density. The straight lines in Figure 5.27 and 5.28 are the linear relationships obtained between the output (predicted) and the target (experimental) data of kinematic viscosity and density used in this present study. The mean squared error (MSE) for kinematic viscosity and density and density network are 8.153×10^{-5} and 8.675×10^{-5} , respectively. The high coefficients of correlation (R) obtained during the training, validation and testing of the kinematic viscosity and density network display very good relationship between the output and the experimental values of kinematic viscosity and density.



Figure 5.27: Regression plots for kinematic viscosity network



Figure 5.28: Regression plots for density network

5.7.4 Effects of Variable Interactions on Biodiesel Properties by ANN

The test values obtained from the ANN model results were compared with experimental values as shown in Figures 5.29, 5.30 and 5.31. As a result, the test values obtained from ANN model were quite compatible with experimental values. In addition, the effects of the biodiesel fraction of WFME on kinematic viscosity, density and dynamic viscosity for different temperatures respectively are shown in the figures as well. It can be concluded that as the temperature increases, the viscosity and density of biodiesel samples decrease. The comparisons of experimental values and ANN values are given in Table 5.16. It is observed that the experimental results and the data obtained by ANN are very close to each other. Moreover, viscosity of biodiesel samples has a maximum absolute relative error (% ϵ) compared to the density of biodiesel as shown in Table 5.16, which contains a comparison of the experimental and predicted data of viscosity and density expressed by their absolute relative error (% ϵ) in percentage. The results are in the range of 0.06% to 9%, which indicates an excellent agreement between the experimental and predicting values.



Figure 5.29: A comparison between experimental and ANN data of kinematic viscosity vs percentage composition



Figure 5.30: A comparison between experimental and ANN data of density vs percentage composition



Figure 5.31: A comparison between experimental and ANN data of dynamic viscosity vs percentage composition

WCME										
	Experiment			ANN			% ε			
Т [℃]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	
20	7.49	879.20	6.58E-03	7.75	876.97	6.80E-03	3.53	0.25	3.27	
40	4.68	868.15	4.06E-03	4.81	869.67	4.19E-03	2.89	0.18	3.07	
90	2.02	828.96	1.68E-03	2.17	829.57	1.80E-03	7.46	0.07	7.54	
140	1.18	769.37	9.06E-04	1.17	767.44	9.00E-04	0.41	0.25	0.66	
270	0.49	662.11	3.23E-04	0.52	678.41	3.53E-04	6.73	2.46	9.36	
				25-W	VFME					
	_	Experime	nt		ANN			% ε		
Т	v	ρ	μ	v	ρ	μ	v	ρ	μ	
[°C]	[mm ² /s]	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	
20	9.75	886.93	8.65E-03	9.70	876.51	8.50E-03	0.53	1.17	1.70	
40	5.75	872.23	5.01E-03	5.39	877.26	4.73E-03	6.19	0.58	5.65	
90	2.32	823.45	1.91E-03	2.51	834.51	2.10E-03	8.24	1.34	9.69	
140	1.36	776.67	1.06E-03	1.29	784.15	1.01E-03	5.32	0.96	4.40	
270	0.55	671.46	3.67E-04	0.58	678.23	3.93E-04	6.15	1.01	7.22	
50-WFME										
		Experime	nt	ANN			% ε			
Т	v	ρ.	μ	v	ρ.	μ	v	ρ.	μ	
[°C]	[mm ² /s]	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	
20	8.82	880.19	7.76E-03	8.64	870.77	7.52E-03	2.08	1.07	3.13	
40	5.42	867.08	4.70E-03	5.25	868.29	4.56E-03	3.16	0.14	3.03	
90	2.26	824.48	1.86E-03	2.12	831.82	1.76E-03	6.35	0.89	5.52	
140	1.35	777.12	1.05E-03	1.27	772.89	9.82E-04	5.71	0.54	6.23	
270	0.56	675.27	3.80E-04	0.60	682.59	4.11E-04	7.01	1.08	8.17	
				75-W	FME					
	Experiment			ANN				%ε		
ר [℃]	v [mm²/s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	v [mm ² /s]	ρ [kg/m ³]	μ [Pa.s]	
20	8.50	887.48	7.54E-03	8.38	878.98	7.37E-03	1.34	0.96	2.29	
40	4.98	873.85	4.35E-03	4.68	871.75	4.08E-03	6.04	0.24	6.27	
90	2.23	840.97	1.87E-03	2.31	839.41	1.94E-03	3.94	0.18	3.75	
140	1.33	780.09	1.04E-03	1.27	784.65	9.97E-04	4.43	0.58	3.87	
270	0.56	670.19	3.73E-04	0.61	676.94	4.11E-04	9.09	1.01	10.19	
				WI	FME					
Experiment ANN % E										
Т	v	0	u	v	Ø	u	v	Ø	u	
[°C]	[mm ² /s]	[kg/m ³]	[Pa.s]	$[mm^2/s]$	[kg/m ³]	[Pa.s]	[mm ² /s]	[kg/m ³]	[Pa.s]	
20	7.36	867.83	6.38E-03	6.98	857.86	5.99E-03	5.13	1.15	6.22	
40	4.67	851.35	3.97E-03	4.65	849.24	3.95E-03	0.28	0.25	0.53	
90	2.03	814.06	1.65E-03	2.10	816.88	1.72E-03	3.44	0.35	3.80	
140	1.19	770.37	9.17E-04	1.42	771.43	1.10E-03	19.29	0.14	19.45	
270	0.52	657.69	3.43E-04	0.55	665.49	3.68E-04	6.13	1.19	7.39	

Table 5.16: Comparison of density and viscosity obtained from experimental data and ANN of the two biodiesel and their blends

5.7.5 Comparison between ANFIS and ANN

A graphical representation of the variation of kinematic viscosity, density and dynamic viscosity values obtained experimentally, using ANFIS and ANN approaches at different temperatures of two biodiesel and their blends are given in Figures 5.32, 5.33, 5.34, respectively. There is an excellent agreement between the measured and predicted values as shown in figures. Increasing the temperatures from 20°C to 270°C, the biodiesel properties decreased. It can be observed from these figures that the predicted values of biodiesel properties of samples at different temperature using ANFIS approach are closer to the experimental values for biodiesel blends compared to ANN approach. Furthermore, these figures show the comparisons of ANFIS and ANN with experimental data for viscosities and density of five biodiesel samples, which also show good agreement between ANFIS predicted data and experimental data. Moreover, the percentage absolute relative error values between experimental data and predicted data using ANFIS of biodiesel properties are lower compared to those of ANN.



Figure 5.32: Comparative illustration of kinematic viscosity biodiesel samples against temperature at various volume fractions of WCME biodiesel



Figure 5.33: Comparative illustration of density biodiesel samples temperature at various volume fractions of WCME biodiesel



Figure 5.34: Comparative illustration of dynamic viscosity biodiesel samples temperature at various volume fractions of WCME biodiesel

CHAPTER 6 CONCLUSION AND FUTURE WORK

6.1 Conclusion

The biodiesel samples those were prepared via the transesterification method were taken from the Mechanical Engineering Laboratory to investigate the biodiesel properties. The kinematic viscosity and density of the prepared biodiesel samples were within ASTM D6751 and EN 14214. In this study, the biodiesel properties (kinematic viscosity, dynamic viscosity and density) and cold flow properties (CP and PP) and kinematic viscosity of the biodiesel samples were measured within the temperature range from 20°C to 270 and -10°C to 20°C, respectively. In addition, the thermo-physical properties of waste vegetable oil, biodiesel and their blends were predicted using adaptive neural-fuzzy inference system (ANFIS), and artificial neural networks (ANN) approaches. Therefore, the predicted values of viscosities and density of five biodiesel samples were determined at wide range temperature (20°C to 270°C). Generalized and empirical equations, validated by using the experimental data, were used for predicting the viscosities and density of the biodiesel samples and compared with ANFIS and ANNS approaches. The following points have been observed based on the results obtained from the experiments and numerical analyses:

- 1. At high temperatures (above 250 °C), the value of the kinematic viscosity is almost equal and the difference between these values is about 3 %.
- 2. It has been noticed that the viscosities and the density of the biodiesel sample decreased with the increase of WFME fraction. It is also seen that the viscosities and density of each sample decrease with an increase in the temperature.
- 3. The Cloud Point and Pour Point of the WCME increased when the WFME contents of the mixture increase.
- 4. Empirical equations to predict the viscosities and densities of the biodiesel sample blends as a function of temperature have been developed. The empirical equations and the measured data closely match with R^2 of 0.995 for density, kinematic viscosity, PP and CP models.
- 5. For the viscosities and densities measured experimentally, the prediction errors indicated by ANFIS, ANN, and mathematical models are very small for all the testes in a wide range temperature.

- 6. According to the results predicted, ANFIS approach is better than ANN approach for calculating viscosity and density of biodiesel samples.
- 7. The empirical equations, ANFIS and ANN approach to predict both viscosity and density of biodiesel samples were developed. In all cases, the viscosity and density of five biodiesel samples decreased with increase in temperature.
- 8. It found that there is an excellent agreement between the experimental and predicted values using mathematical models with high R-squared. Therefore, mathematical models can be used for predicting the viscosity and density of biodiesel without needing experimental measurements.
- 9. It concluded that there is an excellent agreement between the experimental and predicted values using mathematical models with high R-squared. Therefore, mathematical models can be used for predicting the viscosity and density of biodiesel without needing experimental measurements.
- 10. All proposed models provide a satisfactory respond for the estimation of kinematic viscosity, density, and dynamic viscosity. It is remarkable that a better performance is presented in the ANFIS and ANN models that start with the prediction of the thermo-physical properties of biodiesel, as evidenced by their correlation coefficient (closer to unity), and by their lower MSE.
- 11. As a result, it is suggested from the study that it is possible to use the biodiesel obtained from waste oils as an alternative fuel, which can be considered as renewable energy and environmental recycling process from waste oil after frying.

6.2. Future Work

An interesting future study might measure the other properties of the biodiesel samples such as the Cold Filter Plugging Point, flash point and cetane number. Moreover, to improve the cold flow properties of the biodiesel samples, some kind of improvers such as conventional diesel fuel (petrodiesel) or alkyl esters can be added. Since biodiesel can degrade due to oxidation, contact with water, and/or microbial activity, the storage of biodiesel over extended periods may lead to degradation of its fuel properties. Consequently, this research suggests that the degradation process of biodiesel at different temperatures and exposure times should be studied in the future.

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Zhang, X., Peterson, C., Reece, D., Haws, R., & Möller, G. (1998). Biodegradability Of Biodiesel In The Aquatic Environment. *Transactions of the ASAE*, 41(5), 1423-1430. APPENDICES
APPENDIX 1

STANDARD SPECIFICATIONS AND OPERATING INSTRUCTIONS FOR GLASS CAPILLARY KINEMATIC VISCOMETERS

Designation: D 445 – 09



Designation: 71/1/97

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

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

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

1. Scope*

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

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

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

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

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

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

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-

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

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

2. Referenced Documents

- 2.1 ASTM Standards:²
- D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers
- D 1193 Specification for Reagent Water
- D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer
- D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer
- D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer
- D 2162 Practice for Basic Calibration of Master Viscometers and Viscosity Oil Standards
- D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)
- D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer
- D 6071 Test Method for Low Level Sodium in High Purity Water by Graphite Furnace Atomic Absorption Spectroscopy
- D 6074 Guide for Characterizing Hydrocarbon Lubricant Base Oils
- D 6617 Practice for Laboratory Bias Detection Using Single Test Result from Standard Material
- E 1 Specification for ASTM Liquid-in-Glass Thermometers E 77 Test Method for Inspection and Verification of Ther-
- mometers
- 2.2 ISO Standards:³

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

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

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

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

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

2.3 NIST Standards:⁴

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

NIST Special Publication 819

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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

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

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

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

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

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

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

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

4. Summary of Test Method

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

5. Significance and Use

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

6. Apparatus

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

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

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

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

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

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

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

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

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

6.4 Temperature Measuring Device in the Range from 0 to $100^{\circ}C$ —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° C.

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

6.4.3 When using liquid-in-glass thermometers, such as those in Table A2.1, use a magnifying device to read the thermometer to the nearest $\frac{1}{5}$ 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 ± 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.^A

Viscosity of Reference Material, mm ² /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%

^ASupporting 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 μ 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, ν , in mm²/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 ν_1 and ν_2 , respectively, mm²/s,

C = calibration constant of the viscometer, mm²/s², and

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

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

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

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

where:

 η = dynamic viscosity, mPa·s,

 ρ = density, kg/m³, at the same temperature used for the determination of the kinematic viscosity, and

 ν = kinematic viscosity, mm²/s.

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

15. Expression of Results

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

16. Report

16.1 Report the following information:

16.1.1 Type and identification of the product tested,

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

16.1.3 Result of the test (see Section 15),

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

16.1.5 Date of the test, and

16.1.6 Name and address of the test laboratory.

17. Precision

17.1 Comparison of Determined Values:

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

Base oils at 40 and 100°C ⁵	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C ⁶	0.0013 y	(0.13 %)
Formulated oils at 150°C7	0.015 y	(1.5 %)
Petroleum wax at 100°C ⁸	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C ⁹	0.011 (y + 8)	
Residual fuel oils at 50°C9	0.017 y	(1.7 %)
Additives at 100°C ¹⁰	0.00106 y ^{1.1}	

```
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 ⁶	0.0026 x	(0.26 %)
Formulated oils at 150°C7	0.0056 x	(0.56 %)
Petroleum wax at 100°C ⁸	0.0141 x ^{1.2}	
Residual fuel oils at 80 and 100°C9	0.013 (x + 8)	
Residual oils at 50°C ⁹	0.015 x	(1.5 %)
Additives at 100°C ¹⁰	0.00192 x ^{1.1}	
Gas oils at 40°C ¹¹	0.0043 (x+1)	
Jet fuels at -20°C ¹²	0.007 x	(0.7 %)

where: x is the average of results being compared.

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

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

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

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

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

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

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

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

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



Base oils at 40 and 100°C ⁵	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C ⁶	0.0076 x	(0.76 %)
Formulated oils at 150°C7	0.018 x	(1.8 %)
Petroleum wax at 100°C ⁸	0.0366 x ^{1.2}	
Residual fuel oils at 80 and 100°C ⁹	0.04 (x + 8)	
Residual oils at 50°C9	0.074 x	(7.4 %)
Additives at 100°C ¹⁰	0.00862 x ^{1.1}	
Gas oils at 40°C ¹¹	0.0082 (x+1)	
Jet fuels at -20°C ¹²	0.019 x	(1.9 %)

where: x is the average of results being compared.

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

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

18. Keywords

18.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

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

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES AND CERTIFIED VISCOSITY REFERENCE STANDARDS

A1.1 Viscometer Types

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

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

TABLE A1.1 Viscometer Types						
Viscometer Identification K	inematic Viscosity Range, ^A mm ² /s					
A. Ostwald Types for	Transparent Liquids					
Cannon-Fenske routine ^B	0.5 to 20 000					
Zeitfuchs	0.6 to 3 000					
BS/U-tube ^B	0.9 to 10 000					
BS/U/M miniature	0.2 to 100					
SIL ^B	0.6 to 10 000					
Cannon-Manning semi-micro	0.4 to 20 000					
Pinkevitch ^B	0.6 to 17 000					
B. Suspended-level Types	for Transparent Liquids					
BS/IP/SL ^B	3.5 to 100 000					
BS/IP/SL(S) ^B	1.05 to 10 000					
BS/IP/MSL	0.6 to 3 000					
Ubbelohde ^B	0.3 to 100 000					
FitzSimons	0.6 to 1 200					
Atlantic ^B	0.75 to 5 000					
Cannon-Ubbelohde(A), Cannon	0.5 to 100 000					
Ubbelohde dilution ^B (B)						
Cannon-Ubbelohde semi-micro	0.4 to 20 000					
C. Reverse-flow Types for Tran	C. Reverse-flow Types for Transparent and Opaque Liquids					
Cannon-Fenske opaque	0.4 to 20 000					
Zeitfuchs cross-arm	0.6 to 100 000					
BS/IP/RF U-tube reverse-flow	0.6 to 300 000					
Lantz-Zeitfuchs type reverse-flow	60 to 100 000					

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

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

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TABLE A1.2 Certified Viscosity Reference Standards

Designation	Approximate Kinematic Viscosity, mm ² /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

	Tes	st		Te	st	
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

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(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° 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, σ_{site} , from a laboratory quality control program.

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

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

 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

FATTY ACID METHYL ESTER COMPOSITION OF BIODIESEL SAMPLES

Biodiesel produced in mechanical engineering laboratory					literatu	re data			
		M (g/mol)	Mea Comp (wt	sured osition t%)	Calcul	ated Comj (wt%)	oosition	Min. Value	Max. Value
			WFME	WCME	75- WFME	50- WFME	25- WFME		
Methyl caprylate	C8:0	158.2380	0.05	0.00	0.04	0.03	0.01		
Methyl caprate	C10:0	186.2912	0.33	0.00	0.25	0.17	0.08		
Methyl Laurate	C12:0	214.3443	1.18	0.08	0.91	0.63	0.36	0.0	49.2
Methyl myriatate	C14:0	242.3975	0.10	0.00	0.08	0.05	0.03	0.0	25.9
Methyl palmitate	C16:0	270.4507	37.29	5.63	29.38	21.46	13.55	0.9	44.1
Methyl stearate	C18:0	298.5038	4.04	1.57	3.42	2.81	2.19	0.3	23.5
Methyl oleate	C18:1	296.4879	40.42	62.97	46.06	51.70	57.33	1.8	92.5
Methyl linoleate	C18:2	294.4721	17.84	21.34	18.72	19.59	20.47	0.0	77.3
Methyl linolenate	C18:3	292.4562	0.18	6.99	1.88	3.59	5.29	0.0	72.3
Methyl arachidate	C20:0	326.5570	0.00	0.46	0.12	0.23	0.35	0.0	7.5
Methyl erucate	C20:1	324.5411	0.00	1.04	0.26	0.52	0.78	0.0	66.5

Fatty acid methyl ester composition, wt%, (Al-Shanableh et al., 2016)

APPENDIX 3

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

ASTM D941 88 🎟 0759510 0040326 T I



AMERICAN SOCIETY FOR TESTING AND MATERIALS 1916 Race St., Philadelphia, Pa. 19103 Reprinted from the Annual Book of ASTM Standards, Copyright ASTM If not listed in the current combined index, will appear in the next edition.

An American National Standard

H-26-30

Standard Test Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer¹

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

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

1. Scope

1.1 This test method covers the measurement of the density of any hydrocarbon material that can be handled in a normal fashion as a liquid at the specified test temperatures of 20 to 25°C. Its application is restricted to liquids having vapor pressures less than 80 kPa (600 mm Hg) and having viscosities less than 15 mm²/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 Tables²

E 1 Specification for ASTM Thermometers³

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 Method⁴

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

5. Significance and Use

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

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

6. Apparatus

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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 ½ in. (3.2 mm) in thickness by 1 in. (25 mm) in width, of a length suitable for

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

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

² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vois 05.03 and 14.01.

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

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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° 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, ^A plus	W/V	Correction, ^A plus
0.70	0.00036	0.85	0.00018
0.71	0.00035	0.86	0.00017
0.72	0.00033	0.87	0.00016
0.73	0.00032	0.88	0.00014
0.74	0.00031	0.89	0.00013
0.75	0.00030	0.90	0,00012
0.76	0.00029	0.91	0.00011
0.77	0.00028	0.92	0.00010
0.78	0.00026	0.93	0.00009
0.79	0.00025	0.94	0.00007
0.80	0.00024	0.95	0.00006
0.81	0.00023	0,96	0.00005
0.82	0.00022	0.97	0.00004
0.83	0.00020	0.98	0.00003
0.84	0.00019	0.99	0.00001

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

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

where:

C = air buoyancy correction,

 d_a = density of air in the balance case, g/mL

W = weight of sample in pycnometer, and

V = volume of sample in pycnometer.

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 ± 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.

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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 4

STANDARD TEST METHOD FOR CLOUD POINT OF PETROLEUM PRODUCTS





Standard Test Method for Cloud Point of Petroleum Products¹

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

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

1. Scope*

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

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

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

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

2. Referenced Documents

2.1 ASTM Standards:²

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

E 1 Specification for ASTM Liquid-in-Glass Thermometers
2.2 Energy Institute Standard:³

Specifications for IP Standard Thermometers

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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

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

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

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

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

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

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

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

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

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

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

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 ± 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.

		Thermomete Number	
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 Bat	h 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° C above the expected cloud point. Remove any moisture present by a method such as filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature of at least 14° C above the approximate cloud point.

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

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

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

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

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

8.5 Maintain the temperature of the cooling bath at 0 \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 ± 1.5 °C (see Table 2). Do not transfer the jacket. If the specimen does not show a cloud when it has been cooled to -6°C, transfer the test jar to a jacket in a third bath maintained at a temperature of -33 ± 1.5 °C. For the determination of very low cloud points, additional baths are required, each bath to be maintained in accordance with Table 2. In each case, transfer the jar to the next bath, if the specimen does not exhibit cloud point and the temperature of the specimen

TABLE 2 Bath and Sample Temperature Ranges

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

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° C, at which any cloud is observed at the bottom of the test jar, which is confirmed by continued cooling.

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

9. Report

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

10. Precision and Bias

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

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

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

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

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

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

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

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

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



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

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

Note 5—The precision for blends of biodiesel in diesel samples comprised cloud points from about -2 to $+10^{\circ}$ C.

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

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

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

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

11. Keywords

11.1 cloud point; petroleum products; wax crystals

SUMMARY OF CHANGES

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

(1) Revised 6.7.

(2) Revised 7.

(3) Added Table 1.(4) Deleted original Note 2.

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APPENDIX 5

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 (CaCl₂)**, crystals.
- **4.3 Carbon dioxide (CO₂)**, 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)¹⁾ (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.

¹⁾ 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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CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name Nationality Date and Place of Birth Marital Status Kassem, Youssef Palestinian 01 January 1968, Saudi Arabia Marriage



EDUCATION

Degree PhD M.Sc. B.Sc. **Institution** Near East University Near East University Near East University Year of Graduation 2017 2011 2009

WORK EXPERIENCE Year

2012-present

2009-2011

Place Department of Mechanical Engineering Department of Mechanical Engineering Enrollment Lecturer

Teaching Assistant

FOREIGN LANGUAGES

English, fluently spoken and written

PUBLICATIONS IN INTERNATIONAL REFEREED JOURNALS (IN COVERAGE OF SSCI/SCI-EXPANDED AND AHCI):

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Course Given

2009-2012 Laboratory and Teaching Assistant at Near East University.

- Courses given:
 - Thermodynamics I and II
 - Fluid Mechanics,
 - Heat Transfer I and II
 - Theory of Machines II
 - Statics

2012-Present Courses given:

- Advance Calculus,
- Fluid Mechanics,
- Hydraulic Mechanics,
- Mathematics for Mechanical Engineers,
- Heat transfer I, and II
- Thermodynamic I and II

HOBBIES

Reading, Environment and Earth, Music, Travel