BERK AKTUĞ

INFLUENCE OF STORAGE PERIOD ON FUEL PROPERTIES OF BIODIESEL PREPARED FROM
WASTE VEGETABLE OILS

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

By
BERK AKTUĞ

In Partial Fulfillment of the Requirements for
the Degree of Master of Science
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Approval of Director of Graduate School of

Applied Sciences

Prof. Dr. Nadire ÇAVUŞ

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

Name, Last Name :

Signature :

Date:

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ABSTRACT

Rapidly growing world population, rapid modernization of technology, industrialization and thus the energy demand in the world have increased. Reduction of non-renewable energy sources such as natural gas and coal has led people to alternative energy sources. Biodiesel is among one of the most important alternative energy sources. Fats produced from fatty seed plants, waste frying oils or animal fats are fuels produced by reaction of short chain alcohol with a transesterification process in the presence of a catalyst. The biodiesel fuel used in this experiment was produced using waste frying oil by an oil producer in South Cyprus. The purpose of this study was to investigate the influence of storage period of biodiesel sample (B100) which stored at 40 ° C constant temperature on kinematic viscosity and density at different temperatures. In addition to this, pour point and cloud point was investigated. Biodiesel sample parameters which are kinematic viscosity, density, cloud point and pour point had been tested in Near East University Mechanical Engineering laboratory. Acid number and oxidation stability parameters had ben tested at a licensed laboratory in South Cyprus. The experimental measurements in this study were conducted at temperatures between 5°C and 90°C, according to ASTM standards. Experimental results showed that kinematic viscosity and density decrease with increasing temperature. An increase in kinematic viscosity and density is observed with the increase in storage period.

Keyword: Fuel; Biodiesel; Kinematic viscosity; Density; Storage Period

ÖZET

Hızla artan dünya nüfusu, teknolojinin hızla modernleşmesi ve sanayileşme olarak dünyadaki enerji talebini artmıştır. Doğalgaz ve kömür gibi yenilenemez enerji kaynaklarının azalması, insanları alternatif enerji kaynaklarına yöneltmiştir. Biyodizel de önemi gün geçtikçe artan alternatif enerji kaynakları arasında en önemlilerindendir.

Yağlı tohum bitkilerinden elde edilen yağların, evsel kızartma yağlarının veya hayvansal yağların bir katalizör eşliğinde transesterifikasyon süreci ile kısa zincirli bir alkol ile reaksiyonu sonucunda üretilen bir yakıttır. Bu deneyde kullanılan biyodizel yakıt Güney Kıbrıs'taki bir yağ üretim firması tarafından atık kızartma yağı kullanılarak üretilmiştir.

Bu çalışmanın amacı, 40˚Csabit sıcaklıkta depolanan biyodizel numunesinin (B100), depolama süresinin farklı sıcaklıklardaki kinematik viskozite ve yoğunluğu üzerindeki etkisini araştırmaktır. Bunlara ek olarak biyodizel numunesinin Bulutlanma Noktası ve Akma Noktası da incelenmiştir. Biyodizel numunesine ait kinematik viskozite, yoğunluk, bulutlanma noktası ve akma noktası parametreleri Yakın Doğu Üniversitesi Makine Mühendisliği Bölümü Laboratuarı'nda yapılan deneysel çalışmalar sonucu elde edilmiştir. Asit sayısı ve oksidasyon kararlılığı parametreleri ise Güney Kıbrıs'ta sertifikalı bir petrokimya laboratuarı tarafından analiz edilmek suretiyle neticeye ulaşılmıştır. Bu çalışmadaki deneysel ölçümler ASTM standartlarına göre 5˚C ila 90˚C arasındaki sıcaklıklarda yapılmıştır. Elde edilen deneysel sonuçlar neticesinde, sıcaklığın artmasıyla kinematik viskozite ve yoğunluğun azaldığını gözlenmiştir. Depolama süresindeki artış ile birlikte kinematik viskozite ve yoğunlukta bir artış gözlenmektedir.

Keyword: Yakıt; Biyodizel; Kinematik viskozite; Yoğunluk; Depolama süresi

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LIST OF SYMBOLS USED

A	Area
D	Capillary diameter
dv	Changing in velocity
dx	Changing in separation height
F	Force
g	Acceleration due to gravity
G	Universal gas constant
h	Plank’s constant
H	Capillary height
K	Viscometer constant
L	Length of viscometer
P	Flow pressure
Q	Flow rate
R	Capillary radius
R	Radian length
T	Time
T	Absolute temperature
V	Volume
V	Velocity
v	Flow velocity
v_z	Velocity in flow direction
v_r	Velocity in radian direction
v_θ	Velocity in angular direction
X	Elemental length
Y	Correction factor
Z	Length in flow direction
Θ	Angular length
ρ	Density
μ	Dynamic viscosity

ν	Kinematic viscosity
ρ	Density, kg/m^3
τ	Shear stress
$\dot{\gamma}$	Rate of shear

ABBREVIATIONS USED

AN	Acid Number
ANP	Agencia Nacional do Petroleo
ASTM	American Society for Testing Materials
B100	Biodiesel sample with %100 concentration
CFPP	Cold filter plugging point
CIE	Compressor ignition engines
CN	Cetane number
CP	Cloud Point
EU	European union
FA	Fatty acid
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FP	Flash Point
HHV	Higher heating value
IV	Iodine value
KOH	Potassium Hyrdoxide
PP	Pour point
US	United States
WCO	Waste cooking oil
WFCE	World Fuel Charter Committee

CHAPTER 1
INTRODUCTION

1.1 General Information about Energy Sources

Fast growing population, rapid modernization of technology yields industrialization has increased the requirement for energy of the world. Reduction in non-renewable energy resources such as natural gas and coal make the people questing in new type of energy resources. Even scientists say that, all fossil fuel resources will be depleted about 2040 (Showstack, 2016). Because of these facts, experts focus on alternative renewable resources such as solar energy, hydro power, biofuel, biomass, tidal energy, wind energy, nuclear energy etc.

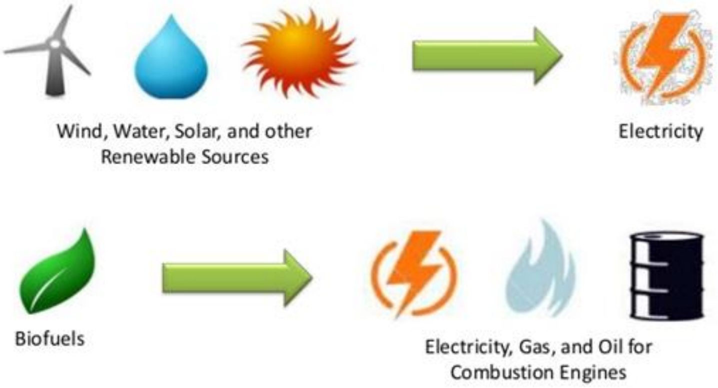

Wind, Water, Solar, and other Renewable Sources
Electricity
Biofuels
Electricity, Gas, and Oil for Combustion Engines

Figure 1.1: Differentiations of biofuels

Renewable energy sources are useful for electric power but they can’t be properly used for transportation sector (Figure 1.1). Biofuels are liquid fuels which are the most suitable renewable energy source type used in transportation so that is why biofuels differ from others. We can obtain these biofuels from a range of sources, forming different type of forms. Source Types;

- Maize
- Grass
- Miscanthus
- Algae
- Waste cooking Oil
- Fertilizer
- Whey
- Plant residues
- Foms
- Ethanol
- Biodiesel
- Biobutanol
- Biomass Pellets
- Synthetic Natural Gas(SNG)

1.2 Definition of Biodiesel

Biodiesel is stated as the mono alkyl esters of vegetable oils or animal fats. Biodiesel can also be used instead of diesel fuel. In today's world, some governments have made that mixing case (biodiesel-diesel) a necessity. For example South Cyprus Government has made a rule that, gasoline stations can sell diesel with the addition of biodiesel. The mixture ratio must be with %5-10 biodiesel addition. Biodiesel is primarily being manufactured from soya bean, rapeseed, and palm oils. When we compare the higher heating values (HHV) of fuels, we consider that gasoline has the highest value with 46 MJ/kg, biodiesels (39 to 41 MJ/kg). Biodisel higher heating value (HVV) is indistinctly lower than petro diesel with the values 39 to 41 MJ/kg and 43 MJ/kg respectively. Petroleum has a HHV around 42 MJ/kg. Coals has the lowest HHV with 32 to 37 MJ/kg. Biodiesel blends (Biodiesel-Petro diesel) are denoted as, ‘’BXX’’with ‘’XX’’ representing the percentage of biodiesel caontained in the biodiesel blend (i.e., a B30 blend is 30% biodiesel and 70% petro diesel) (Demirbas, 2008).

To produce biodiesel, the vegetable oil or animal fat is exposed to a chemical reaction called transesterification. In that chemical reaction (Figure 1.2) short-chain alcohols are being reacted with vegetable or animal fats. The alcohols used in these chemical reactions are mostly Methanol or Ethanol. The case is that alcohols having lower molecular weight are mostly chosen for transesterification process. Ethanol is being preferred furthest for its low charge. However by using methanol greater transformations into biodiesel is possible. Either acids or bases are used as catalyze for the transesterification process. Bases are most commonly used to catalyze transesterification to lower reaction period. Also they have lower cost compare to acid catalysis (Anastopoulos et al, 2009).

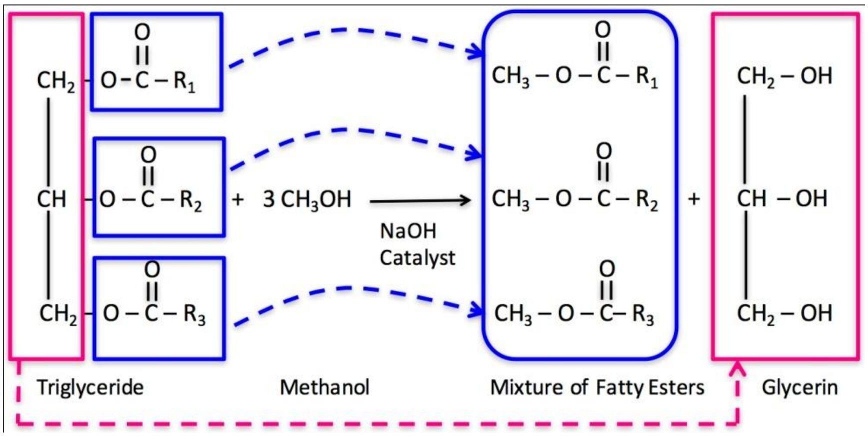


Figure 1.2: Chemical process of biodiesel production

In this thesis, the tests and researches has been conducted with Biodiesel (methyl ester) prepared from waste cooking oil (WCO). WCO defined as the used vegetable oil obtained from cooking. High free fatty acid (FFA) occurred as a result of repeated frying of vegetable oils especially at fast food restaurants. Waste frying oil has many extermination harms such as water and soil contamination, human health problems etc. So much WCO can be used as a raw material (Figure 1.3) for biodiesel production (Nanthagopal et al, 2014).

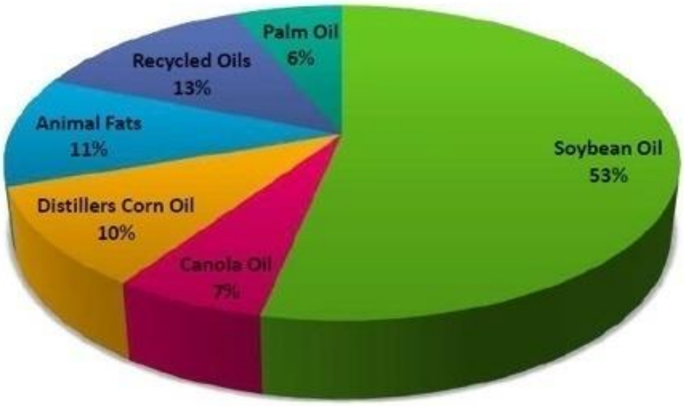


Figure 1.3: Raw material percentage for biodiesel production

The properties of WCO can change depending on the frying conditions, such as temperature, cooking time, number of cooks etc. Chemical and physical properties of cooking oil under a thermal stress can be completely modified. Triglyceride in the vegetable oil to break-down to forming, diglycerides, monoglycerides, and free fatty acids (FFAs) while the cooking duration occurs. Heat and water in the frying process increases the hydrolysis of triglycerides, for this reason the amount of FFA increasing in the WCO (Carlinia et al, 2014). In addition to this, oxidation and polymerization processes cause a rise in the viscosity of WCO.

1.3 Aim of Thesis

The aim of this work is to determine influence of storage period and storage temperature (40°C) on the properties of B100 biodiesel sample prepared from waste vegetable oils. Fuel properties that we want to examine are as following;

- Kinematic viscosity,
- Density
- Cold flow properties
- Acid value
- Oxidation stability

1.4 Thesis Outline

Chapter 1, includes a general information about biodiesel, general aim of this work discussed.

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

Chapter 3, explains the measurement procedure and experimental setup for measuring biodiesel properties.

Chapter 4, is a discussion of the results obtained from the experimental work.

Chapter 5, includes conclusions and suggestions for future work.

CHAPTER 2
BIODIESEL PROPERTIES

2.1 Concept of Viscosity

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

2.1.1 Types of viscosity

Dynamic viscosity

Dynamic (absolute) viscosity is the parallel force per unit area (tangent) required to move one horizontal plane with respect to another plane at a monad velocity. Dynamic Viscosity sometimes refers to shear viscosity. When a materials sidewards deformed by a (shear) force acting in the same direction, a shear stress τ is produced between the layers and a corresponding shear strain γ is produced. Shear strain is defined as follows;

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

The rate of shear strain;

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

Rate of shear strain is directly proportional shear stress between layers in oil, air and water. Dynamic viscosity formula can be expressed as follows;

$$\mu = \frac{\tau}{\dot{\gamma}} = \tau\frac{dy}{du} \tag{2.4}$$

Kinematic viscosity

The kinematic viscosity (m^2/s) that is express in Equation 2.5 defined as the ratio of the dynamic viscosity μ (Pa.s) to the density of the fluid ρ (m^3/kg).

$$v = \frac{\mu}{\rho} \tag{2.5}$$

2.1.2 Importance of viscosity

Viscosity of the biodiesel directly affect the behavior and performance of engines that is why it is accepted as an important property. Creation of engine sediment caused by viscosity affecting the atomization of a fuel upon injection into the combustion chamber (Knothe et al, 2005b). That means, fluids having lower viscosities flow easier compared that having higher viscosity value ones, even so it does not mean that we want a fuel with low viscosity or high viscosity. Right proportion is the real issue for getting the best engine efficiency. Low viscosities don’t ensure sufficient lubrication for the sensitive fit of fuel injection pumps. In contrast high viscosities guide to the formation of large droplets on injection (resulting in poor combustibility, raised exhaust smoke and emissions) (Cennatek Bioanalytical Services, 2013). EU and ASTM standards are given in Table 2.1

Table 2.1: Kinematic viscosity diesel fuel standards (Knothe, 2005)

Standard	Place	Method	Fuel type	Kinematic viscosity [mm^2/s]
EN 14214	E.U	ISO 3104	Biodiesel	3.5 - 5.0
ASTM D6751	U.S	ASTM D445	Biodiesel	1.9 - 6.0
EN 590	E.U	ISO 3104	Petro diesel	2.0 - 4.5
ASTM D975	U.S	ASTM D445	Petro diesel	1.9 - 4.1

There are some factors such as pressure and temperature which affects the viscosity of fuel:

- *Temperature:* Viscosity is decreasing with the increasing temperature. For all materials, viscosity and temperature are inversely proportional to each other. Sometimes for some specific fluids viscosity may increase with a percentage of 10-12 % with a decrease in temperature of 1-2°C.

- *Pressure:* Generally increasing pressure affects viscosity to rise up. Although pressure has an impact on the viscosity, it is lower than the temperatures impact since the liquids are nearly non-compressible at low pressures. Change in pressure from 0.1 to 30-32 MPa has the same effect with a temperature change of about 1-2°C, on the viscosity for most of the liquids

2.1.3 Measurement of viscosity

The instruments used for measuring viscosity are known as viscometers. Generally viscometers are categorized in six groups as following;

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

2.1.4 Capillary viscometers

Capillary viscometers are using to determine the viscosity of Newtonian fluids. Time period is measured for a specific quantity of fluid which flows through a capillary with a specific diameter and specific length. Under idealized conditions,

- Laminar, isothermal, steady flow condition

- Newtonian flow behavior of the liquid
- Pressure independence of the viscosity
- Incompressibility of the liquid
- Wall adherence of the liquid
- Neglect of the flow influences at the entry and exit of capillary of sufficient length

The liquid moves in coaxial layers toward the pressure drop through the capillary, in which a parabolic velocity profile is formed.

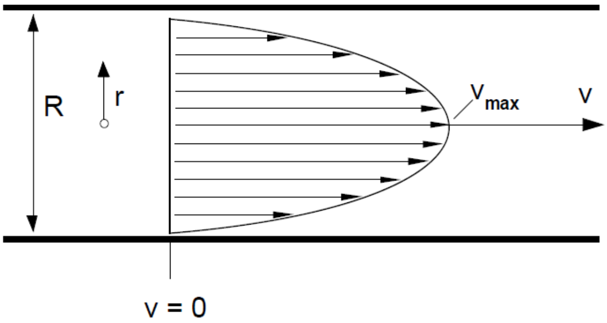


Figure 2.1: Velocity profile with laminar tube flow

Capillary viscometer was chosen for this study. The Ubbelohde viscometer used in this work will be explained in later sections

2.1.4.1 Theory of capillary viscometers

The calculation of viscosity from the data measured using glass capillary viscometer is based on Hagen-Poiseuille’s equation of a Newtonian fluid (Tushar et al, 2007).

In cylindrical coordinates,

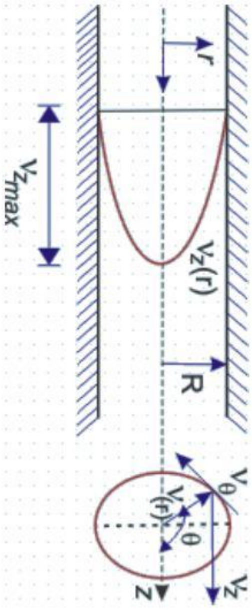


Figure 2.2: Hagen-Poiseuille flow through a vertical pipe

If z-axis is taken as the axis of the tube along which all the fluid particle travels and considering rotational symmetry to make the flow two-dimensional axi symmetry, then;

$$v_z \neq 0, \qquad v_r = 0, \qquad v_\theta = 0 \tag{2.6}$$

From continuity equation;

$$\frac{\partial v_r}{\underbrace{\partial_r}_{0}} + \frac{v_r}{\underbrace{r}_{0}} + \frac{\partial v_z}{\partial z} = 0 \tag{2.7}$$

For rotational symmetry,

$$\frac{1}{r}\frac{\partial v_\theta}{\partial \theta} = 0; \quad v_z = v_z\,(r, t) \quad or \quad \frac{\partial}{\partial \theta}(any\ quantity) = 0 \tag{2.8}$$

Inserting equations 2.6, 2.7 and 2.8 into the Navier Stoke's Equation in cylindrical coordinates (z-direction) it can be obtained;

$$\frac{\partial v_z}{\partial t} = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial z} + v\left(\frac{\partial^3 v_z}{\partial r^3} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right) \; in\; z\; direction \tag{2.9}$$

For steady flow the equation becomes

$$\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r} = \frac{1}{\mu}\frac{\partial p}{\partial z} \tag{2.10}$$

Solving the differential equation 2.10 with boundary conditions

$$r = 0\,;\; v_z\; is\; finite \tag{2.11}$$

$$r = R\,;\; v_z = 0 \tag{2.12}$$

Yields

$$v_z = \frac{R^3}{4\mu}\left(-\frac{\partial p}{\partial z}\right)\left(1 - \frac{r^3}{R^3}\right) \tag{2.13}$$

While

$$-\frac{\partial p}{\partial z} = \frac{\Delta p}{L} \tag{2.14}$$

The volume flow rate discharge is given by

$$Q = \int_0^R 2\pi v_z r dr \tag{2.15}$$

Inserting 2.13 and 2.14 into 2.15, we obtain

$$Q = \pi \frac{R^3}{8\mu}\left(\frac{\Delta p}{L}\right) \qquad (2.16)$$

Also

$$Q = \frac{V}{t} \qquad (2.17)$$

Q is overall flow rate, V is volume and t is time.

$$v = \frac{\mu}{\rho} \qquad (2.18)$$

$$\Delta p = \rho g h \quad \text{as in Pressure} - \text{Height relationship} \qquad (2.19)$$

Then,

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

K, calibration constant for viscometer

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

Then,

$$v = Kt \qquad (2.22)$$

Equation 2.22 is similar to ASTM kinematic viscosity equation (ASTM D 446-07) with an exception of the correction factor.

$$v = \frac{10\pi g D^4 H t}{138LV} - \frac{E}{t^3} \qquad (2.23)$$

Where E is the correction factor.

2.1.4.2 Types of capillary viscometers

The list and specification of different types of capillary viscometers are given in Appendix 2. The Ubbelohde viscometer used in this work will be explained in details in later sections.

2.2 Density of Fuel

Fuel qualification is also affected by density. Kinematic viscosity of biodiesel and engine efficiency connected also to density parameter. Percentage of fatty acid compounds affects the value of the density. Measurement of the density made according to ASTM D941-88 (Appendix 3) or EN ISO 12185.

2.3 Cold Flow Properties of Biodiesel

Liquidity of biodiesel at low temperatures can be explained by the cold flow properties are properties of biodiesel. Generally, fuels have ignition troubles at low temperatures, because of the deterioration of the fuelss flow attributes at low temperatures. Cold flow properties can be divided into three which are the cloud point (CP), the pour point (PP) and cold filter plugging point (CFPP). Petroleum diesel fuel have lower CP, PP and CFPP than traditional B10 blends.

2.3.1 Cloud point

Temperature when wax crystals appear firstly is defined as cloud point. At this phase, the fuel forms a cloudy appearance. When we compare biodiesel and petro-diesel, petro-diesel has lower cloud point than biodiesel. ASTM D2500 standard (Appendix 4) is the reference for cloud point measurement.

2.3.2 Pour point

Temperature which fuel becomes partly stiff and loses its flow characteristics is defined as pour point. In some sources, pour point can describes as the minimum temperature which a vehicle can run. At this stage biodiesel fuel comprises so much collected crystals that it is in fact a gel and can’t flow anymore. It is know that the Pour Point is always lower than the cloud point. When we compare biodiesel and petro-diesel, biodiesel has higher pour point than petro-diesel. The PP measurement was made according to ASTM Standard D97-05 (Appendix 5).

2.3.3 Cold filter plugging point

Lowest temperature which a type of fuel with a specific volume passes through a uniform filter instrument within a certain time when cooled under precise conditions. Since CFPP experiment utilize rapid cooling conditions, it can’t be the visualization of the exact limit of temperature which fuel can operate. The CFPP measurement was made according to ASTM Standard D6371-05 (Appendix 6).

2.4 Some Other Important Properties of Biodiesel

Acid number

The acid number (AN) is the mass of potassium hydroxide (KOH) in milligrams that is necessary to neutralize the acidic constituents per gram of a sample. Profit-making biodiesel consists of fatty acid methyl esters (FAMEs). It may also contain small amounts fatty acids, which are quantified by an acid number, expressed as milligrams of potassium hydroxide required to neutralize 1 g of sample. ASTM D 664-04 (Appendix 7) is the standard reference method for measuring the acid number of biodiesel.

Calorific value

Calorific value or heat of combustion is the amount of heat transferred to the chamber during combustion. This value indicates the energy available in the fuel (Klopfenstein, 1985), (Krisnangkura et al., 1986). Biodiesel has a calorific value which is about 12% lower than diesel, showing that biodiesel has lower energy content compared to diesel. This leads to a higher utilization of biodiesel in order to achieve yield of diesel in the engine (Lin et al., 2011).

Cetane number

Cetane number (CN) illustrates the ignition quality of fuels for compression ignition engines (CIE). Since the CIE burning of the fuel-air mixture is launched by compression ignition of the fuel, the cetane number is a key indicator of fuel quality as it describes the facilitate of its self-ignition. Cetane number is needed for ignition and operability. EN

15195 and D 613 are the standard reference methods for measuring the cetane number biodiesel.

Flash point

The minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel will flash on application of an ignition source under specified conditions is known as the flash point. The flash point does not affect the combustion directly. However, higher values indicate safer fuels with regards to storage, fuel handling and transportation. ASTM D 93 is the standard reference method for measuring the flash point of biodiesel.

Iodine value

The iodine value (IV) or iodine number was introduced in biodiesel quality standards for evaluating their stability to oxidation. The IV is a measurement of total unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample, during addition of iodine to the double bonds. When in contact with air, biodiesel with high IV is easily oxidized. EN 14111 is the standard reference method for measuring the iodine value of biodiesel.

Oxidation stability

A disadvantage of biodiesel is poor oxidation stability. Oxidation can result in acidity and increasing viscosity due to formation of insoluble gums that can plug fuel filters (Gerpen, 2001).The poor oxidation stability of biodiesels make them unsuitable for use in engines due to the damaging effects of oxidation products on the engines of vehicles. EN15751:2014 (Appendix 8) is the standard reference method for measuring the oxidation of biodiesel.

Sulfated ash

Sulfated ash is a measure of ash formed from inorganic metallic compounds. Requirement for sulfated ash is crucial to limit the amount of potassium, sodium, magnesium, and calcium in the finished biodiesel fuel. These metals can contribute to injector, fuel pump, piston and ring wear, engine deposits, and filter plugging. These impurities may be the result of the process chemicals used in biodiesel production. ASTM D 874, ISO 3987 are the standard reference methods for measuring the sulfated ash of biodiesel.

Water Content

Water content indicates the purity of the biodiesel. Once the biodiesel is washed, it should be dried to get the water specification below 500 ppm (0.050 %).Although the biodiesel is dried properly by the producer, water may still remainduring storage and transportation. The moisture formed in biodiesel leads to an increased free fatty acid concentration. This may result in corrosion on the metal parts of the engine.

2.5 Required Standards for Biodiesel

Biodiesel quality is the examined by inclusion of its physical and chemical properties into the necessities of the adequate standard. Standards of biodiesel are continually updated, owing to the changes of engines, emission standards, reevaluation of the qualification of raw materials used for the production of biodiesel, etc. The produced biodiesel must meet the international biodiesel standard specifications. The standards provide manufacturers to determine how the fuel will affect the performance and lifespan of their products. These specifications include The American Society for Testing and Materials or the European Union standards and some other standards in the world such as (DIN 51606) in Germany, (CSN) in Czech Republic, (ON) in Austria and etc. Table 2.2 introduces some of the biodiesel quality standards in the world which are mostly used. In this work, the ASTM D 445-09 is used for kinematic viscosity, ASTM D 941-8 for density, ASTM D 2500-09 for cloud point and ASTM D 97-05 for pour point.

Table 2.2: Biodiesel quality standards (Brabás, 2011)

Standards	**Place**	**Caption**
EN 14213	EU	Heating fuels - FAME - Requirements and test methods
EN 14214	EU	EN 14214 Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods
ASTM D 6751	U.S	ASTM D6751 - 11a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
	Australia	Fuel Standard (Biodiesel) Determination 2003
ANP42	Brazil	Brazilian Biodiesel Standard
IS15607	India	Bio-diesel (B 100) blend stock for diesel fuel - Specification
JASO M360	Japan	Automotive fuel - Fatty acid methyl ester (FAME) as blend stock
SANS 1925	South Africa	Automotive biodiesel fuel

CHAPTER 3

MATERIALS AND METHODS

3.1 Biodiesel Sample

A biodiesel sample produced from waste frying oils by the Ambrosia Oils Ltd. used in this experimental study. Table 3.1 illustrates the property values for biodiesel sample according to some standards when it was produced.

Table 3.1: Biodiesel sample properties

NAME	METHOD	UNIT	SPECS		RESULT
			MİN	MAX	
FAME content	EN 14103	mass %	96.5		> 99.5
Density at 15°C	ISO 12185	kg/m^3	860.0	900.0	878.4
Kinematic Viscosity at 40°C	EN ISO 3104	mm^2/s	3.500	5.000	4.483
Flash point (rapid equilibrium)	ISO 3679	°C	101		> 140
Cetane Number	EN 15195	-	51.0		59.7
Copper Corrosion (3 hrs/50°C)	EN ISO 2160	-		Class 1	1A
Oxidation Stability (110°C)	EN 14112	hours	8.0		> 11
Acid Number	EN 14104	mg KOH/g		0.50	0.31
Iodine value	EN 14111	gI2/100g		120	74
Linolenic acid methyl ester	EN 14103	mass %		12.0	2.6
Polyunsaturated methyl esters (>=4 double bounds)	EN 15779	mass %		1.0	< 0.10
Methanol	EN 14110	mass %		0.20	0.02
Glyceride Content	EN 14105				
Mono-glyceride		mass %		0.70	0.21
Di-glyceride		mass %		0.20	0.02
Tri-glyceride		mass %		0.20	< 0.03
Free glycerol		mass %		0.02	< 0.010
Total glycerol		mass %		0.25	0.065
Water Karl Fischer	EN ISO 12937	mg/kg		300	160
Contamination	EN 12662-98	mg/kg		24	< 6
Sulphated ash	ISO 3987	mass %		0.02	< 0.005

Table 3.1: Continued

Sulphur (S)	EN ISO 20846	mg/kg	10.0	9.8
Group I metals (Na+K)	EN 14538	mg/kg	5.0	< 2.0
Group II metals (Ca+Mg)	EN 14538	mg/kg	5.0	< 2.0
Phosphorus content	EN 14107	mg/kg	4.0	< 4
Cold Filter Plugging Point	EN 116	°C	+5	+5
Melting Point of organic chemicals	ISO 6321	°C		+10
Kinematic Viscosity at 20°C	ASTM D 445	mm^2/s		7.2

3.2 Experimental Set-Up and Methods

The biodiesel sample was analyzed to determine their viscosity, density, oxidation stability, total acid number and cold flow properties. We want to observe the properties of the biodiesel sample as if it was held up in a furnace kept at a constant temperature at 40 °C as shown in the Figure 3.1. That furnace was designed from an old dish washer machine. Temperature in the furnace was controlled by a digital calibrated thermometer. Thus it is able to hold biodiesel samples at a constant temperature. When the thermocouple of thermometer inside the furnace gauge the ambience temperature lower than 40 °C, it gives signal to the relay to open the circuit and lamps turn on, as a result heating the ambience. When the temperature reaches 40 °C, relay cuts of the circuit so lamps turn off as shown in Figure 3.2.

The effect of temperature on the biodiesel properties including kinematic viscosity and density was tested within the temperature range of 5°C to 20°C and 30°C to 90°C. Cold flow properties were also measured. Total acid number and oxidation stability was analyzed by a petrochemical laboratory.

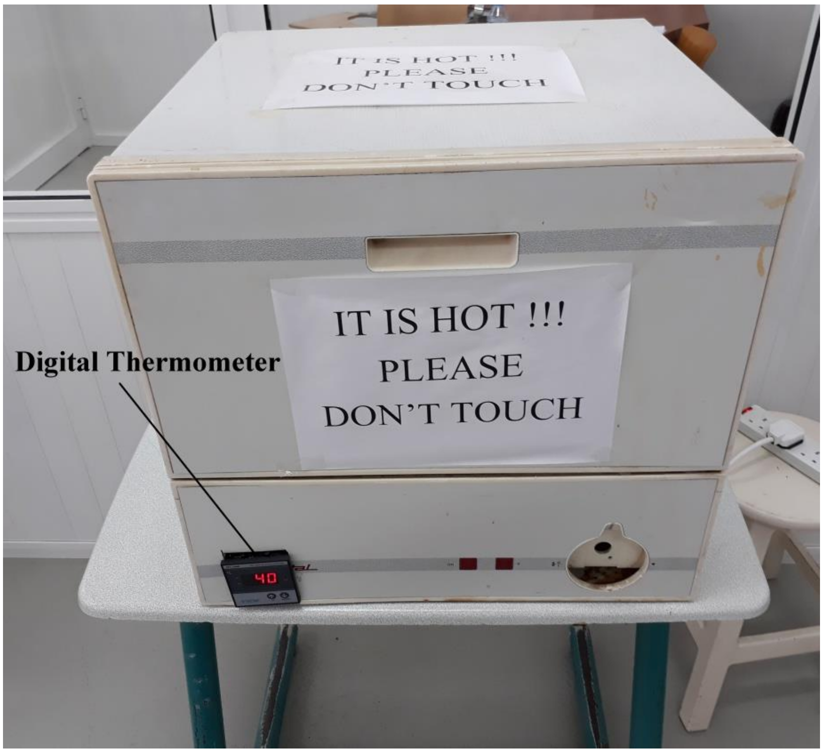


Figure 3.1: Constant temperature furnace controlled by digital thermomer

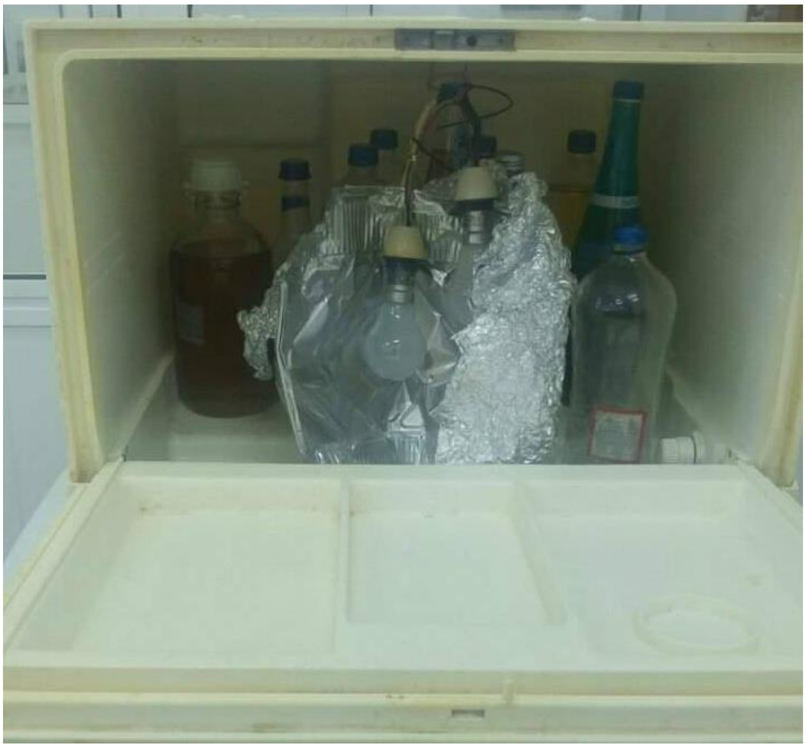


Figure 3.2: Constant temperature furnace

3.2.1 Kinematic viscosity

An Ubbelohde type viscometer (Figure 3.3) is an instrument that uses a capillary based method of measuring viscosity and it is recommended for higher viscosity cellulosic polymer solutions. The advantage of this type of viscometer is that the values obtained are independent of the total volume. The device was developed by the German chemist Leo Ubbelohde (1877-1964) (Viswanath, 2007).

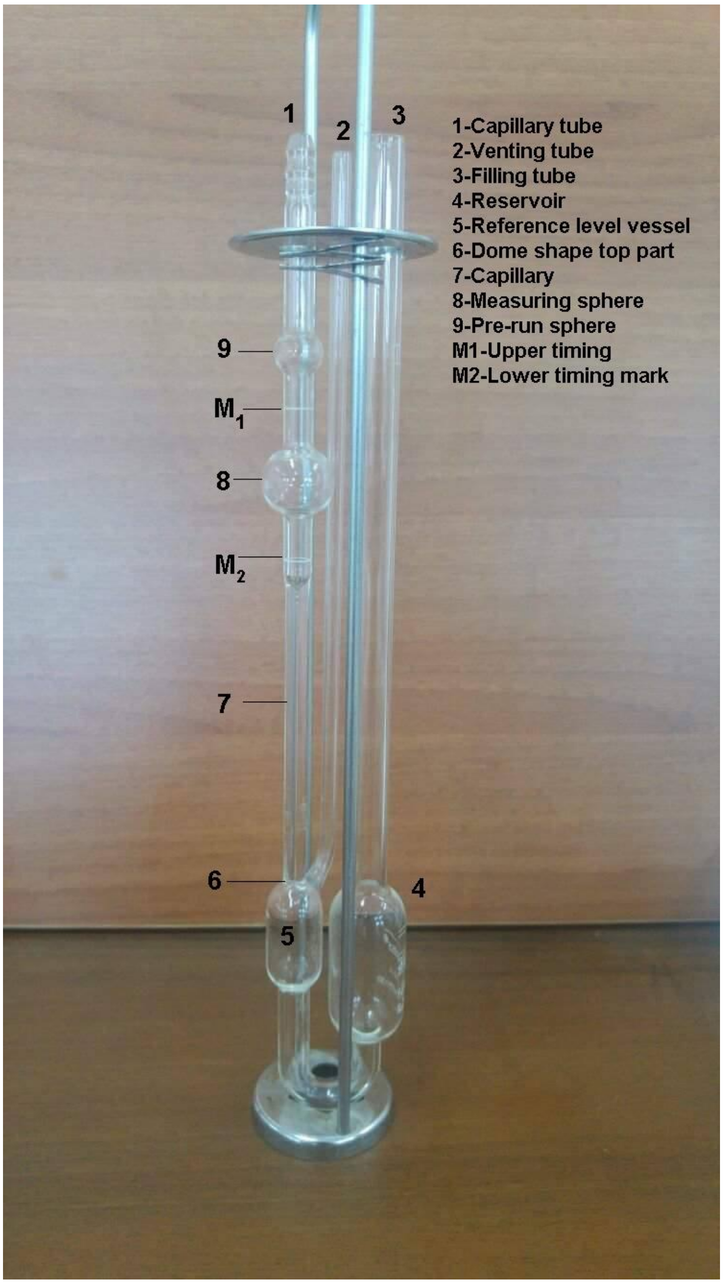


Figure 3.3: Ubbelohde viscometer

The Ubbelohde viscometer as shown in Figure 3.3 is closely related to the Ostwald viscometer. Both are U-shaped pieces of glassware with a reservoir on one side and a measuring bulb with a capillary on the other. A liquid is introduced into the reservoir then sucked through the capillary and measuring bulb. The liquid is allowed to travel back through the measuring bulb and the time it takes for the liquid to pass through two calibrated marks is a measure for viscosity. The Ubbelohde device has a third arm extending from the end of the capillary and open to the atmosphere. In this way the pressure head only depends on a fixed height and no longer on the total volume of liquid.
The ubbelohde viscometer was chosen because of its wide range of using application and accuracy. It enables transparent and high temperature measurement. According to their kinematic viscosity range, three viscometer of size 0c, I and Ic were chosen in this work for measuring kinematic viscosity. They were calibrated by the manufacturer. Appendix 8 shows the manufacturer's certificate for these viscometers.

The ubbelohde viscometer constant, K, [(mm^2/s)/s] was determined with the Table 3.2 given by the manufacturer company.

Table 3.2: Ubbelohde viscometer technical specifications

Capillary No.	**Capillary Dia. I ± 0.01[mm]**	**Constant , K, (mm^2/s)/s**	**Measuring range [mm^2/s]**
0c	0.36	0.002856	0.6 ……… 3
I	0.58	0.009820	2 ………10
Ic	0.78	0.02944	6 ………30

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

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

Where ν, K, t, and y represent the kinematic viscosity, the calibration constant, measured time of flow and kinetic energy correction, respectively. In the experiment formula in the Equation 3.1 was used to obtain the kinematic viscosity values. The kinetic energy correction y is given by the manufacturer and tabulated for each viscometer in term of flow time as shown in Table 3.3 below.

Table 3.3: 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 (s)	**0**	**0c**	**0a**	**I**	**Ic**	**Ia**	**1**
40	-^{B}	-^{B}	-^{B}	1.03	0.45	0.15	
50	-^{B}	-^{B}	-^{B}	3.96	0.66	0.29	0.10
60	-^{B}	-^{B}	-^{B}	2.75	0.46	0.20	0.07
70	-^{B}	-^{B}	-^{B}	2.02	0.34	0.15	0.05
80	-^{B}	-^{B}	4.78^{B}	1.55	0.26	0.11	0.04
90	-^{B}	-^{B}	3.78^{B}	1.22	0.20	0.09	0.03
100	-^{B}	7.07^{B}	3.06^{B}	0.99	0.17	0.07	0.02
110	-^{B}	5.84^{B}	2.53	0.82	0.14	0.06	0.02
120	-^{B}	4.91^{B}	2.13	0.69	0.12	0.05	0.02
130	-^{B}	4.18^{B}	1.81	0.59	0.10	0.04	0.01
140	-^{B}	3.61^{B}	1.56	0.51	0.08	0.04	0.01
150	-^{B}	3.14^{B}	1.36	0.44	0.07	0.03	0.01
160	-^{B}	2.76	1.20	0.39	0.06	0.03	0.01
170	-^{B}	2.45	1.06	0.34	0.06	0.02	0.01
180	-^{B}	2.18	0.94	0.30	0.05	0.02	0.01
190	-^{B}	1.96	0.85	0.28	0.05	0.02	0.01
200	10.33^{B}	1.77	0.77	0.25	0.04	0.02	0.01
225	8.20	1.40	0.60	0.20	0.03	0.01	0.01
250	6.64	1.13	0.49	0.16	0.03	0.01	<0.01
275	5.47	0.93	0.40	0.13	0.02	0.01	<0.01
300	4.61	0.79	0.34	0.11	0.02	0.01	<0.01
325	3.90	0.66	0.29	0.09	0.02	0.01	

Table 3.3: Continued

Flow	**Capillary no**						
Time (s)	**0**	**0c**	**0a**	**I**	**Ic**	**Ia**	**1**
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		
800	0.65	0.11	0.05				
850	0.57	0.10	0.04				
900	0.51	0.09	0.04				
950	0.46	0.08	0.03				
1000	0.42	0.07	0.03				

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

[B] For precision measurement, these flow times should not be applied. Selection of a viscometer with a smaller capillary diameter is suggested

3.2.1.1 Procedure of measuring the kinematic viscosity using Ubbelohde viscometer

As already mentioned before, kinematic viscosity was measured using the capillary viscometer named as Ubbelohde viscometer. Figure 3.4 summarizes the measuring procedure of kinematic viscosity using Ubbelohde viscometer.

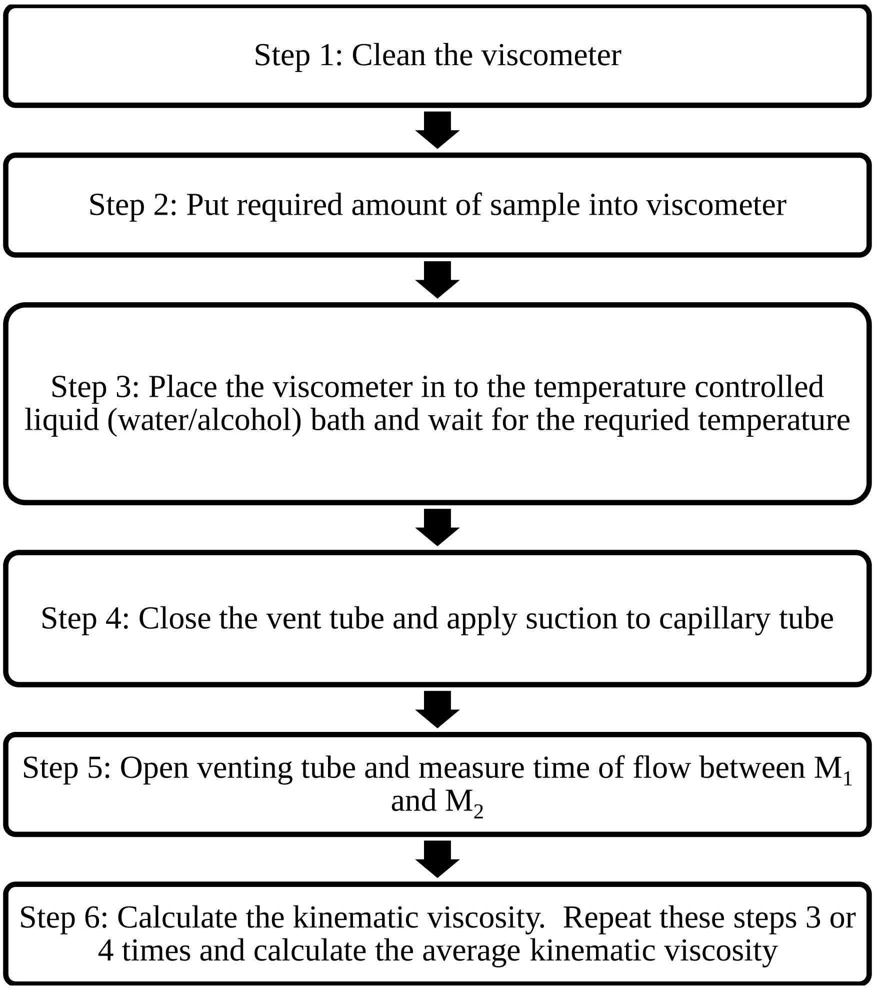

Step 1: Clean the viscometer
Step 2: Put required amount of sample into viscometer
Step 3: Place the viscometer in to the temperature controlled liquid (water/alcohol) bath and wait for the requried temperature
Step 4: Close the vent tube and apply suction to capillary tube
Step 5: Open venting tube and measure time of flow between M_1 and M_2
Step 6: Calculate the kinematic viscosity. Repeat these steps 3 or 4 times and calculate the average kinematic viscosity

Figure 3.4: Flow chart for measuring procedure of kinematic viscosity using Ubbelohde viscometer

Step One

Clean the viscometer with the cleaning material. Cleaning material must be with the right proportions. (%70 distilled water, %15 hydrogen peroxide, %15 muriatic acid). Then apply acetone to finish the cleaning process. To start the experiment process, capillary tube must be dry.

Step Two

Fill the viscometer with sufficient quantity of biodiesel. Be sure that biodiesel is between the two lines on the tube so that the amount of liquid charged will not obstruct the air tube during use.

Step Three

Place the viscometer in a temperature controlled liquid bath. Here, the capillary must be vertical. The sample liquid must come to the same temperature in the bath, and this will take about 20 minutes.

Step Four

Next, seal off venting tube and apply gently suction to the capillary tube with the suction instrument which is shown in Figure 3.4. Apply suction to the capillary tube until the liquid reaches about 5 mm above the upper timing mark. Hold the liquid at this level by venting tube. Make sure that this point is at least 2 cm below the bath liquid level.

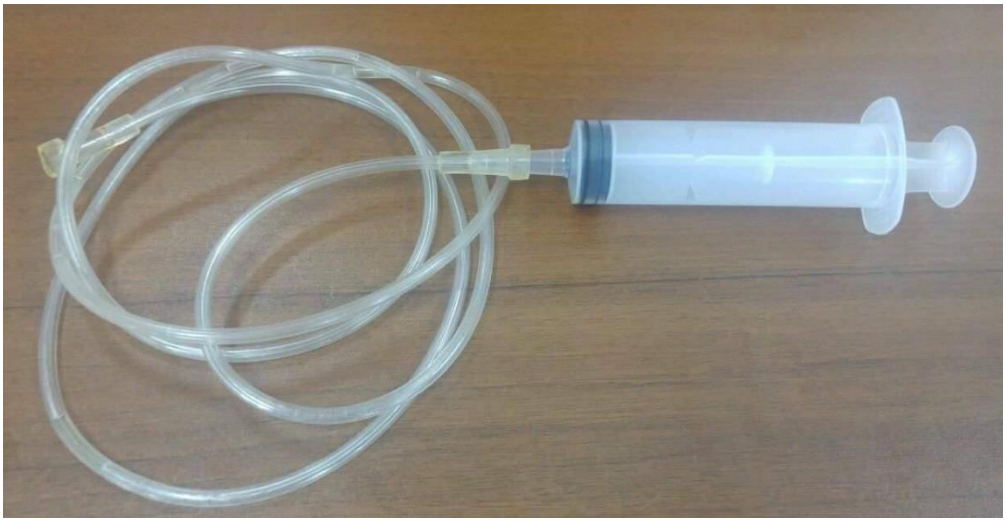


Figure 3.5: Suction instrument

Step five

Next, release the timing tube and allow the liquid to flow. Measure the flow time in seconds for the bottom of the meniscus to pass from the top edge of the top Mark Line to the top edge of the Mark Line below it. The time it takes for the liquid to pass through the two calibrated marks is a measure for the viscosity.

Step six

Calculate the kinematic viscosity of the sample using formula in equation 3.1. Repeat processes 3 or 4 times. Take average of the measurements and pass to the next measurement with a different temperature value.

3.2.1.2 Kinematic viscosity setup between 30˚C to 90˚C

Figure 3.6 shows experimental setup and its components used to measure the viscosity of a biodiesel samples in the temperature range 30˚C - 90˚C. As described above, we are applying a procedure for using Ubbelohde viscometer.

Components of the setup kinematic viscosity setup between 30˚C to 90˚C

1- Thermometer
2- Capillary Holder
3- Heat Resistant Beaker Thermometer
4- Water
5- Capillary viscometer
6- Biodiesel Sample
7- Electromagnetic hot plate

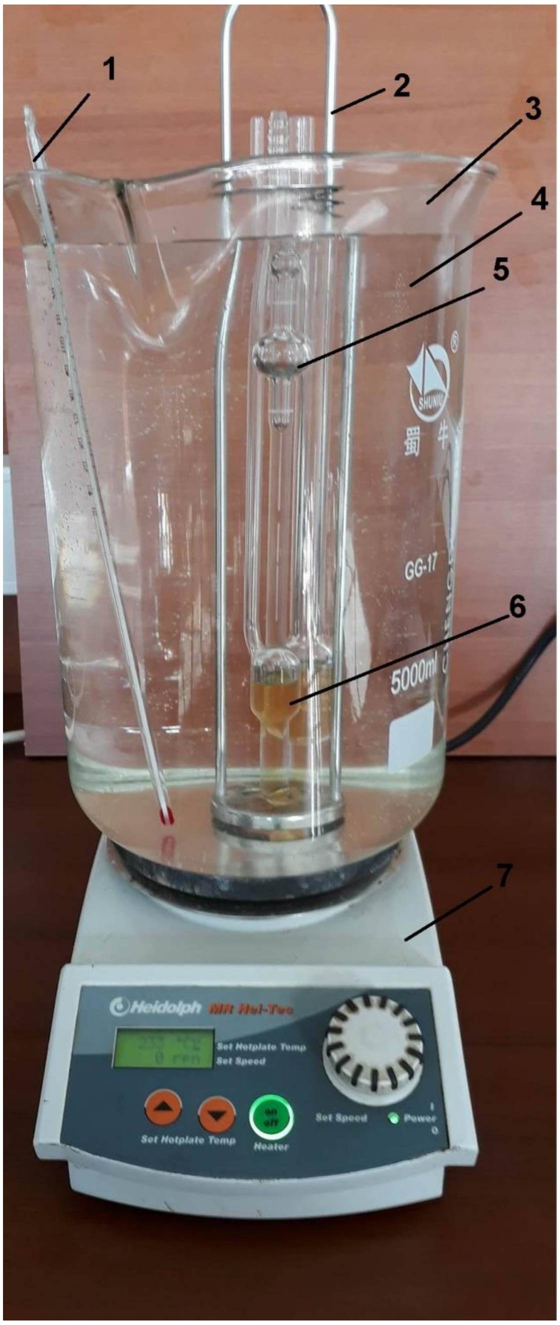


Figure 3.6: Experimental setup used to measure the viscosity of a biodiesel sample in the temperature range 30˚C - 90˚C

Water (4) in a heat resistant standard beaker (2) is used as fluid bath. The capillary viscometer (5) is placed in its holder (2) which holds it in an upright position in the water bath. The water bath is heated by an electromagnetic plate (7) and its temperature is controlled by a standard thermometer (1).

3.2.1.3 Kinematic viscosity setup between 5˚C to 20˚C

Figure 3.7 shows experimental setup used to measure the viscosity of a biodiesel samples in the temperature range 8˚C to 20˚C. The water is freezing by 0°C but pure alcohol will not be frozen up to -114°C. Thus, alcohol (ethanol) was used as a cooling bath liquid. The purity of alcohol that used as bath liquid was 97% and purchased from a local alcohol factory in Cyprus. We are applying the same procedure for measuring the kinematic viscosity with the Ubbelohde viscometer in the cooling bath as shown in Figure 3.7.

Components of the setup kinematic viscosity setup between 5˚C to 20˚C

1- Cooling bath reservoir
2- Capillary viscometer with holder
3- Alcohol (ethanol)
4- Coil
5- Insulator (Styrofoam)
6- Radiator
7- Thermostat
8- Compressor

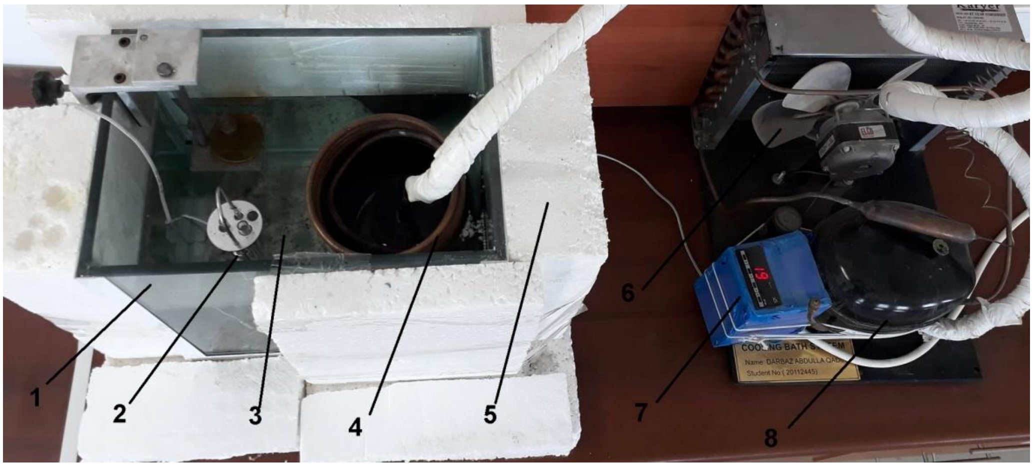


Figure 3.7: Experimental setup used to measure the viscosity of a biodiesel sample in the temperature range 5˚C-20˚C

Alcohol (ethanol) (3) in a cooling bath reservoir (1) is used as a fluid bath. The bath temperature was controlled using a thermostat (7), by automatically starting up and shutting down the compressor (8). A coil (4) connected to a compressor cools down the liquid bath, and the compressor is cooled down by a radiator (6). The cooling bath was insulated by thick Styrofoam layer (5).

3.2.2 Density

Density of biodiesel was measured with a device called Pycnometer which is a device used to determine the density of a liquid. A pycnometer is usually made of glass, with a close-fitting ground glass stopper with a capillary tube through it, so that air bubbles and the excess fluid may escape from the apparatus. This device enables a liquid's density to be measured accurately by reference to an appropriate working fluid, such as water, using an electronicall. The density value of the biodiesel sample was measured for temperatures between 5°C to 20^{0}C and 30^{0}C to 90^{0}C. For the measurement result, we subtract the empty pycnometer mass [g] from pycnometer mass [g] filled with biodiesel. We divide that value with the volume of the pycnometer [ml] to obtain the density of biodiesel sample in kg/m^3 as given in Equation (3.2)

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

3.2.2.1 Procedure for measuring density with a pycnometer

Before starting the measurement procedure, the volume of the pycnometer is determined by filling it with water, as the density of water already known temperature. Figure 3.8 summarizes the measuring procedure of density using a pycnometer. By following the steps, the density measurement will be finalized successfully.

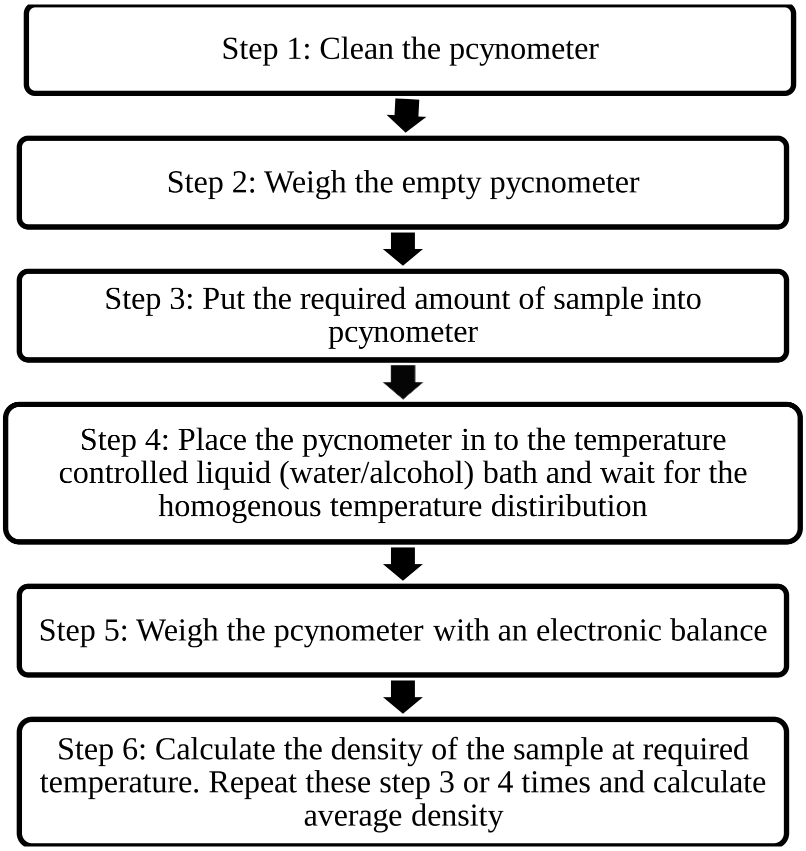

Step 1: Clean the pcynometer
Step 2: Weigh the empty pycnometer
Step 3: Put the required amount of sample into pcynometer
Step 4: Place the pycnometer in to the temperature controlled liquid (water/alcohol) bath and wait for the homogenous temperature distiribution
Step 5: Weigh the pcynometer with an electronic balance
Step 6: Calculate the density of the sample at required temperature. Repeat these step 3 or 4 times and calculate average density

Figure 3.8: Flow chart of procedure for measuring density using pycnometer

Step 1

Clean the pycnometer with the cleaning material. Cleaning material must be with the right proportions. (%70 distilled water, %15 hydrogen peroxide, %15 muriatic acid). Then apply acetone to finish the cleaning process. To start the experiment process, pycnometer must be dry.

Step 2

Weigh the empty pycnometer with an electronic balance before filling it with sample as shown in Figure 3.9. To use the Equation 3.2, empty mass of the pycnometer is needed.

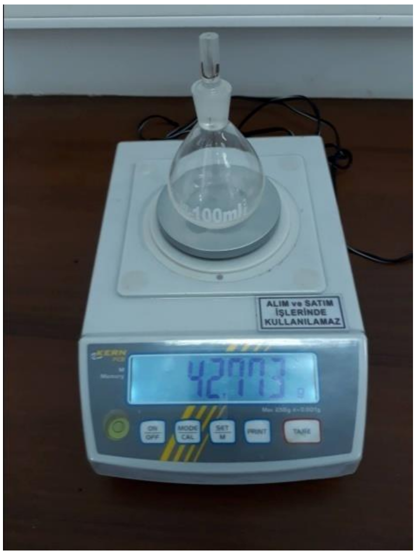


Figure 3.9: Pycnometer weigh

Step 3

Completely fill the pycnometer with biodiesel. Excess biodiesel and air gaps will overflow from the pycnometer as shown in Figure 3.10.

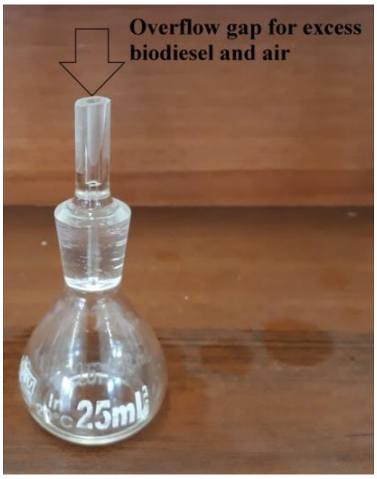


Figure 3.10: Overflow gap of pycnometer

Step 4

Placed the Pycnometer in heating bath (Figure 3.11) or cooling bath (Figure 3.12) and wait for the needed temperature. Wait at required temperature for 15 minutes minimum until the temperature becomes homogeneous in the beaker or cooling bath.

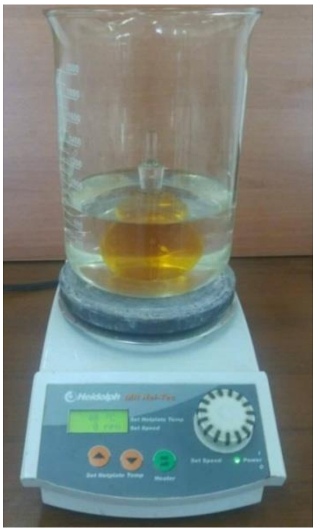


Figure 3.11: Experimental setup used to measure the density of a biodiesel sample in the temperature range 30˚C - 90˚C

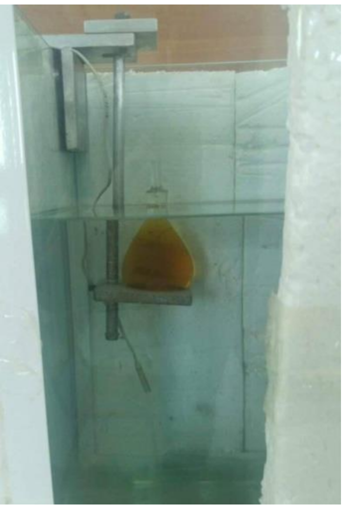


Figure 3.12: Experimental setup used to measure the density of a biodiesel sample in the temperature range 5˚C - 20˚C

Step 5

Weigh the full Pycnometer on an electronic balance as shown in Figure 3.13

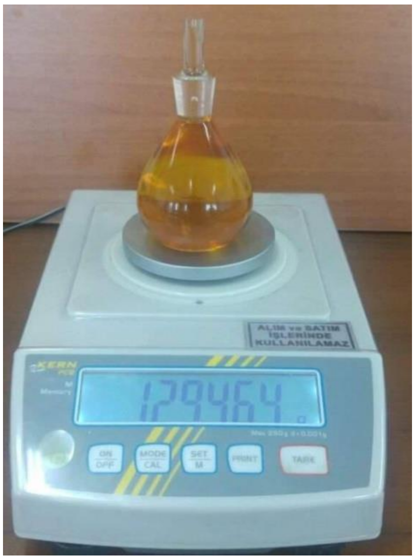


Figure 3.13: Pycnometer on an electronic balance

Step 6

Calculate the density of biodiesel at selected temperature using the Equation 3.2. Repeat these steps 3 or 4 times and calculate the average density value.

3.2.3 Cold Flow Properties

Experimental setup used for measuring the cold flow properties such as cloud point, cold filter plugging point and pour point is shown in Figure 3.14. The sample was tested as per American standard test method for cloud point, cold filter plugging point and pour point, ASTM D2500, ASTM D6371-05 and ASTM D97 respectively.

Main components of the setup

1- Data system
2- Cooling bath
3- Compressor system

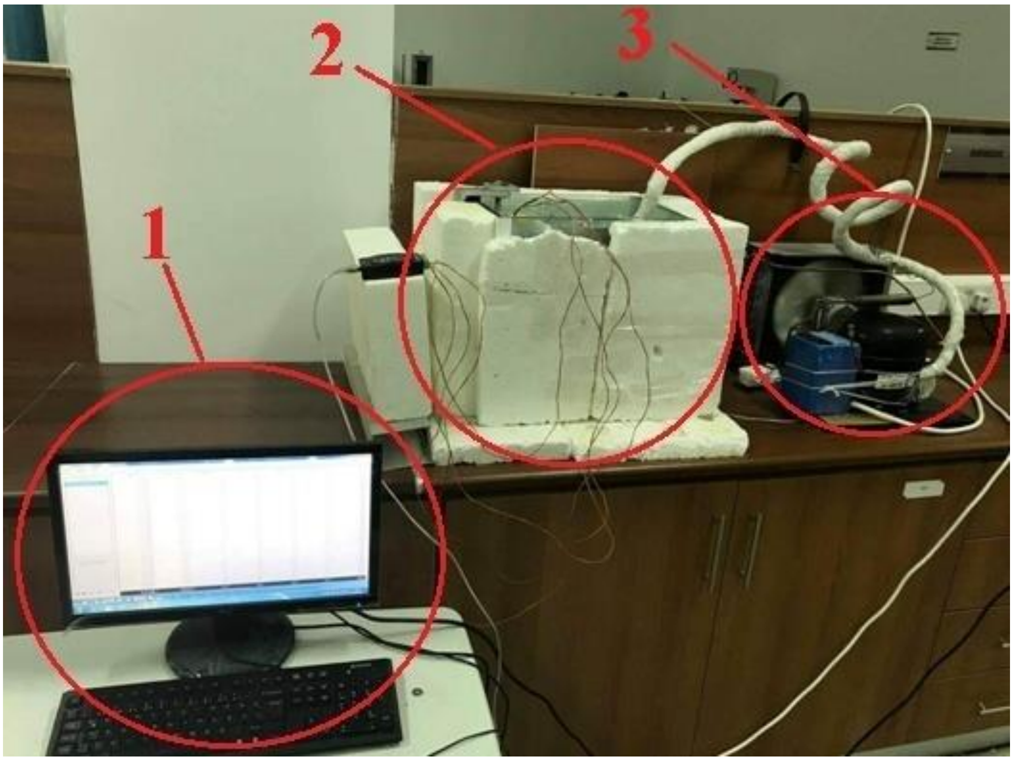


Figure 3.14: Cold flow properties measurement apparatus

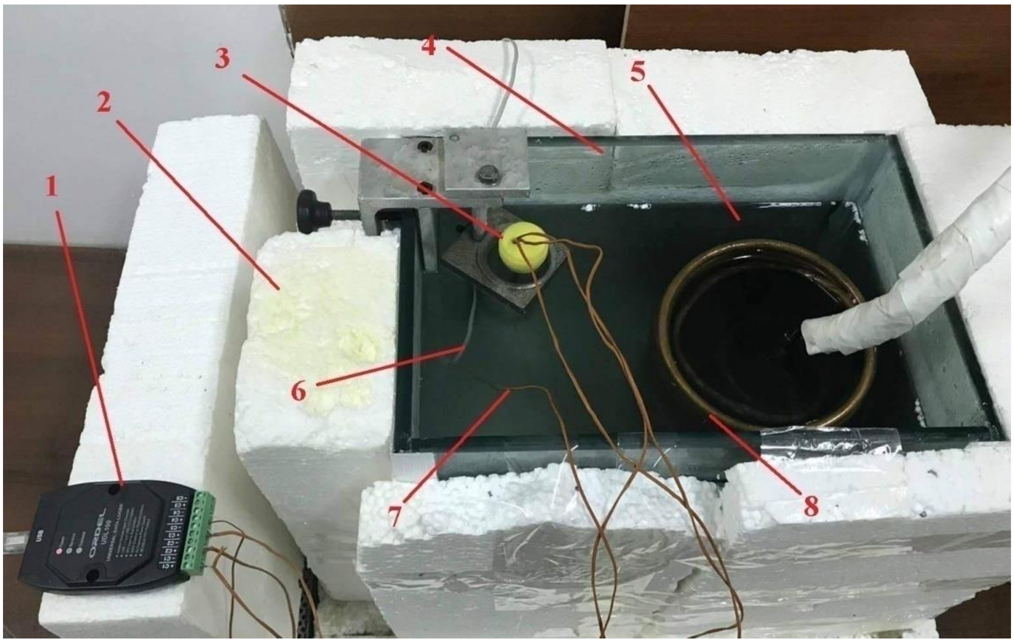


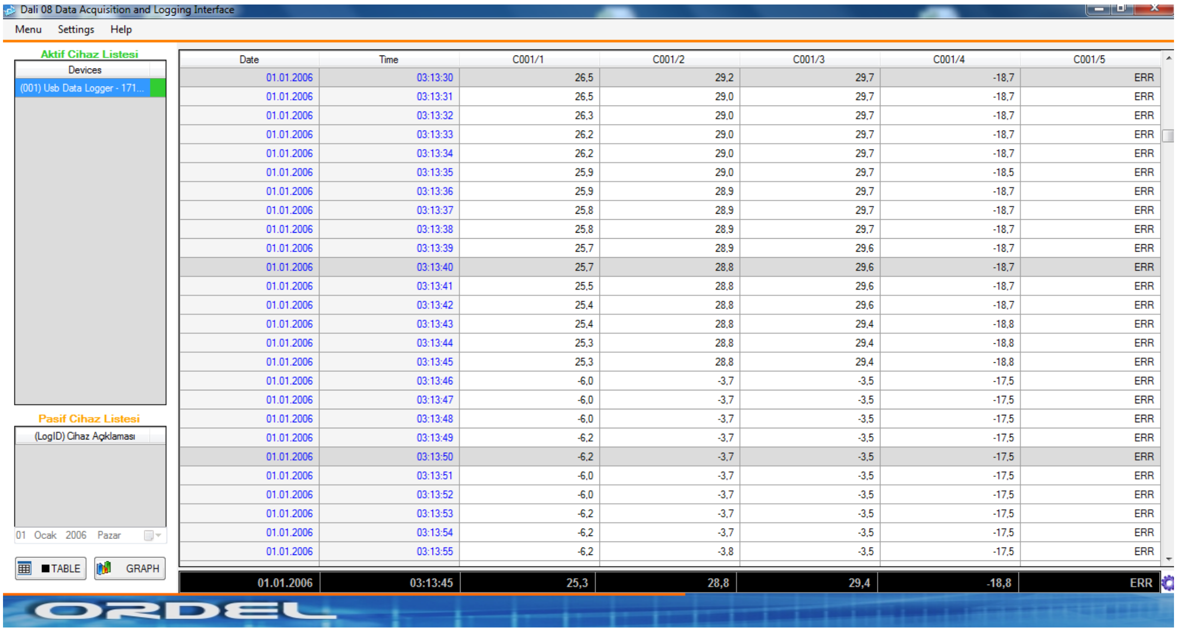
Figure 3.15: Particular components of cold flow properties measurement apparatus

Particular components of the setup

1- Data logger
2- Insulator (Styrofoam)
3- Glass of test jar
4- Cooling bath reservoir
5- Alcohol
6- Thermocouple of compressor system
7- Fourth thermocouple of data logger
8- Coil of compressor system

Alcohol (ethanol) (5) in a cooling bath reservoir (4) is used as a fluid bath. The bath temperature was controlled using a thermocouple (6) in the alcohol connected to a thermostat. Thermostat is automatically starting up and shutting down the compressor system. The cooling bath was insulated by thick Styrofoam layer (2).

Data logger (1) is a device that can be operated from the computer using a special software program (Figure 3.16) to save the data obtained from thermocouples.



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

Figure 3.16: Software program for data logger

Test sample is poured into the glass of test jar by amount of 45ml (3) shown in Figure 3.17.

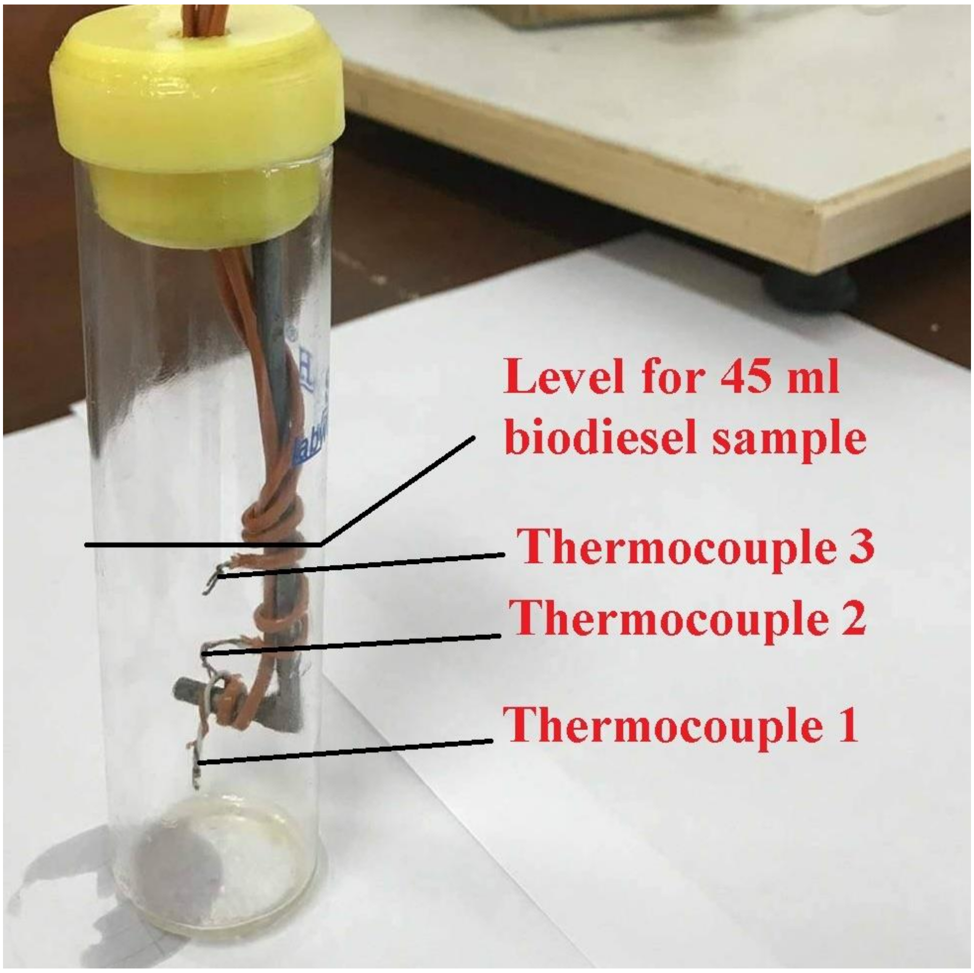


Figure 3.17: Glass of test jar with thermocouples

It is able to link five different thermocouples to the data logger. In this setup four thermocouples were placed at the bottom, middle, and upper layer of the glass test jar to measure the cloud point, cooling curve and the pour point respectively. Cold filter plugging point can be determined using the cooling curve. Fourth thermocouple (7) was placed in the alcohol bath to measure the temperature of the alcohol bath which is the same function with the compressor systems thermostat.

Cloud Point

As described in ASTM D 2500 (Appendix 4), the cloud point is determined by visually inspecting for a fog in the normally clear fuel, while the fuel is cooled under carefully controlled conditions. Also it can be analyzed from the cooling curve graph created with the readied data by the data logger.

Steps for measuring procedure of the cloud point

Step 1

By using the cooling bath set up in figure 3.13, alcohol was cooled down to -20˚C.

Step 2

Put required amount of biodiesel sample into the glass test jar (45ml).

Step 3

Place the glass test jar into aluminum cylinder which was immersed in the cooling bath.

Step 4

Place the thermocouple at the bottom of the glass test jar because temperature at the bottom of the jar is normally higher than the top.

Step 5

Record the temperature using thermocouple 1, named as cloud point, at which the fog appeared inspected at stepwise of 1˚C.

Pour Point

A second measure of the low temperature performance (cold flow property) of diesel/biodiesel fuels is the pour point. The pour point is the lowest temperature at which a fuel sample will flow. Therefore, the pour point provides an index of the lowest temperature of the fuel’s utility for certain applications. The standard procedure for measuring the pour point of fuels is ASTM D 97-05 (Appendix 5) as mentioned in the previous chapter.

Steps for measuring procedure the poor point

Step 1

By using the cooling bath set up in figure 3.13, alcohol was cooled down to -20˚C.

Step 2

Put required amount of biodiesel sample into the glass test jar (45ml).

Step 3

Place the glass test jar into aluminum cylinder which was immersed in the cooling bath.

Step 4

Place the thermocouple which was placed was placed at the top layer of the sample.

Step 5

Record the temperature using thermocouple 3, named as pour point, at which the biodiesel samples is totally ceased to flow inspected at stepwise of 1˚C.

3.2.4 Acid number and oxidation stability

Acid number and oxidation stability was measured by a certificate laboratory at Greek side, Nortest Petrochemical laboratory according to test methods ASTM D664-04(2017) and EN15751:2014 respectively. One time measurement cost for both of the experiments was 72.5 euro with %50 discount for the students.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Accuracy for Kinematic Viscosity

Capillary viscometers (Oc, I and Ic) which are used in the experimental work were calibrated by the manufacturer company. In order to check the accuracy of the result values, an accuracy and repeatability test were accomplished. Pure water used as the basic kinematic viscosity standard. Kinematic viscosity value for pure water at 30˚C is given as 0.80908 mm^2/s in the literature (Streeter et al., 1998). With the same experimental conditions, the kinematic viscosity value of pure water at 30˚C was measured as 0.803 mm^2/s. The percent error of the result value was calculated to be less than 1% that means calibrations of the capillary viscometers are well done.

4.2 Kinematic Viscosity

Quite a lot of studies have shown that with an increase in biodiesel storage duration and temperature are associated with approval of biodiesel properties and quality of biodiesel. As a result of these studies, we know that the fatty acid methyl ester molecules are broken down during degradation process (storage duration) into fatty acid chains. Fatty acid chain oxidation accelerated by exposure to air during storage and at high temperature may yield polymerized compounds. Oxidation of sample can cause degradation of fuel quality by affecting the oxidation and thermal stability. Oxidation instability results with the formation of oxidation products alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel. Thermal instability cause rate of oxidation at higher temperature to increase which in turn, increases the weight of oil and fat due to the formation of insolubles. Thus due to the production of soluble polymeric material during degradation process, decreasing in fuel stability significantly and increased viscosity of the biodiesel sample [Leung, 2006; Kwancheraeon, 2007].

In brief we suppose to the effect storage duration of biodiesel to increase the viscosity. Table 4.1 provides the kinematic viscosity of biodiesel samples with respect to days. Experimental measurements were carried out for every ten days of storage period of 90 days. Although viscosity result values were increasing with the storage period, it has been noticed that kinematic viscosity of the sample at 40˚C temperature ensures the 1.9-6.0 mm^2/s range according to ASTM D6751 standard.

Table 4.1: Influence of storage period (days) on kinematic viscosity of biodiesel at 40˚C temperature

B100 Sample	
Day	**Viscosity at 40˚C [mm^2/s]**
0	4.545
10	4.581
20	4.618
30	4.630
40	4.667
50	4,704
60	4.729
70	4.770
80	4.779
90	4.792

At Figure 4.1, viscosity measurements are plotted at 40 ˚C since kinematic viscosities are given at 40 ˚C in international standards (ASTM). As a result of the expectation, we can observe also from Figure 4.1 that, there is a slight rising of viscosity as the storage period increases.

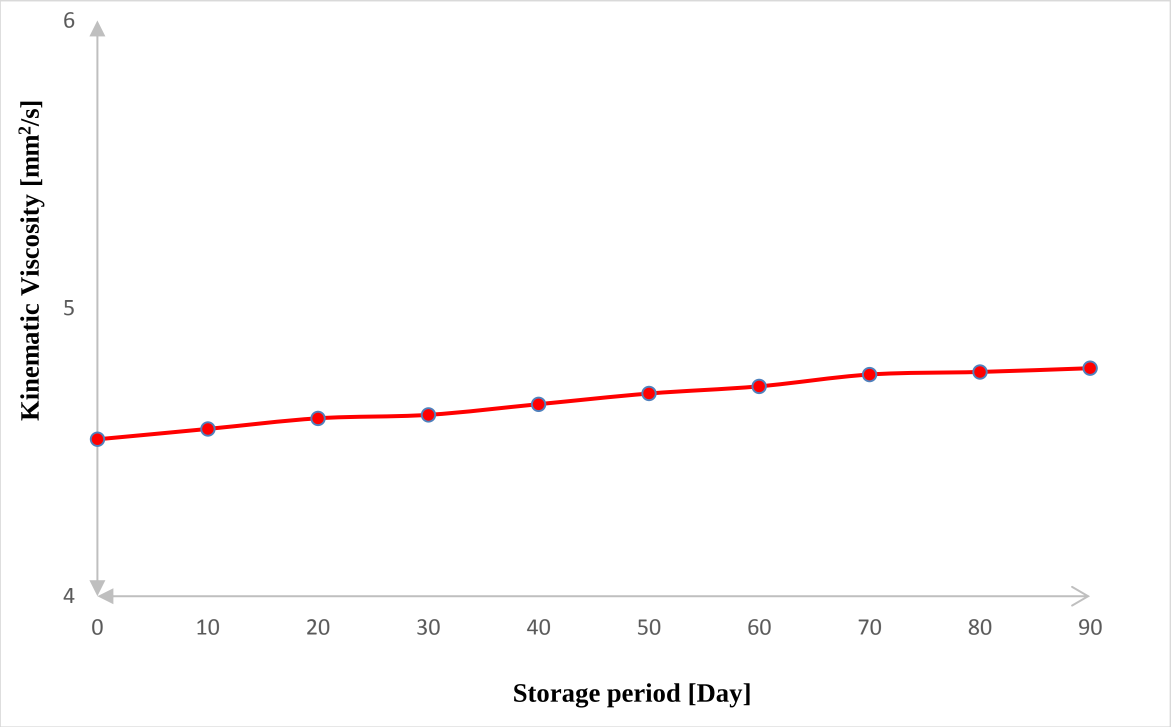


Figure 4.1: Kinematic viscosity-storage period relationship at 40˚C

In contrast with the storage period, kinematic viscosity decreases as the temperature increases. The gas viscosity will increase with temperature. According to the kinetic theory of gases, kinematic viscosity should be proportional to the square root of the absolute temperature, in practice, it increases more rapidly. In a liquid there will be molecular interchange similar to gas. In liquid form there are additional substantial attractive, cohesive forces between the molecules of a liquid. Both cohesion and molecular interchange contribute to liquid kinematic viscosity.

The former effect causes a decrease in the shear stress while the latter causes it to increase. That means that liquids show a decrease in kinematic viscosity value with rising up temperature.

Table 4.2 summarizes the kinematic viscosities measured at once every 4 weeks for a period of 12 weeks. Temperature range is between at 5 ˚C to 90 ˚C.

Table 4.2: Influence of storage period (days) and testing temperatures on kinematic viscosity of biodiesel

B100 Sample				
Temperature [˚C]	**Weeks**			
	0	**4**	**8**	**12**
5	13,52			
8	10,658	10.944	11.071	11.689
10	9.685	9.859	9.974	10.530
15	7.860	8.285	8.381	8.449
20	7.300	7.365	7.451	7.537
30	5.524	5.737	5.848	5.969
40	4.545	4.630	4.720	4.792
50	3.564	3.722	3.765	3.747
60	3.034	3.222	3.260	3.279
70	2.640	2.809	2.842	2.873
80	2.247	2.464	2.493	2.562
90	1.860	2.189	2.215	2.254

From Figure 4.2 it can be concluded that like similar to expectations, with the increasing temperature, kinematic viscosity is decreasing. Also kinematic viscosity is increasing over the storage period for each temperature slightly.

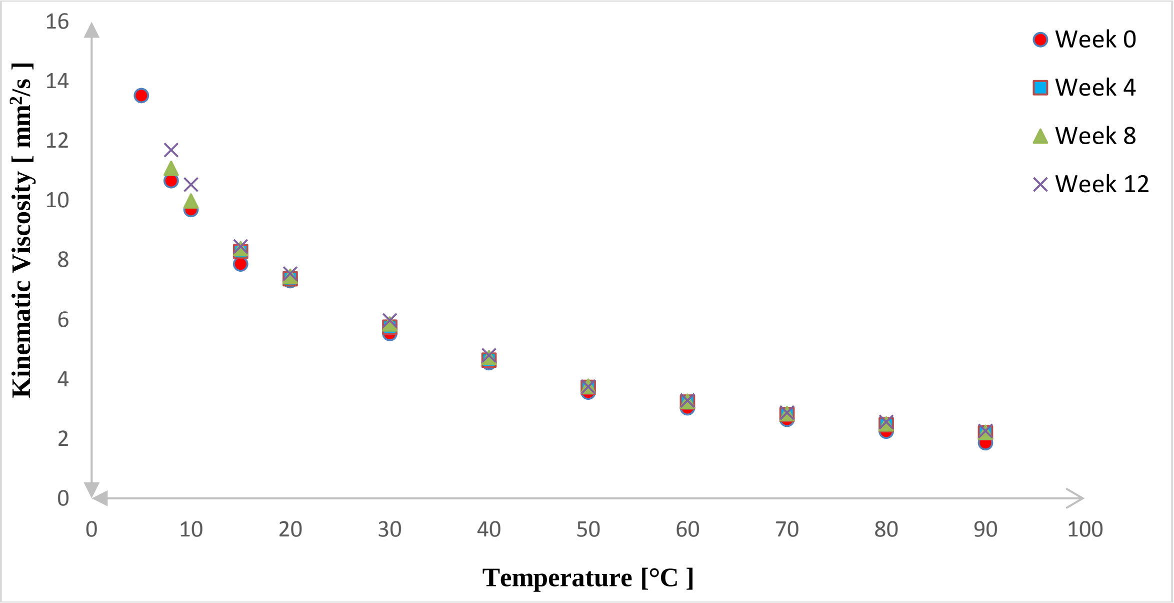


Figure 4.2: Kinematic viscosity-storage period-temperature relationship

4.3 Density

In the previous section 4.2, we discuss that an increase in storage period results with the oxidation and thermal instability. Oxidation stability results with the formation of oxidation products alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel. Thermal instability cause rate of oxidation at higher temperature to increase which in turn increases the weight of oil and fat due to the formation of insolubles. Biodiesel, because it's made from a vegetable or animal fat, is more at risk under attack and breakdown from oxygen exposure. Even though they are chemically processed to burn like diesel fuel in an engine, biodiesel molecules aren't exactly the same in structure as petroleum molecules. They have more areas on their molecular structure that are weak points for oxygen and free radicals to attack, reacting and breaking the molecules away from each other. Thus with the formation of new impurities in the sample during the storage period, it was expected for biodiesel density to increase.

At Table 4.3 we can observe the rise in density values of biodiesel sample with to storage period. Experimental measurements were carried out for every ten days of storage period of 90 days.

Table 4.3: Influence of storage period (days) on density of biodiesel at 15˚C temperature

B100 Sample	
Day	**Density at 15˚C [kg/m^3]**
0	867.779
10	868.907
20	870.037
30	875.910
40	877.049
50	878.189
60	881.249
70	882.346
80	883.493
90	886.396

At Figure 4.3, density measurements are plotted at 15˚C since densities are at 15 ˚C given at international standards (ASTM). As a result of our expectation, there is a slight rising in density value plotted in Figure 4.3 proportional to the storage period

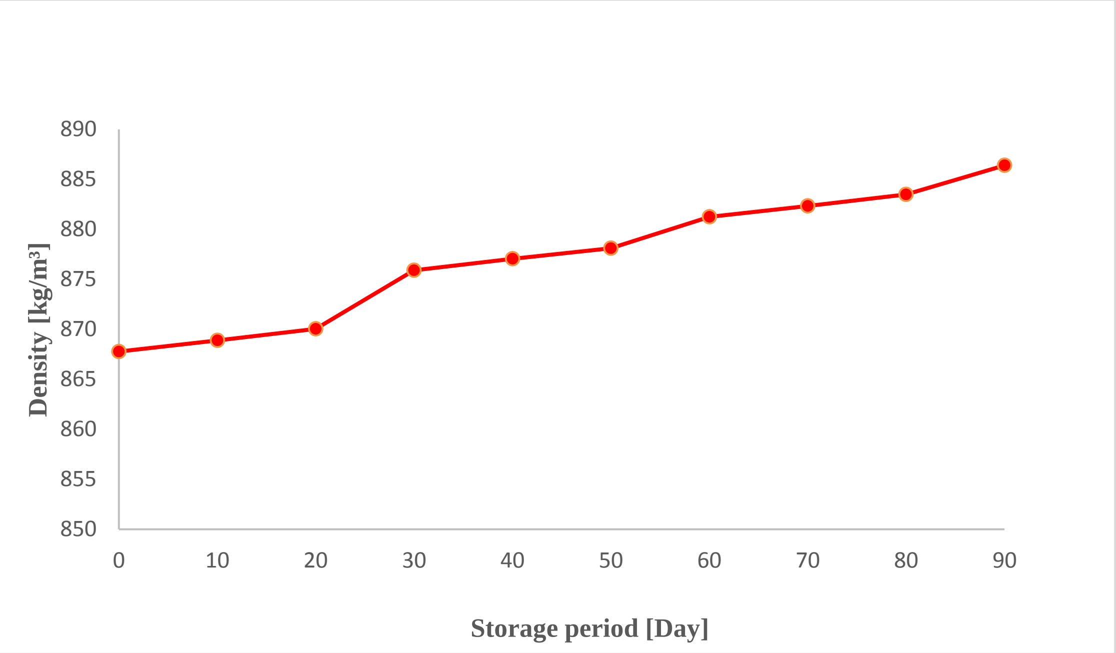


Figure 4.3: Density-storage period relationship at 15˚C

Temperature is a measurement of the average kinetic energy of the molecules in a system. By increasing temperature of the biodiesel sample, kinetic energy of the molecules in sample is increased. In other words solubility of the molecules in the sample increased. Consequently volume of the sample increases. Exemplarily as discussed in previous chapter, excess biodiesel will come out from the pycnometer to outside with the increasing temperature. Thus that results decreasing of the density value.

Table 4.4 summarizes for density values measured at every 4 weeks for a storage period of 12 week at different temperatures. Temperature range is between at 5 ˚C to 90 ˚C.

Table 4.4: Influence of storage period (weeks) and testing temperatures on density of biodiesel

B100 Sample				
	Weeks			
Temperature [˚C]	**0**	**4**	**8**	**12**
5	893,165			
8	884.676	892.965	898.367	903.656
10	876.187	884.396	889.746	894.984
15	867.779	875.910	881.249	886.396
20	859.372	864.745	872.671	877.808
30	850.964	858.937	864.133	869.220
40	840.910	848.789	853.923	858.950
50	838.982	846.843	851.966	856.981
60	829.741	837.516	842.582	847.542
70	822.864	830.574	835.598	840.518
80	809.284	816.867	821.808	826.646
90	802.949	810.473	815.375	820.176

From Figure 4.4 it can be concluded that like similar to expectations, with the increasing temperature, density is decreasing. Storage period-density relationship can be observed at all temperature values. As the storage period increases, density is increasing for each week.

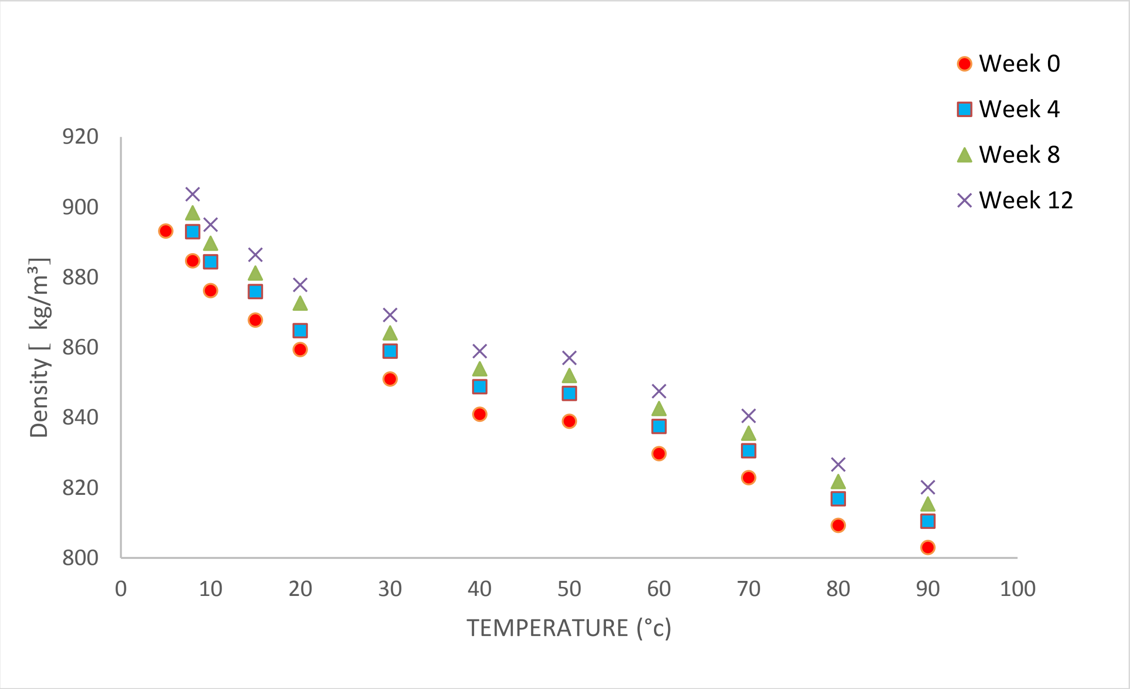


Figure 4.4: Density-storage period-temperature relationship

4.4 Acid Number and Oxidation Stability

Acid number and oxidation stability were measured by a certificate laboratory at Greek side, Nortest Petrochemical Laboratory. Table 4.5 indicates the measurements for acid number and oxidation stability with a difference of one month between the two measurements.

Table 4.5: Total acid number and oxidation number values

B100 Sample				
TEST DESCRIPTION UNITS	**TEST METHOD**	**SPEC. LİMİTS**	**TEST RESULT (1st Month)**	**TEST RESULT (2nd Month)**
Total Acid Number (mgKOH/gr)	D664-04(2018	-	0.40	0.42
Oxidation Stability (Hours)	EN15751:2014	-	0.1	0.1

Similar to expectations, with the increasing storage period acid number of the biodiesel sample increased. When the storage period increased oxidation in the biodiesel is increasing forming fatty acid chains in the sample results with the higher acid number. Expectation for oxidation stability was to decrease with the storage period increase. Since the time difference for the two measurements is one month, it couldn’t be observed a change in the oxidation stability value.

4.5 Cold Flow Properties

Cold flow properties of the biodiesel were investigated using DSC (data logger). Calibration of the data logger had been done by measuring the temperature of the cooling bath with data logger and comparing it with the real temperature measured by the thermostat. This comparison had been done for three times as shown in Figure 4.5, Figure 4.6 and Figure 4.7.

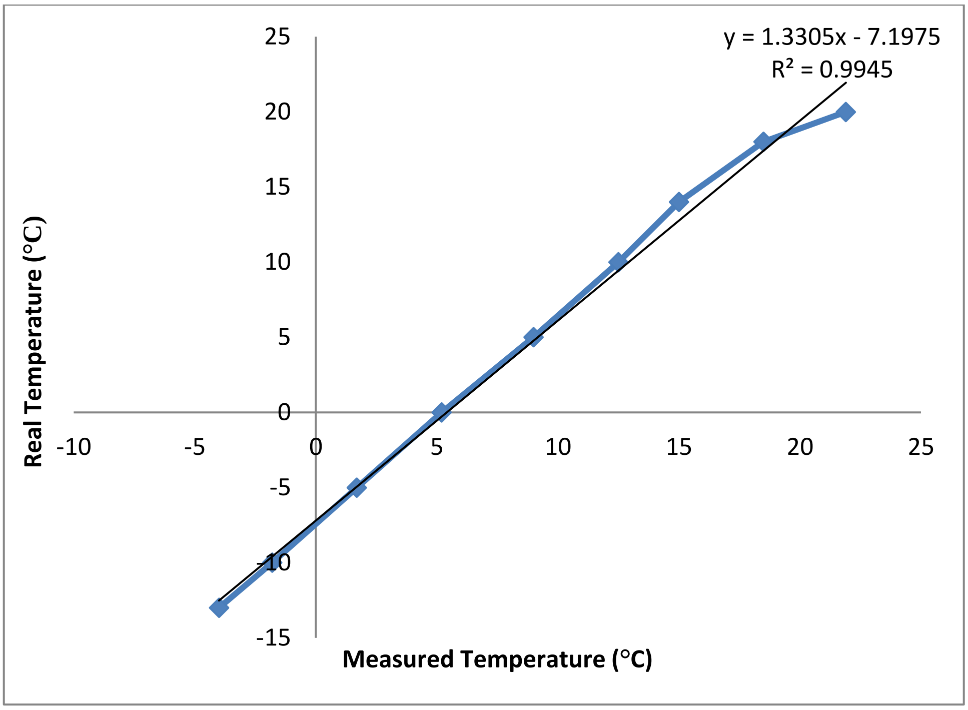


Figure 4.5: First comparison for the temperature of cooling bath

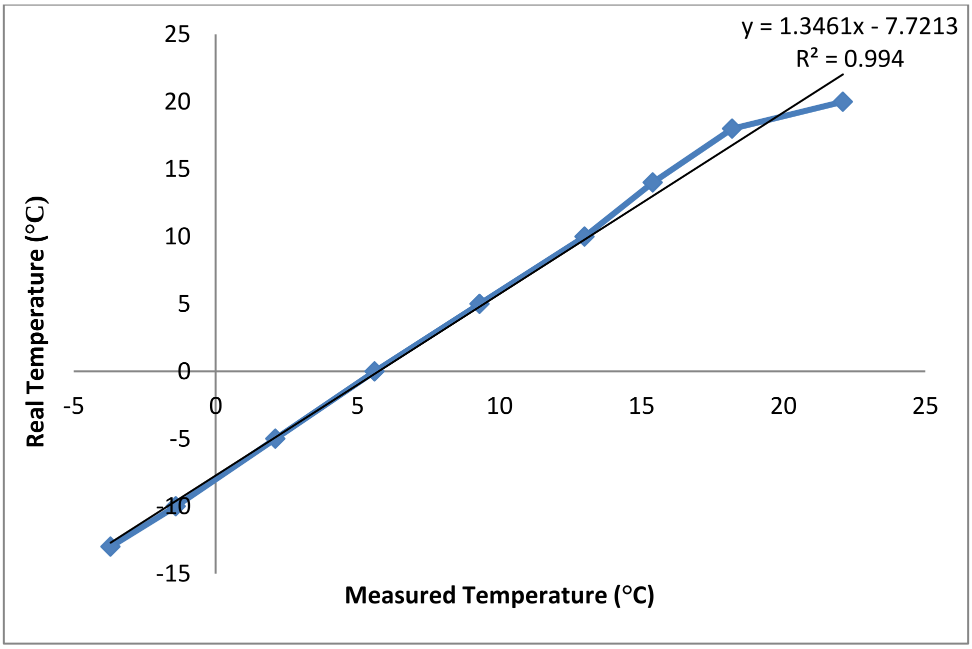


Figure 4.6: Second comparison for the temperature of cooling bath

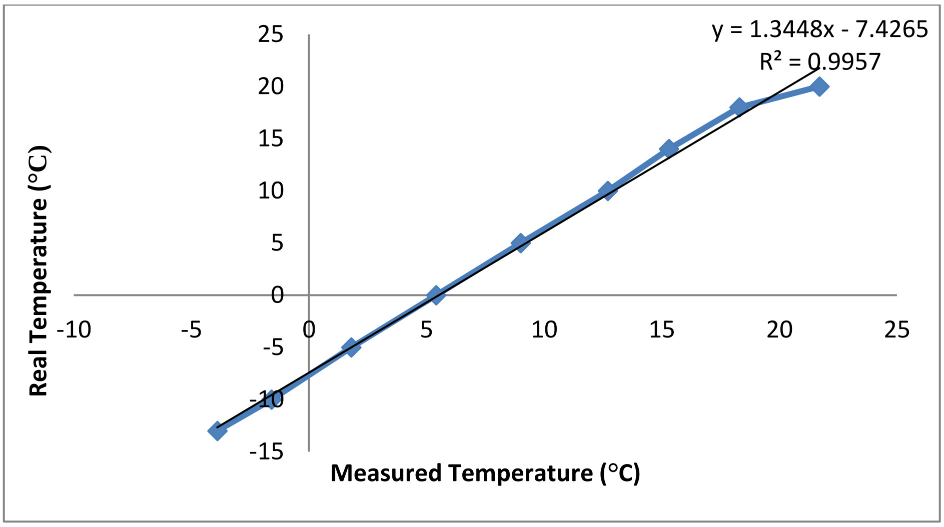


Figure 4.7: Third comparison for the temperature of cooling bath

Figure 4.8 shows the cooling curve and bath temperature during both the cooling cycle scans. In order to know the values of cold flow properties, the second derivative of temperature (as function of time) has been calculated and plotted. It has been observed that the value of CP, CFPP and PP from cooling curve and observation data from the experimental setup were almost equals which are 11˚C, 7˚C and 6˚C respectively.

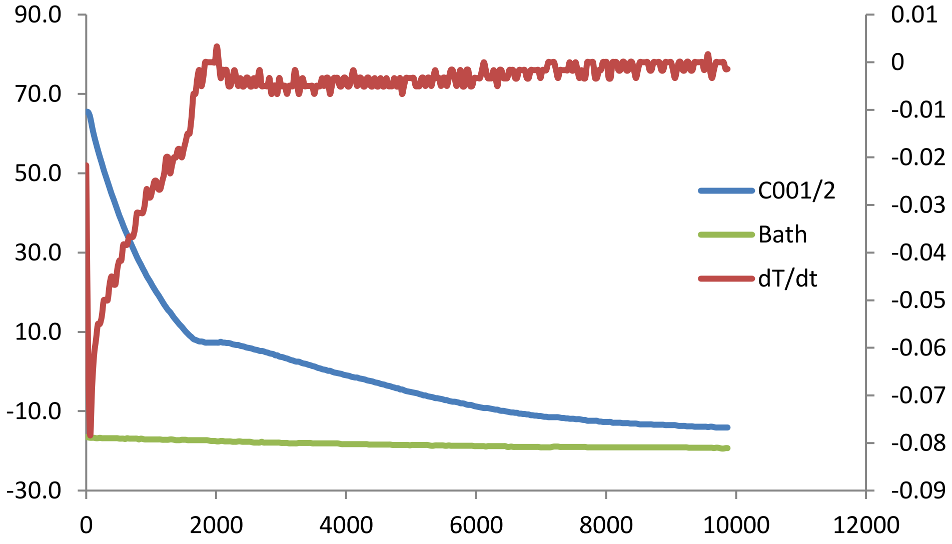


Figure 4.8: Cooling curve

CHAPTER 5
CONCLUSIONS

5.1 Conclusion

B100 biodiesel sample was stored in a furnace at a constant temperature of 40˚C in the Mechanical Engineering Laboratory. The kinematic viscosity of biodiesel sample was measured from 5˚C to 90˚C by using Ubbelohde viscometer according to standard ASTM D445-09 and the experimental data were listed. Also density of biodiesel sample was measured from 5˚C to 90˚C by using pycnometer according to standard ASTM D 941-88 and experimental data were listed. Total acid number and oxidation stability were analyzed by a certificate laboratory which is locate in Southern part of Cyprus using the test methods ASTM D664-04(2017) and EN15751:2014 respectively. In consequence of the experimental results listed, the following points have been observed:

- Kinematic viscosity of the biodiesel sample increases with the storage period.
- Kinematic viscosity of the biodiesel sample decreases with the increasing testing temperature.
- Kinematic viscosity of the biodiesel sample cannot be determined below 8˚C because of the solidification of sample.
- It has been noticed that kinematic viscosity of the sample below 20˚C temperature exceeds the upper limit of 1.9-6.0 mm^2/s range according to ASTM D6751 standard. Above 20˚C, kinematic viscosity test results are in the suitable range according to ASTM D6751 standard.
- Density of the biodiesel sample also increases with the storage period.
- In contrast with the storage period, temperature rise decrease the density value.

- Experimental measurements show that density values above 20˚C temperature stay below the lower limit of 860-890 kg/m^3 range according to EN ISO 12185 standard.
- Acid number increases with the storage period. In contrast oxidation value decreases with the storage period.
- Results show that that the values of cold flow properties observed from the cooling curve were almost equal with the observation data from the experimental setup.

All of the experiments were conducted as accurate as possible but there are some factors affecting the results and cause errors:

1- Reading and averaging error.
2- Non-uniform distribution of temperature in the cooling and heating bath.
3- Quickly changing temperature in the heating bath during measurements.
4- We had to use five different thermometers in total due to the break of other four thermometers and as a result of this measured temperature values were affected.
5- Due to the electricity cut-off in the city network, sometimes biodiesel stored at 40˚C was cooled down affecting the experimental results.
6- Vibration in the test environment can cause may lead to measurement errors.
7- Electronic balance calibration.

5.2 Recommendations

A future work suggested to be done such as investigation of pressure effect on the biodiesel sample. Also some other important properties of the biodiesel sample such as the flash point, cetane number, iodine value might be measured.

Consequently, in the light of this study, storage time might be increased or storage temperature might be changed to get different experimental results.

REFERENCES

Anastopoulos, G., Zannikou, Y., Stournas, S., & Kalligeros, S. (2009). Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies*, 2(2), 362-376 doi:10.3390/en20200362.

ASTM D 446-07: Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers (1995). Philadelphia

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

Changes in Diesel Fuel; The Service Technician Guide to Compression Ignition Quality; (2007). *National Institute of Automotive Service Excellence.*

Cennatek Bioanalytical Services, (2013). Kinematic Viscosity According to ASTM D445;, fromhttp://cennatek.ca/analytical/biodiesel/kinematic-viscosity-according-to-astm-d445/.

Carlini, M., Castellucci, S. & Cocchia, S. (2014). A Pilot-Scale Study of Waste Vegetable Oil Transesterification with Alkaline and Acidic Catalysts. *Energy Procedia*, 45, 198 – 206. doi:10.1016/j.egypro.2014.01.022

Demirbas, A. (2008). *Biodiesel: A realistic fuel alternative for diesel engines*. London: Springer.

Gerpen, V. J., Knothe, G. & Krahl J. (2005). The Basics of Diesel Engines and Diesel Fuel. *The Biodiesel Handbook*, 2nd Edition. AOCS Press.

Gopal, K. N., Pal, A., Sharma, S., Samanchi, C., Sathyanarayanan, K., & Elango, T. (2014). Investigation of emissions and combustion characteristics of a CI engine fueled with waste cooking oil methyl ester and diesel blends. *Alexandria Engineering Journal, 53*(2), 281-287. doi:10.1016/j.aej.2014.02.003

Groschen, R., (2009). *Petroleum Diesel Fuel and Biodiesel Technical Cold Weather Issues. Report to the Legislature*. St. Paul, MN: Minnesota Dept. of Agriculture.

Hodac, I., McCurdy, D., Mandel, J., R. & Nao Y. (2009). Biodiesel Guidelines, World Fuel Charter Committee (Washington D.C.: Alliance of Automobile Manufacturers).

Kassem, Y., & Çamur, H. (2016). A Laboratory Study of the Effects of Wide Range Temperature on the Properties of Biodiesel Produced from Various Waste Vegetable Oils. Waste and Biomass Valorization, 8(6), 1995-2007. doi:10.1007/s12649-016-

9753-4

Klopfenstein, W. E. (1985). Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels. *Journal of the American Oil Chemists Society*, 62(6), 1029-1031. doi:10.1007/bf02935708

Krahl, J., Knothe, G., & Harlan, V. G. (2010). Biodiesel Handbook (2nd ed.). AOCS Press.

Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology, 86*(10), 1059-1070.

Knothe, G., & Steidley, K. R. (2005). Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. *Fuel,84*(9), 1059-1065. doi:10.1016/j.fuel.2005.01.016

Krisnangkura, K. (1986). A simple method for estimation of cetane index of vegetable oil methyl esters. *Journal of the American Oil Chemists Society,* 63(4), 552-553. doi:10.1007/bf02645752

Kwanchareon, P., Luengnaruemitchai, A., & Jai-In, S. (2007). Solubility of a diesel–biodiesel–ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel, 86*(7-8), 1053-1061. doi:10.1016/j.fuel.2006.09.034

Lin, L., Zhou, C., Saritporn V., Xiangqian, S., Mingdong, D. (2011). Opportunities and challenges for biodiesel fuel. *Applied Energy, 88*(1020–1031).

Leung, D., Koo, B., & Guo, Y. (2006). Degradation of biodiesel under different storage conditions. *Bioresource Technology, 97*(2), 250-256. doi:10.1016/j.biortech.2005.02.006

Monyem A., Van Gerpen JH. (2001). The Effect ofBiodiesel Oxidation on Engine Performance and Emissions, *Biomass and Bioenergy, 20*, 317-, 2001.

Serway, R. A. (1996). *Physics for scientists & engineers*. Philadelphia: Saunders College Pub.

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

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

Tat, M., E. & Gerpen, J. V. (2000). The Specific Gravity of Biodiesel and Its Blends with Diesel Fuels, *Journal of the American Oil Chemists Society*, 77(2), 115-119. doi:10.1007/s11746-000-0019-3

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

APPENDICES

APPENDIX 1

ASTM D 6751

Designation: D6751 – 09a

Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels[1]

This standard is issued under the fixed designation D6751; 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.

1. Scope*

1.1 This specification covers biodiesel (B100) Grades S15 and S500 for use as a blend component with middle distillate fuels.

1.2 This specification prescribes the required properties of diesel fuels at the time and place of delivery. The specification requirements may be applied at other points in the production and distribution system when provided by agreement between the purchaser and the supplier.

1.3 Nothing in this specification shall preclude observance of federal, state, or local regulations which may be more restrictive.

NOTE 1—The generation and dissipation of static electricity can create problems in the handling of distillate fuel oils with which biodiesel may be blended. For more information on the subject, see Guide D4865.

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

1.4.1 *Exception*—In Annex A1, the values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D93 Test Methods for Flash Point by Pensky-Martens Closed Cup Tester
D130 Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test
D189 Test Method for Conradson Carbon Residue of Petroleum Products
D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
D524 Test Method for Ramsbottom Carbon Residue of Petroleum Products
D613 Test Method for Cetane Number of Diesel Fuel Oil
D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D874 Test Method for Sulfated Ash from Lubricating Oils and Additives
D974 Test Method for Acid and Base Number by Color-Indicator Titration
D975 Specification for Diesel Fuel Oils
D976 Test Method for Calculated Cetane Index of Distillate Fuels
D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure
D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)
D1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)
D2274 Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
D2500 Test Method for Cloud Point of Petroleum Products
D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
D2709 Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge
D2880 Specification for Gas Turbine Fuel Oils
D3117 Test Method for Wax Appearance Point of Distillate Fuels
D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
D3242 Test Method for Acidity in Aviation Turbine Fuel
D3828 Test Methods for Flash Point by Small Scale Closed Cup Tester
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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[1] This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.E0 on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels.

Current edition approved Dec. 1, 2009. Published February 2010. Originally approved in 1999 as PS 121–99. Adopted as a standard in 2002 as D6751–02. Last previous edition approved in 2009 as D6751–09. DOI: 10.1520/D6751-09a.

[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.

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

D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
D4530 Test Method for Determination of Carbon Residue (Micro Method)
D4737 Test Method for Calculated Cetane Index by Four Variable Equation
D4865 Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems
D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
D5452 Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration
D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
D5771 Test Method for Cloud Point of Petroleum Products (Optical Detection Stepped Cooling Method)
D5772 Test Method for Cloud Point of Petroleum Products (Linear Cooling Rate Method)
D5773 Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)
D6217 Test Method for Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
D6450 Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester
D6469 Guide for Microbial Contamination in Fuels and Fuel Systems
D6584 Test Method for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography
D6890 Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber
D7039 Test Method for Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
D7397 Test Method for Cloud Point of Petroleum Products (Miniaturized Optical Method)

2.2 *Government Standard:*

40 CFR Part 79 Registration of Fuels and Fuel Additives Section 211(b) Clean Air Act[3]

2.3 *Other Documents:*[4]

UOP 389 Trace Metals in Oils by Wet Ashing and ICP-OES
UOP 391–91 Trace Metals in Petroleum Products or Organics by AAS
EN 14112 Fat and oil derivatives—Fatty acid methyl esters (FAME)—Determination of oxidation stability (Accelerated oxidation test)[5]
EN 14110 Fat and oil derivatives—Fatty acid methyl esters (FAME)—Determination of methanol content[5]
EN 14538 Fat and oil derivatives—Fatty acid methyl esters (FAME)—Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *biodiesel, n*—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*, as defined above, is registered with the U.S. EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act. There is, however, other usage of the term biodiesel in the marketplace. Due to its EPA registration and the widespread commercial use of the term biodiesel in the U.S. marketplace, the term biodiesel will be maintained for this specification.

3.1.1.2 *Discussion*—Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin, which is removed. The finished biodiesel derives approximately 10 % of its mass from the reacted alcohol. The alcohol used in the reaction may or may not come from renewable resources.

3.1.2 *biodiesel blend (BXX), n*—blend of biodiesel fuel with diesel fuel oils.

3.1.2.1 *Discussion*—In the abbreviation BXX, the XX represents the volume percentage of biodiesel fuel in the blend.

3.1.3 *biodiesel fuel, n*—synonym for *biodiesel.*

3.1.4 *diesel fuel, n*—middle petroleum distillate fuel.

3.1.5 *free glycerin, n*—a measure of the amount of glycerin remaining in the fuel.

3.1.6 *Grade S15 B100, n*—a grade of biodiesel meeting ASTM Specification D6751 and having a sulfur specification of 15 ppm maximum.

3.1.7 *Grade S500 B100, n*—a grade of biodiesel meeting ASTM Specification D6751 and having a sulfur specification of 500 ppm maximum.

3.1.8 *middle distillate fuel, n*—kerosines and gas oils boiling between approximately 150°C and 400°C at normal atmospheric pressure and having a closed-cup flash point above 38°C.

3.1.9 *total glycerin, n*—the sum of the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat.

4. Requirements

4.1 The biodiesel specified shall be mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats.

4.2 Unless otherwise specified, samples for analysis shall be taken by the procedure described in Practices D4057 or D4177.

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[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

[4] Available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA. Visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org.

[5] Available from the National CEN Members listed on the CEN website (www.cenorm.be) or from the CEN/TC19 secretariat (astm@nen.nl).

4.3 The biodiesel specified shall conform to the detailed requirements shown in Table 1.

Note 2—A considerable amount of experience exists in the U.S. with a 20 % blend of biodiesel, primarily produced from soybean oil, with 80 % diesel fuel (B20). Experience with biodiesel produced from animal fat and other oils is similar. Experience with B20 and lower blends in other applications is not as prevalent. Although biodiesel (B100) can be used, blends of over 20 % biodiesel with diesel fuel (B20) should be evaluated on a case by case basis until further experience is available.

Note 3—The user should consult the equipment manufacturer or owner's manual regarding the suitability of using biodiesel or biodiesel blends in a particular engine or application.

5. Test Methods

5.1 The requirements enumerated in this specification shall be determined in accordance with the following methods.

5.1.1 *Flash Point*—Test Methods D93, except where other methods are prescribed by law. Test Methods D3828 or D6450 can also be used. The precision and bias of Test Methods D3828 and D6450 with biodiesel is not known and is currently under investigation. Test Methods D93 shall be the referee method.

5.1.2 *Water and Sediment*—Test Method D2709. Test Method D1796 may also be used. Test Method D2709 shall be the referee method. The precision and bias of these test methods with biodiesel is not known and is currently under investigation.

5.1.3 *Viscosity*—Test Method D445.

5.1.4 *Sulfated Ash*—Test Method D874.

5.1.5 *Oxidation Stability*—Test Method EN 14112.

5.1.6 *Sulfur*—Test Method D5453. Test Method D7039 may also be used. Other test methods may also be suitable for determining up to 0.05 % (500 ppm) sulfur in biodiesel fuels such as Test Methods D1266, D2622, D3120 and D4294 but may provide falsely high results (see X1.5) although their precision and bias with biodiesel is unknown. Test Method D5453 shall be the referee test method.

5.1.7 *Corrosion*—Test Method D130, 3 h test at 50°C.

5.1.8 *Cetane Number*—Test Method D613. Test Method D6890 may also be used. Test Method D613 shall be the referee method.

5.1.9 *Cloud Point*—Test Method D2500. Test Method D5771, D5772, D5773, or D7397 may also be used. Test Method D3117 may also be used because it is closely related. Test Method D2500 shall be the referee test method. The precision and bias of Test Method D3117 for biodiesel is not known and is currently under investigation.

5.1.10 *Acid Number*—Test Method D664. Test Methods D3242 or D974 may also be used. Test Method D664 shall be the referee test method.

5.1.11 *Carbon Residue*—Test Method D4530. A100 % sample shall replace the 10 % residual, with percent residue in the original sample reported using the 10 % residual calculation (see X1.9.1). Test Methods D189 or D524 may also be used. Test Method D4530 shall be the referee method.

5.1.12 *Total Glycerin*—Test Method D6584.

5.1.13 *Free Glycerin*—Test Method D6584.

5.1.14 *Phosphorus Content*—Test Method D4951.

5.1.15 *Distillation Temperature, Reduced Pressure*—Test Method D1160.

5.1.16 *Calcium and Magnesium, combined*—Test Method EN 14538. Test Method UOP 389 may also be used. Test Method EN 14538 shall be the referee test method.

TABLE 1 Detailed Requirements for Biodiesel (B100) (All Sulfur Levels)

Property	Test Method[A]	Grade S15 Limits	Grade S500 Limits	Units
Calcium and Magnesium, combined	EN 14538	5 max	5 max	ppm (µg/g)
Flash point (closed cup)	D93	93 min	93 min	°C
Alcohol control				
One of the following must be met:				
1. Methanol content	EN 14110	0.2 max	0.2 max	mass %
2. Flash point	D93	130 min	130 min	°C
Water and sediment	D2709	0.050 max	0.050 max	% volume
Kinematic viscosity, 40°C	D445	1.9-6.0[B]	1.9–6.0[B]	mm^2/s
Sulfated ash	D874	0.020 max	0.020 max	% mass
Sulfur[C]	D5453	0.0015 max (15)	0.05 max (500)	% mass (ppm)
Copper strip corrosion	D130	No. 3 max	No. 3 max	
Cetane number	D613	47 min	47 min	
Cloud point	D2500	Report[D]	Report[D]	°C
Carbon residue[E]	D4530	0.050 max	0.050 max	% mass
Acid number	D664	0.50 max	0.50 max	mg KOH/g
Cold soak filterability	Annex A1	360 max[F]	360 max[F]	seconds
Free glycerin	D6584	0.020 max	0.020 max	% mass
Total glycerin	D6584	0.240 max	0.240 max	% mass
Phosphorus content	D4951	0.001 max	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered	D1160	360 max	360 max	°C
Sodium and Potassium, combined	EN 14538	5 max	5 max	ppm (µg/g)
Oxidation stability	EN 14112	3 minimum	3 minimum	hours

[A] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 5.1.

[B] See X1.3.1. The 6.0 mm^2/s upper viscosity limit is higher than petroleum based diesel fuel and should be taken into consideration when blending.

[C] Other sulfur limits can apply in selected areas in the United States and in other countries.

[D] The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending.

[E] Carbon residue shall be run on the 100 % sample (see 5.1.11).

[F] B100 intended for blending into diesel fuel that is expected to give satisfactory vehicle performance at fuel temperatures at or below –12°C shall comply with a cold soak filterability limit of 200 s maximum.

5.1.17 *Sodium and Potassium, combined*—Test Method EN 14538. Test Method UOP 391 may also be used. Test Method EN 14538 shall be the referee test method.

5.1.18 *Cold Soak Filterability*—The test method in Annex A1 shall be used to determine the cold soak filterability. B100 intended for blending into diesel fuels that is expected to give satisfactory vehicle performance at fuel temperatures at or below –12°C shall comply with a cold soak filtration limit of 200 s maximum. A cold soak filterability standard test method is under development.

NOTE 4—Interim precision information is provided in Annex A1 for the cold soak filterability test to give the user some indication of the repeatability and reproducibility expected.

6. Workmanship

6.1 The biodiesel fuel shall be visually free of undissolved water, sediment, and suspended matter.

7. Keywords

7.1 alternative fuel; biodiesel fuel; diesel fuel oil; fuel oil; renewable resource

ANNEX

(Mandatory Information)

A1. DETERMINATION OF FUEL FILTER BLOCKING POTENTIAL OF BIODIESEL (B100) BLEND STOCK BY COLD SOAK LABORATORY FILTRATION

A1.1 Scope

A1.1.1 This test method covers the determination by filtration time after cold soak of the suitability for a Biodiesel (B100) Blend Stock for blending with middle distillates to provide adequate low temperature operability performance to at least the cloud point of the finished blend.

A1.1.2 The interim precision of this test method has been determined.

A1.1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

A1.1.4 *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.*

A1.2 Referenced Documents

A1.2.1 *ASTM Standards*:[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4865 Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems

D5452 Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration

A1.3 Terminology

A1.3.1 *Definitions*:

A1.3.1.1 *biodiesel, n*—fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

A1.3.1.2 *bond, v*—to connect two parts of a system electrically by means of a conductive wire to eliminate voltage differences.

A1.3.1.3 *ground, v*—to connect electrically with earth.

A1.3.2 *Definitions of Terms Specific to this Standard*:

A1.3.2.1 *filtered flushing fluids, n*—either of two solvents, heptane or 2,2, 4–trimethylpentane, filtered through a nominal 0.45 µm glass fiber filter.

A1.3.2.2 *glass fiber filter, n*—the 0.7 µm glass fiber filters used in this test method.

A1.3.3 *Abbreviations*:

A1.3.3.1 *CSFT*—cold soak filtration test.

A1.4 Summary of Test Method

A1.4.1 In this test method, 300 mL of biodiesel (B100) is stored at 4.4°C (40°F) for 16 h, allowed to warm to 20 to 22°C (68 to 72°F), and vacuum filtered through a single 0.7 µm glass fiber filter.

A1.4.2 In this test method, the filtration time is reported in seconds.

A1.5 Significance and Use

A1.5.1 Some substances that are soluble or appear to be soluble in biodiesel at room temperature will, upon cooling or standing at room temperature for extended periods, come out of solution. These substances can cause filter plugging. This test method provides an accelerated means of assessing the propensity for these substances to plug filters.

A1.5.1.1 Fuels that give short filtration times are expected to give satisfactory operation down to the cloud point of biodiesel blends.

A1.5.2 The test method can be used in specifications as a means of controlling levels of minor filter plugging components in biodiesel and biodiesel blends.

A1.6 Apparatus

A1.6.1 *Filtration System*—Arrange the following components as shown in Fig. A1.1.

A1.6.1.1 *Funnel and Funnel Base*, with a stainless steel filter support for a 47–mm diameter glass fiber filter and a locking ring or spring action clip capable of receiving 300 mL.

NOTE A1.1—Sintered glass supports were found to give much higher filtration times during initial studies and should not be used.

A1.6.1.2 *Ground/Bond Wire*, 0.912 to 2.59 mm (No. 10 through No. 19) bare-stranded flexible stainless steel or copper installed in the flasks and grounded as shown in Fig. A1.1.

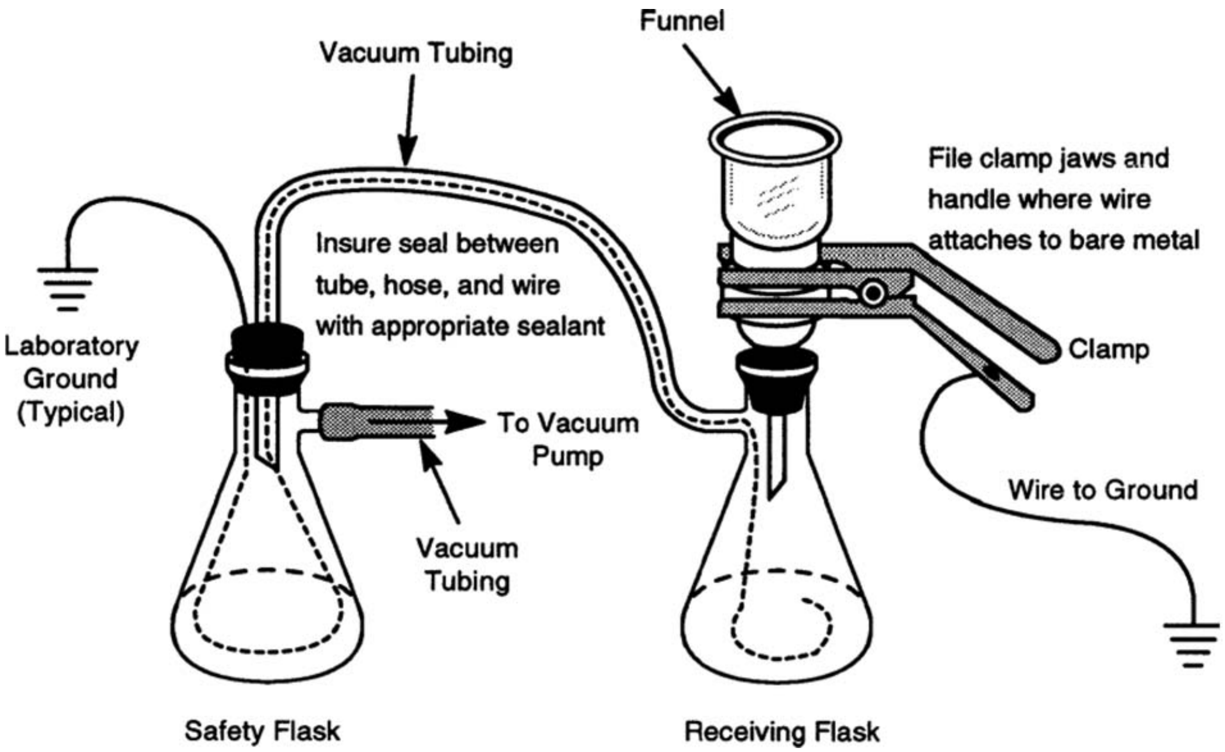

FIG. A1.1 Schematic of Filtration System

NOTE A1.2—The electrical bonding apparatus described in Test Method D5452 or other suitable means of electrical grounding which ensure safe operation of the filtration apparatus and flask can be used. If the filtrate is to be subsequently tested for stability it is advisable not to use copper as copper ions catalyze gum formation during the stability test.

A1.6.1.3 *Receiving Flask*, 1-L borosilicate glass vacuum filter flask, into which the filtration apparatus fits, equipped with a sidearm to connect to the safety flask.

A1.6.1.4 *Safety Flask*, 1-L borosilicate glass vacuum filter flask equipped with a sidearm to connect the vacuum system. A fuel and solvent resistant rubber hose, through which the grounding wire passes, shall connect the sidearm of the receiving flask to the tube passing through the rubber stopper in the top of the safety flask.

A1.6.1.5 *Vacuum System*, a vacuum system capable of producing a vacuum of 70 to 100 kPa below atmospheric pressure when measured at the receiving flask. A mechanical vacuum pump may be used if it has this capability.

NOTE A1.3—Water aspirated vacuum will not provide relative vacuum within the prescribed range.

A1.6.2 *Other Apparatus*:

A1.6.2.1 *Forceps*, approximately 12-cm long, flat-bladed, with non-serrated, non-pointed tips.

A1.6.2.2 *Graduated Cylinders*, to contain at least 0.5 L of fluid and marked at 10-mL intervals. Graduated cylinders, 100-mL, may be required for samples which filter slowly.

A1.6.2.3 *Petri Dishes*, approximately 12.5 cm in diameter, with removable glass supports for glass fiber filters.

NOTE A1.4—Small watch glasses, approximately 5 to 7 cm in diameter, have also been found suitable to support the glass fiber filters.

NOTE A1.5—B100 will dissolve some plastics. This can cause the filters to adhere to the plastic.

A1.6.2.4 *Glass Fiber Filters*, plain, 47-mm diameter, nominal pore size 0.7-µm.

A1.6.2.5 *Protective Cover*, polyethylene film or clean aluminum foil.

A1.6.2.6 *Liquid or Air Bath or Chamber*, capable of sustaining a temperature of 4.4 ± 1.1°C (40 ± 2°F) for 16 h.

A1.6.2.7 *Timer*, capable of displaying elapsed times of at least 900 s to the nearest 0.1 s.

A1.7 Reagents and Materials

A1.7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

A1.7.2 *Flushing Fluids*—Flushing fluids are not required for the test as the filter is not weighed. However, heptane or isooctane may be used to wash the apparatus after filtration to remove any residue. Alternatively soap and water may be used in accordance with A1.7.3.

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

A1.7.2.1 *Heptane*, (**Warning**—Flammable).

A1.7.2.2 *2,2,4-trimethylpentane (isooctane)*, (**Warning**—Flammable).

A1.7.3 *Liquid or Powder Detergent*, water-soluble, for cleaning glassware.

A1.8 Preparation of Apparatus and Sample Containers

A1.8.1 Clean all components of the filtration apparatus using the reagents described in A1.7.2 and A1.7.3.

A1.8.1.1 Remove any labels, tags, and so forth.

A1.9 Sampling

A1.9.1 The sample container should be 500 ± 15 mL in volume and have a screw-on cap with an inert liner. Glass containers are preferred to facilitate a visual inspection of the contents and the container before and after filling. Glass containers also allow for visual inspection of the container, after the sample is emptied, to confirm complete emptying of the container. Epoxy-lined sample cans, polytetrafluoroethylene (PTFE) bottles, and high density linear polyethylene bottles have also been found suitable as sample containers but are less desirable since visual inspection of the interior of the container is more difficult.

A1.9.2 Precautions to avoid sample contamination shall include selection of an appropriate sampling point. It is preferred to obtain samples dynamically from a sampling loop in a distribution line, or from the flushing line of a field sampling kit. Ensure that the line to be sampled is flushed with fuel before collecting the sample.

A1.9.2.1 Use clean sample containers.

A1.9.2.2 Keep a clean protective cover over the top of the sample container until the cap is installed. Similarly protect the funnel opening of the assembled filtration apparatus with a clean protective cover until ready for use.

A1.9.2.3 Where it is desirable or only possible to obtain samples from static storage, follow the procedures given in Practice D4057 or equivalent, taking precautions for cleanliness of all equipment used. The sample should pass through a minimum number of intermediate containers prior to placement in the prepared container.

A1.9.2.4 Samples obtained from static storage can give results that are not representative of the bulk contents of the tank because of particulate matter settling. Where possible, the contents of the tank should be circulated or agitated before sampling, or the sampling should be performed shortly after a tank has been filled.

A1.9.3 Visually inspect the sample container before taking the samples to verify that there are no visible particles present inside the container. Fill the sample container to contain 300 mL. Protect the fuel sample from prolonged exposure to light by wrapping the container in aluminum foil or storing it in the dark to reduce the possibility of particulate formation by light-promoted reactions. Do not transfer the fuel sample from its original sample container into an intermediate storage container. If the original sample container is damaged or leaking, then a new sample shall be obtained.

A1.9.3.1 If a 500-mL bottle is not available, or the sample has already been received in a container not suitable for this test, follow A1.9.5.

A1.9.4 Analyze fuel samples as soon as possible after sampling.

A1.9.4.1 Upon receipt of a Biodiesel Blend Stock (B100) sample, the entire sample shall be heated to 40°C for at least 3 h under an inert atmosphere to erase any thermal history and to dissolve any solids that might have precipitated during transit unless it is known that the sample has never been cooled below 20°C. If the sample has never been exposed to temperatures below 20°C then proceed to A1.9.5.

A1.9.4.2 After heating for the required time, allow the sample to sit for 24 h at a temperature no lower than 20°C.

A1.9.5 Shake the sample vigorously for 1 min, and transfer 300 mL to a clean fresh 500 ± 15 mL bottle.

A1.10 Preparation of Glass Fiber Filter

A1.10.1 Each filtration uses one filter. The glass fiber filter used for each individual test shall be identified by marking the petri dishes used to hold and transport the filters.

A1.10.2 Clean all glassware used in preparation of glass fiber filter as described in A1.8.1.

A1.10.3 Using forceps, place the filters on clean glass support rods or watch glasses in petri dish.

A1.10.4 Place the petri dish with its lid slightly ajar in a drying oven at 90 ± 5°C, and leave it for 30 min.

A1.10.5 Remove the petri dish from the drying oven. Keep the petri dish cover ajar, such that the filter is protected from contamination from the atmosphere. Allow 30 min for the filter to come to equilibrium with room air temperature and humidity.

A1.10.6 Using clean forceps, place the filter centrally on the filter support of the filtration apparatus (see Fig. A1.1). Install the funnel and secure with locking ring or spring clip. Do not remove the plastic film from the funnel opening until ready to start filtration.

A1.11 Procedure

A1.11.1 Place 300 mL of sample in a glass 500–mL bottle, and set in a liquid or air bath or chamber at 4.4 ± 1.1°C (40 ± 2°F) for 16 ± 0.5 h.

A1.11.2 After the 16-h cold soak is completed, allow the sample to come back to room temperature at 20 to 22°C (68 to 72°F) on its own without external heating. The sample shall be completely liquid before filtration. The sample shall be filtered within 1 h after reaching 20 to 22°C (68 to 72°F).

A1.11.3 Complete assembly of the receiving flask, 0.7 µm glass fiber filter and funnel as a unit (see Fig. A1.1) before swirling the sample. To minimize operator exposure to fumes, the filtering procedure should be performed in a fume hood.

A1.11.4 Start the vacuum system. Record the pressure in the system after 1 min of filtration. The vacuum shall be between 71.1 and 84.7 kPa (21 and 25 in. Hg) below atmospheric pressure. If the vacuum is not within the specified range, make adjustments to the vacuum system.

A1.11.5 Thoroughly clean the outside of the sample container in the region of the cap by wiping it with a damp, lint-free cloth. Swirl the container vigorously for about 2 to 3 s to dislodge any particles that may have adhered to the walls of the container.

A1.11.6 Immediately after swirling, pour the entire contents of the sample container into the filtration funnel and simultaneously start the timer. The entire contents of the sample container shall be filtered through the glass fiber filter to ensure a correct measure of the contamination in the sample.

NOTE A1.6—Take care not to shake the sample vigorously, as this could cause some of the solids to go back into solution.

A1.11.7 If the filtration is not complete when 720 s (12 min) has elapsed, turn off the vacuum system and record the duration of the filtration to the nearest second. Record the pressure in the system and the volume filtered just before the termination of the filtration.

A1.12 Reporting

A1.12.1 Report the time for the 300–mL B100 to be completely filtered as B100 filtration time in seconds.

A1.12.2 If the filtration of the 300 mL failed to be completed after 720 s, report the volume that was filtered after 720 s.

A1.13 Precision and Bias

A1.13.1 *Precision*—The precision of this test method for B100 filtration has not yet been determined.

A1.13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material for B100 filtration has not yet been determined.

A1.13.1.2 *Reproducibility*—The difference between the two single and independent results obtained by different operators working in different laboratories on identical test material for B100 filtration has not yet been determined.

A1.13.1.3 *Interim Precision*—Repeatability and reproducibility determinations were made using data from the ASTM Biodiesel Low Temperature Operability Task Force. The analysis of the data is the subject of a research report, RR:D02-1649.[7] The report is an attempt to supply such an analysis based on well-established methodologies. Subsequent to test method publication a more thorough round robin is planned.

	200 s	360 s
Repeatability	34.0	61.0
Reproducibility	115.9	208.1

NOTE A1.7—The degree of freedom associated with the repeatability estimate from this round robin study is 25 for repeatability which is below 30 but acceptable. The degree of freedom associated with the reproducibility estimate from this round robin study is 10 and below acceptable limits. For that reason only the repeatability is included in A1.13.1.4. Since the minimum requirement of 30 (in accordance with Practice D6300) is not met, users are cautioned that the actual repeatability/reproducibility may be significantly different than these estimates. An ASTM ILS will be conducted in the future.

A1.13.1.4 The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material for B100 filtration would in the long run, in the normal and correct operation of this test method, exceed 0.1689(X + 1.2018) time(s) only in one case in twenty.

A1.13.2 *Bias*—The procedure given for the determination of B100 filtration time has no bias because the value of the filtration time is defined in terms of this test method.

A1.14 Keywords

A1.14.1 biodiesel; diesel fuel; glass fiber filter; biodiesel; filter blocking potential, cold soak filtration test, CSFT, biodiesel blend; laboratory filtration; glass fiber filter; low temperature operability, middle distillate fuel.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1649.

APPENDIXES

(Nonmandatory Information)

X1. SIGNIFICANCE OF PROPERTIES SPECIFIED FOR BIODIESEL FUEL

X1.1 Introduction

X1.1.1 The properties of commercial biodiesel fuel depends upon the refining practices employed and the nature of the renewable lipids from which it is produced. Biodiesel, for example, can be produced from a variety of vegetable oils or animal fats which produce similar volatility characteristics and combustion emissions with varying cold flow properties.

X1.1.2 The significance of the properties in this appendix are based primarily on the commercial use of biodiesel in on-road and off-road diesel engine applications. Some of the properties may take on other significance if biodiesel is used as a fuel or blending component in other applications. See the respective finished product specifications for additional information on significance of properties of those applications.

X1.2 Flash Point

X1.2.1 The flash point, as specified, is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage that are normally specified to meet insurance and fire regulations.

X1.2.2 The flash point for biodiesel has been set at 93°C (200°F) minimum, so biodiesel falls under the non-hazardous category under National Fire Protection Association codes.

X1.3 Viscosity

X1.3.1 For some engines it may be advantageous to specify a minimum viscosity because of power loss due to injection pump and injector leakage. Maximum allowable viscosity, on the other hand, is limited by considerations involved in engine design and size, and the characteristics of the injection system. The upper limit for the viscosity of biodiesel (6.0 mm^2/s at 40°C) is higher than the maximum allowable viscosity in Specification D975 Grade 2-D and 2-D low sulfur (4.1 mm/s at 40°C). Blending biodiesel with diesel fuel close to its upper limit could result in a biodiesel blend with viscosity above the upper limits contained in Specification D975.

X1.4 Sulfated Ash

X1.4.1 Ash-forming materials may be present in biodiesel in three forms: (*1*) abrasive solids, (*2*) soluble metallic soaps, and (*3*) unremoved catalysts. Abrasive solids and unremoved catalysts can contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but may contribute to filter plugging and engine deposits.

X1.5 Sulfur

X1.5.1 The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can also affect emissions control systems performance and various limits on sulfur have been imposed for environmental reasons. B100 is essentially sulfur-free.

NOTE X1.1—Test Method D5453 should be used with biodiesel. Use of other test methods may provide falsely high results when analyzing B100 with extremely low sulfur levels (less than 5 ppm). Biodiesel sulfur analysis from RR:D02-1480[8], *Biodiesel Fuel Cetane Number Testing Program, January-April, 1999*, using Test Method D2622 yielded falsely high results due to the presence of the oxygen in the biodiesel. Sulfur results using Test Method D2622 were more accurate with B20 than with B100 due to the lower oxygen content of B20. Potential improvements to Test Method D2622 may provide more accurate values in the future.

X1.6 Copper Strip Corrosion

X1.6.1 This test serves as a measure of possible difficulties with copper and brass or bronze parts of the fuel system. The presence of acids or sulfur-containing compounds can tarnish the copper strip, thus indicating the possibility for corrosion.

X1.7 Cetane Number

X1.7.1 Cetane number is a measure of the ignition quality of the fuel and influences white smoke and combustion roughness. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions.

X1.7.2 The calculated cetane index, Test Methods D976 or D4737, may not be used to approximate the cetane number with biodiesel or its blends. There is no substantiating data to support the calculation of cetane index with biodiesel or biodiesel blends.

X1.8 Cloud Point

X1.8.1 Cloud point is of importance in that it defines the temperature at which a cloud or haze of crystals appears in the fuel under prescribed test conditions which generally relates to the temperature at which crystals begin to precipitate from the fuel in use. Biodiesel generally has a higher cloud point than petroleum based diesel fuel. The cloud point of biodiesel and its impact on the cold flow properties of the resulting blend should be monitored by the user to ensure trouble-free operation in cold climates. For further information, consult Appendix X4 of Specification D975.

X1.9 Carbon Residue

X1.9.1 Carbon residue gives a measure of the carbon depositing tendencies of a fuel oil. While not directly correlating with engine deposits, this property is considered an approximation. Although biodiesel is in the distillate boiling range, most biodiesels boil at approximately the same temperature and it is difficult to leave a 10 % residual upon distillation. Thus, a 100 % sample is used to replace the 10 % residual sample, with the calculation executed as if it were the 10 % residual. Parameter E (final weight flask charge/original weight flask charge) in 8.1.2 of Test Method D4530-93 is a constant 20/200.

X1.10 Acid Number

X1.10.1 The acid number is used to determine the level of free fatty acids or processing acids that may be present in biodiesel. Biodiesel with a high acid number has been shown to increase fueling system deposits and may increase the likelihood for corrosion.

NOTE X1.2—Acid number measures a different phenomenon for biodiesel than petroleum based diesel fuel. The acid number for biodiesel measures free fatty acids or degradation by-products not found in petroleum based diesel fuel. Increased recycle temperatures in new fuel system designs may accelerate fuel degradation which could result in high acid values and increased filter plugging potential.

X1.11 Free Glycerin

X1.11.1 The free glycerin method is used to determine the level of glycerin in the fuel. High levels of free glycerin can cause injector deposits, as well as clogged fueling systems, and result in a buildup of free glycerin in the bottom of storage and fueling systems.

X1.12 Total Glycerin

X1.12.1 The total glycerin method is used to determine the level of glycerin in the fuel and includes the free glycerin and the glycerine portion of any unreacted or partially reacted oil or fat. Low levels of total glycerin ensure that high conversion of the oil or fat into its mono-alkyl esters has taken place. High levels of mono-, di-, and triglycerides can cause injector deposits and may adversely affect cold weather operation and filter plugging.

X1.13 Phosphorus Content

X1.13.1 Phosphorus can damage catalytic converters used in emissions control systems and its level must be kept low. Catalytic converters are becoming more common on diesel-powered equipment as emissions standards are tightened, so low phosphorus levels will be of increasing importance. Biodiesel produced from U.S. sources has been shown to have

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[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1480.

low phosphorus content (below 1 ppm) and the specification value of 10 ppm maximum is not problematic. Biodiesel from other sources may or may not contain higher levels of phosphorus and this specification was added to ensure that all biodiesel, regardless of the source, has low phosphorus content.

X1.14 Reduced Pressure Distillation

X1.14.1 Biodiesel exhibits a boiling point rather than a distillation curve. The fatty acids chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357°C, thus the specification value of 360°C is not problematic. This specification was incorporated as an added precaution to ensure the fuel has not been adulterated with high boiling contaminants.

NOTE X1.3—The density of biodiesel meeting the specifications in Table 1 falls between 0.86 and 0.90, with typical values falling between 0.88 and 0.89. Since biodiesel density falls between 0.86 and 0.90, a separate specification is not needed. The density of raw oils and fats is similar to biodiesel, therefore use of density as an expedient check of fuel quality may not be as useful for biodiesel as it is for petroleum based diesel fuel. This section has been added to provide users and engine interests with this information.

NOTE X1.4—In certain items of fuel injection equipment in compression ignition engines, such as rotary/distributor fuel pumps and injectors, the fuel functions as a lubricant as well as a source for combustion. Blending biodiesel fuel with petroleum based compression-ignition fuel typically improves fuel lubricity.

X1.15 Alcohol Control

X1.15.1 Alcohol control is to limit the level of unreacted alcohol remaining in the finished fuel. This can be measured directly by the volume percent alcohol or indirectly through a high flash point value.

X1.15.2 The flash point specification, when used for alcohol control for biodiesel, is intended to be 100°C minimum, which has been correlated to 0.2 vol % alcohol. Typical values are over 160°C. Due to high variability with Test Method D93 as the flash point approaches 100°C, the flash point specification has been set at 130°C minimum to ensure an actual value of 100°C minimum. Improvements and alternatives to Test Method D93 are being investigated. Once complete, the specification of 100°C minimum may be reevaluated for alcohol control.

X1.16 Calcium and Magnesium

X1.16.1 Calcium and magnesium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston, and ring wear, as well as to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of calcium and magnesium compounds may also be collected in exhaust particulate removal devices, are not typically removed during passive or active regeneration, and can create increased back pressure and reduced time to service maintenance.

X1.17 Sodium and Potassium

X1.17.1 Sodium and potassium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of sodium or potassium compounds may also be collected in exhaust particulate removal devices, are not typically removed during passive or active regeneration, and they can create increased back pressure and reduced period to service maintenance.

X1.18 Oxidation Stability

X1.18.1 Products of oxidation in biodiesel can take the form of various acids or polymers, which, if in high enough concentration, can cause fuel system deposits and lead to filter clogging and fuel system malfunctions. Additives designed to retard the formation of acids and polymers can significantly improve the oxidation stability performance of biodiesel. See Appendix X2 for additional information on long-term storage.

X2. LONG-TERM STORAGE OF BIODIESEL

X2.1 Scope

X2.1.1 This appendix provides guidance for consumers of biodiesel (B100) who may wish to store quantities of fuels for extended periods. Consistently successful long-term fuel storage requires attention to fuel selection, storage conditions, and monitoring of properties prior to and during storage. This appendix is directed toward biodiesel (B100) and may be more or less applicable to blends of biodiesel with petroleum based diesel fuel.

X2.1.2 Normally produced biodiesel has adequate stability properties to withstand normal storage without the formation of troublesome amounts of insoluble degradation products, although data suggests some biodiesel may degrade faster than petroleum based diesel fuel. Biodiesel that is to be stored for prolonged periods should be selected to avoid formation of sediments, high acid numbers, and high viscosities that can clog filters, affect fuel pump operation or plug combustor nozzles or injectors. The selection of biodiesel should result from supplier-user discussions.

X2.1.3 These suggested practices are general in nature and should not be considered substitutes for any requirement imposed by the warranty of the distillate fuel equipment manufacturers or by federal, state, or local government regulations. Although they cannot replace knowledge of local conditions or good engineering and scientific judgment, these suggested practices do provide guidance in developing an individual fuel management system for the biodiesel fuel user. They include suggestions in the operation and maintenance of existing fuel storage and handling facilities and for identifying where, when, and how fuel quality should be monitored.

X2.2 Terminology

X2.2.1 *bulk fuel*—fuel in the storage facility in quantities over 50 gallons.

X2.2.2 *combustor fuel*—fuel entering the combustion zone of the burner or engine after filtration or other treatment of bulk fuel.

X2.2.3 *fuel contaminants*—foreign materials that make fuel less suitable or unsuitable for the intended use. Fuel contaminants include materials introduced subsequent to the manufacture of fuel and fuel degradation products.

X2.2.4 *fuel-degradation products*—those materials formed in fuel after it is produced. Insoluble degradation products may combine with other fuel contaminants to reinforce deleterious effects. Soluble degradation products (acids and gums) may be more or less volatile than the fuel and may cause an increase in injector and nozzle deposits. The formation of degradation products may be catalyzed by contact with metals, especially those containing copper and, to a lesser extent, iron.

X2.2.5 *long-term storage*—storage of fuel for longer than 6 months after it is received by the user.

X2.3 Fuel Selection

X2.3.1 The stability properties of biodiesel are not fully understood and appear to depend on the vegetable oil and animal fat sources, severity of processing, and whether additional production plant treatment has been carried out or stability additives are present.

X2.3.2 The composition and stability properties of biodiesel produced at specific production plants may be different. Any special requirements of the user, such as long-term storage, should be discussed with the supplier.

X2.4 Fuel Additives

X2.4.1 Available fuel additives appear to improve the long term storage of biodiesel. Most additives should be added as close to the production site as possible to obtain maximum benefits.

X2.4.2 Biocides or biostats destroy or inhibit the growth of fungi and bacteria which can grow at fuel-water interfaces to give high particulate concentrations in the fuel. Available biocides are soluble in the fuel phase or the water phase, or both. Refer to Guide D6469 for a more complete discussion.

X2.5 Tests for Fuel Quality

X2.5.1 Test methods for estimating the storage stability of biodiesel (B100) are being developed. Modifications of Test Method D2274 to use glass fiber filters, varying times and temperatures, and the measurement of pre-test and post-test acid number and viscosity appear promising. However, correlation of this test with actual storage stability is unknown, and may depend upon field conditions and fuel composition.

X2.5.2 Performance criteria for accelerated stability tests that ensure satisfactory long-term storage of biodiesel (B100) have not been established.

X2.6 Fuel Monitoring

X2.6.1 A plan for monitoring the quality of bulk fuel during prolonged storage is an integral part of a successful monitoring program. A plan to replace aged fuel with fresh product at established intervals is also desirable.

X2.6.2 Stored fuel should be periodically sampled and its quality assessed. Practice D4057 provides guidance for sampling. Fuel contaminants and degradation products may settle to the bottom of a quiescent tank although detrimental changes to biodiesel can occur (rising acid value) without causing sediment formation. A *Bottom* or *Clearance* sample, as defined in Practice D4057, should be included in the evaluation along with an *All Level* sample.

X2.6.3 The quantity of insoluble fuel contaminants present in biodiesel can be determined using Test Method D6217 with glass fiber filters and abundant washing although no precision or bias testing has been performed with biodiesel using Test Method D6217.

X2.6.4 The acid value of biodiesel appears to exceed its specified maximum before other deleterious fuel property changes occur. A conscientious program of measuring the acid value of biodiesel may be sufficient for monitoring biodiesel stability.

X2.7 Fuel Storage Conditions

X2.7.1 Contamination levels in fuel can be reduced by storage in tanks kept free of water, and tankage should have provisions for water draining on a scheduled basis. Water promotes corrosion, and microbiological growth may occur at a fuel-water interface. Refer to Guide D6469 for a more complete discussion. Underground or isothermal storage is preferred to avoid temperature extremes; above-ground storage tanks should be sheltered or painted with reflective paint. High storage temperatures accelerate fuel degradation. Fixed roof tanks should be kept full to limit oxygen supply and tank breathing. The use of airtight sealed containers, such as drums or totes, can enhance the storage life of biodiesel.

X2.7.2 Copper and copper-containing alloys should be avoided with biodiesel due to increased sediment and deposit formation. Contact with lead, tin, and zinc can also cause increased sediment levels that can rapidly plug filters and should be avoided.

X2.7.3 Appendix X3 of Specification D2880 discusses fuel contaminants as a general topic. The discussion in Specification D2880 pertains to gas turbine combustion which may or may not be applicable to diesel engine combustion.

SUMMARY OF CHANGES

Subcommittee D02.E0 has identified the location of selected changes to this standard since the last issue (D6751–09) that may impact the use of this standard. (Approved Dec. 1, 2009.)

(*1*) Added Test Method D5771 and D5772 to 5.1.9 and to the Referenced Documents.

Subcommittee D02.E0 has identified the location of selected changes to this standard since the last issue (D6751–08) that may impact the use of this standard. (Approved April 15, 2009.)

(*1*) Added Test Method D7397 cloud point as an option to Test Method D2500 in 5.1.9 and to the Referenced Documents.

Subcommittee D02.E0 has identified the location of selected changes to this standard since the last issue (D6751–07b$^{\varepsilon 1}$) that may impact the use of this standard. (Approved Oct. 1, 2008.)

(*1*) Added Annex A1.
(*2*) Revised Table 1.
(*3*) Added 5.1.18.
(*4*) Added Note 4.

APPENDIX 2

ASTM D 445-09

Designation: D 445 – 09

British Standard 2000: Part 71:1990

Designation: 71/1/97

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

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

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

1. Scope*

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

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

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

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

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

2.2 *ISO Standards:*[3]

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

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

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

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

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

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

ISO 3104 Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity

ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions

ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods

ISO 5725 Accuracy (trueness and precision) of measurement methods and results.

ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use

ISO 17025 General Requirements for the Competence of Testing and Calibration Laboratories

2.3 *NIST Standards:*[4]

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

NIST GMP 11

NIST Special Publication 819

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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

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

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

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

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

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

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

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

4. Summary of Test Method

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

5. Significance and Use

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

6. Apparatus

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7. Reagents and Materials

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

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

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

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

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

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

8. Certified Viscosity Reference Standards

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

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

9. Calibration and Verification

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

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

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

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

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

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

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

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

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 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.

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%

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

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 µm screen, either prior to or during charging (see Specifications D 446).

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

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

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

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

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

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

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

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

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

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

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

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

12. Procedure for Opaque Liquids

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

13. Cleaning of Viscometer

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

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

14. Calculation

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

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

where:

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

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

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

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

where:

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

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

15. Expression of Results

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

16. Report

16.1 Report the following information:

16.1.1 Type and identification of the product tested,

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

16.1.3 Result of the test (see Section 15),

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

16.1.5 Date of the test, and

16.1.6 Name and address of the test laboratory.

17. Precision

17.1 *Comparison of Determined Values*:

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

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

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

17.2 *Comparison of Results*:

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

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

where: x is the average of results being compared.

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

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

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

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

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

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

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

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

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

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

where: x is the average of results being compared.

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

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

18. Keywords

18.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

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

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES AND CERTIFIED VISCOSITY REFERENCE STANDARDS

A1.1 Viscometer Types

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

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

TABLE A1.1 Viscometer Types

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

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

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

TABLE A1.2 Certified Viscosity Reference Standards

Designation	Approximate Kinematic Viscosity, mm^2/s					
	20°C	25°C	40°C	50°C	80 °C	100°C
S3	4.6	4.0	2.9	...	...	1.2
S6	11	8.9	5.7	...	...	1.8
S20	44	34	18	...	...	3.9
S60	170	120	54	...	...	7.2
S200	640	450	180	...	...	17
S600	2400	1600	520	280	67	32
S2000	8700	5600	1700	...	...	75
S8000	37 000	23 000	6700	...	...	...
S30 000	...	81 000	23 000	11 000	...	...

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

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

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

A2.2 Calibration

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

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

TABLE A2.1 General Specification for Thermometers

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

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

TABLE A2.2 Complying Thermometers

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

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

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

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

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

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

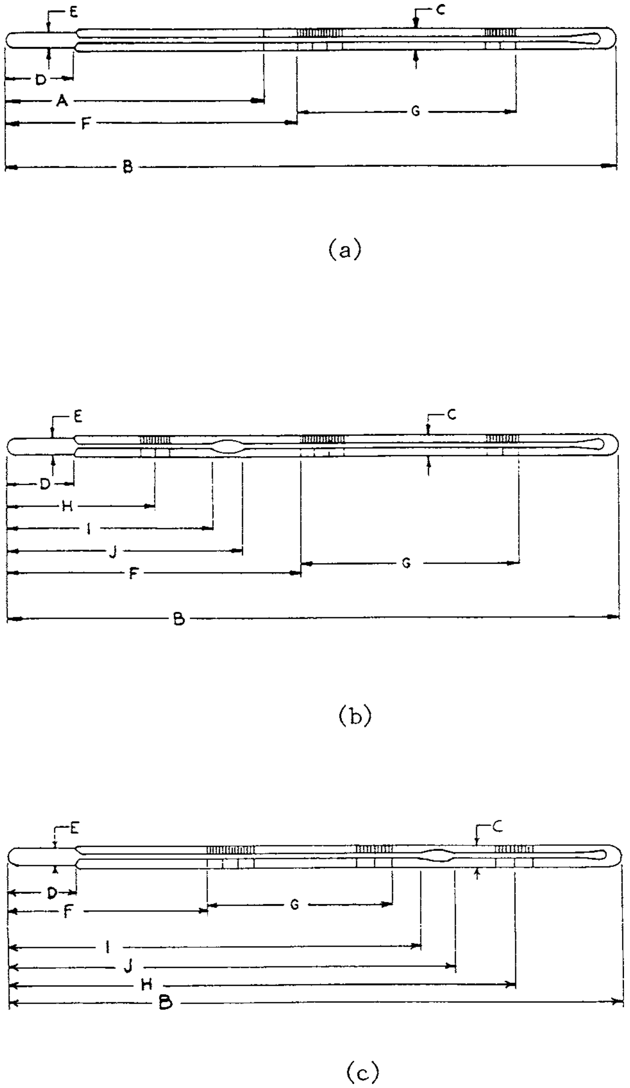

FIG. A2.1 Thermometer Designs

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

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

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

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

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

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

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

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

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

A3. TIMER ACCURACY

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

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

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

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

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

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

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

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

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

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

A4.4 Construct the acceptable tolerance zone:

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

SUMMARY OF CHANGES

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

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

APPENDIX 3

ASTM D941-88

Designation: D 941 – 88

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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If not listed in the current combined index, will appear in the next edition.

An American National Standard

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

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

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

1. Scope

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

1.2 Two procedures are covered as follows:

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

1.2.2 *Procedure B*, for highly volatile mixtures.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 1250 Petroleum Measurement Tables[2]

E 1 Specification for ASTM Thermometers[3]

3. Terminology

3.1 *density*—mass per unit volume.

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

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

4. Summary of Test Method[4]

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

5. Significance and Use

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

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

6. Apparatus

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

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

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

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

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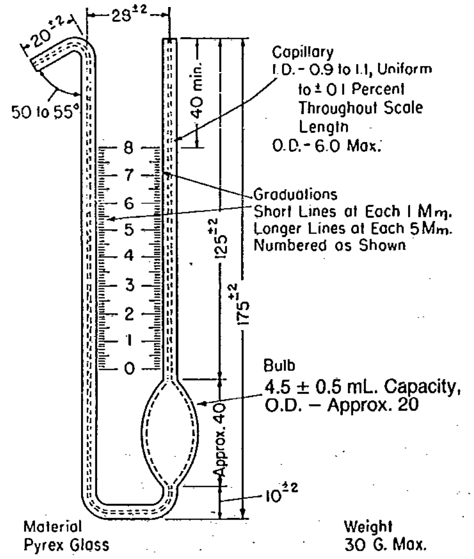
[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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

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

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

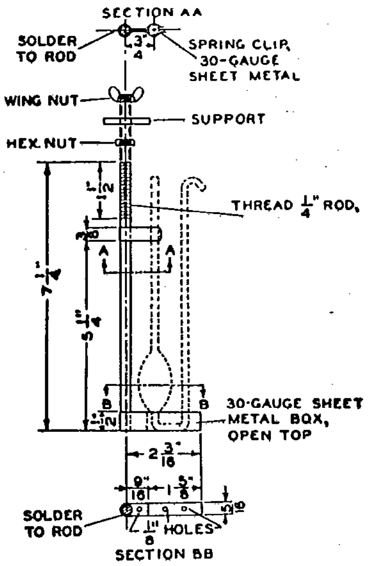
[4] For a more complete discussion of this method, see Davidson, J. A., Harvey, T., Kurtz, S. S., Jr., Lipkin, M. R., "Pycnometer for Volatile Liquids," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA Vol 16, No. 1, 1944, p. 55 and H. M. Smith, and Cooperators, "Measurement of Density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



All Dimensions in Millimetres

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

FIG. 1 Pycnometer



Metric Equivalents

in.	mm	in.	mm
5⁄16	7.94	¾	19
9⁄16	14.3	1½	38
⅛	3.2	1⅝	41.3
⅜	9.53	2³⁄16	55.6
¼	6.4	5¼	133.4
½	12.7	7¼	184.2

FIG. 2 Pycnometer Holder

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

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

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

7. Preparation of Apparatus

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

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

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

8. Calibration of Apparatus

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

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

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

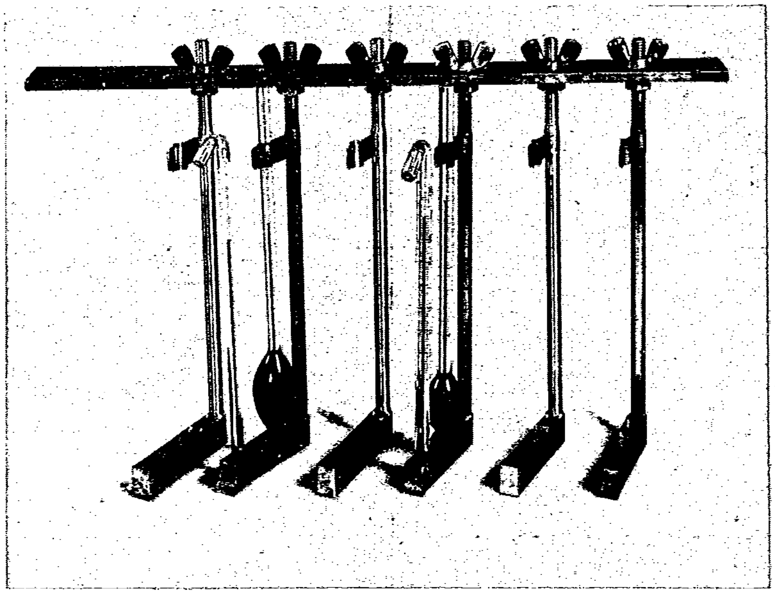


FIG. 3 Holder Mounting

9. Procedure A

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

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

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

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 ½ h it can be detected by touching the pycnometer to the wire hook on the balance and then drawing it away slowly. If the pycnometer exhibits an attraction for the wire hook, it may be considered to have a static charge.

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

10. Procedure B

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

10.2 Weigh the pycnometer as described in 9.2.

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

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

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

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

TABLE 2 Density of Water

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

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

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

11. Calculation

11.1 Calculate the density of the sample as follows:

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

where:

D = density, g/mL at 20 or 25°C,

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

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

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

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

12. Report

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

13. Precision and Bias

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

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

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

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

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Chromic Acid (Cleaning Solution)

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

A1.2 Isopentane

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

A1.3 Acetone

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

APPENDIX 4

ASTM D 2500

Designation: D 2500 – 09

An American National Standard
British Standard 4458

Designation: 219/82

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

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

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

1. Scope*

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

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standard:*[3]

Specifications for IP Standard Thermometers

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4. Summary of Test Method

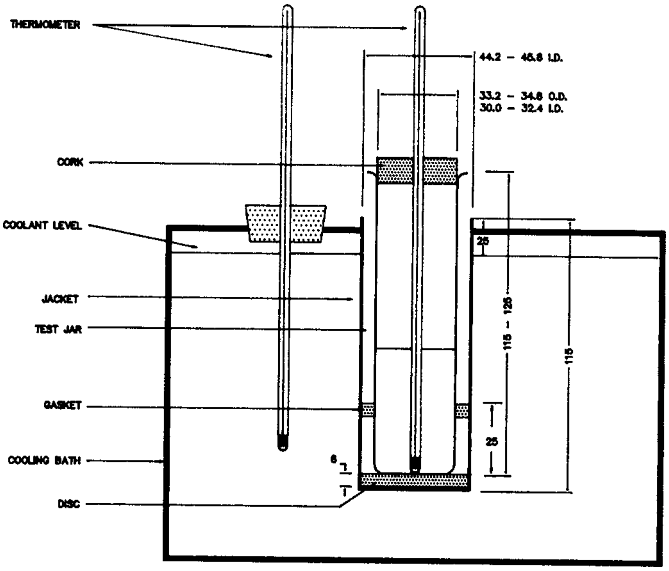
4.1 The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

5. Significance and Use

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

6. Apparatus (see Fig. 1)

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



NOTE—All dimensions are in milllimetres.

FIG. 1 Apparatus for Cloud Point Test

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

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

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

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

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

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

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

7. Reagents and Materials

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

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

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

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

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

TABLE 1 Cooling Mixtures and Bath Temperatures

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

8. Procedure

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

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

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

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

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

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

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

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

TABLE 2 Bath and Sample Temperature Ranges

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

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

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

9. Report

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

10. Precision and Bias

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

11. Keywords

11.1 cloud point; petroleum products; wax crystals

SUMMARY OF CHANGES

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

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

APPENDIX 5

ASTM D 97-05

Designation: D 97 – 05

An American National Standard

Designation: 15/95

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

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

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

1. Scope*

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 117 Guide for Sampling, Test Methods, and Specifications for Electrical Insulating Oils of Petroleum Origin

D 396 Specification for Fuel Oils

D 1659 Test Method for Maximum Fluidity Temperature of Residual Fuel Oil[4]

D 2500 Test Method for Cloud Point of Petroleum Products

D 3245 Test Method for Pumpability of Industrial Fuel Oils

D 5853 Test Method for Pour Point of Crude Oils

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standards:*

Specifications for IP Standard Thermometers [5]

3. Terminology

3.1 *Definitions:*

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

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

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

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

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

4. Summary of Test Method

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

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

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

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

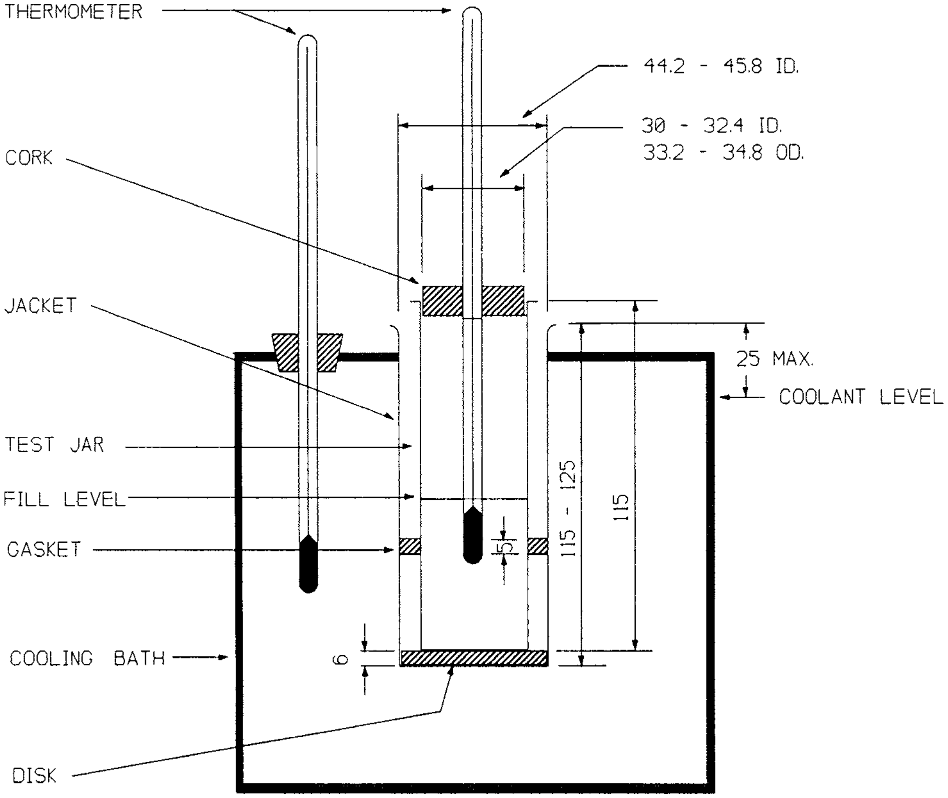
[2] Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in Guide D 117.

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

[4] Withdrawn.

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

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



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

FIG. 1 Apparatus for Pour Point Test

5. Significance and Use

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

6. Apparatus

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

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

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

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

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

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

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

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

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

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

7. Reagents and Materials

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

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

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

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

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

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

8. Procedure

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

9. Calculation and Report

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

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

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

10. Precision and Bias

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

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

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

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

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

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

APPENDIX

(Nonmandatory Information)

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

X1.1 General

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

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

X1.2 Scope

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

X1.3 Definition

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

X1.4 Summary of Test Method

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

X1.5 Significance and Use

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

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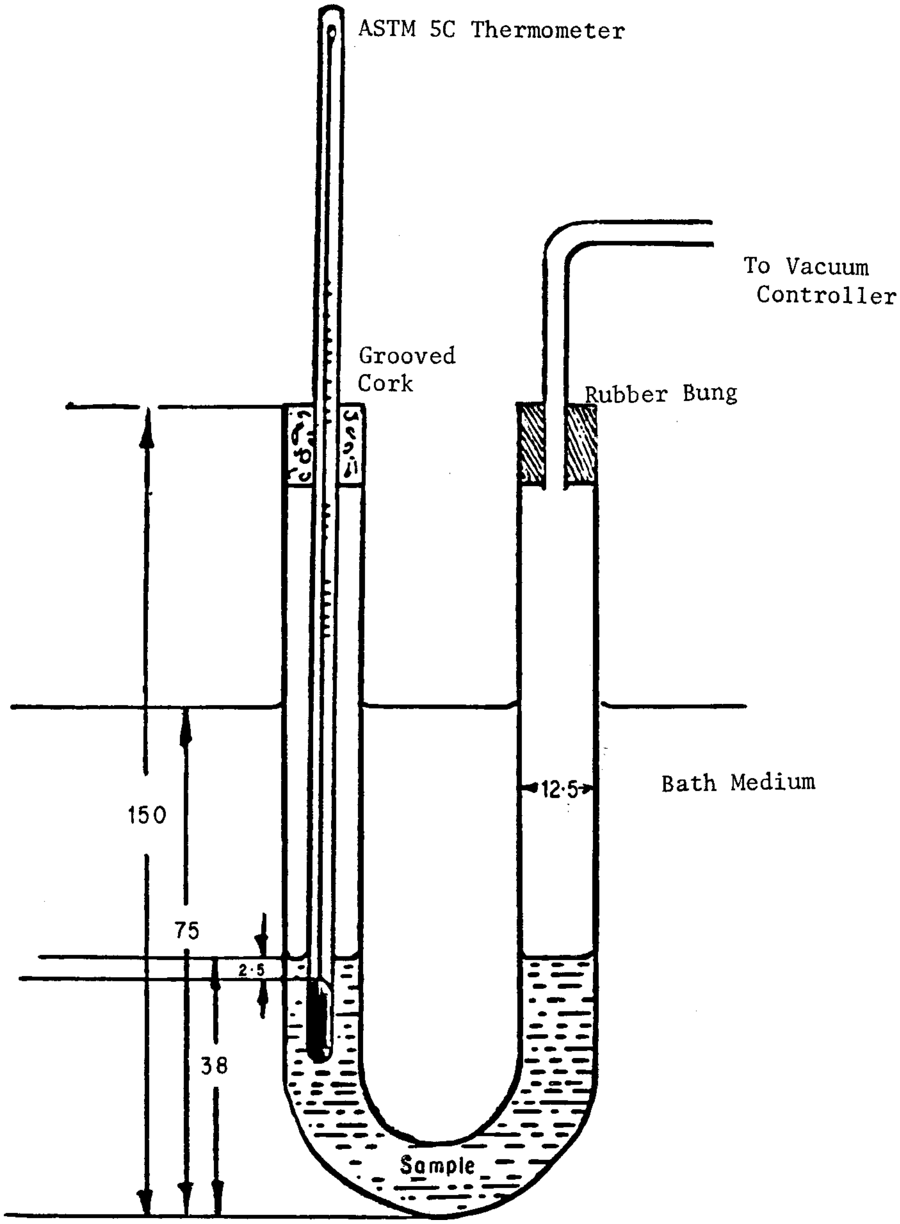
[7] The cloud point procedure formerly part of this test method now appears as Test Method D 2500.



NOTE—All dimensions are in millimetres

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

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

X1.6 Apparatus

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

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

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

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

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[8] A kinematic viscosity bath is usually satisfactory.

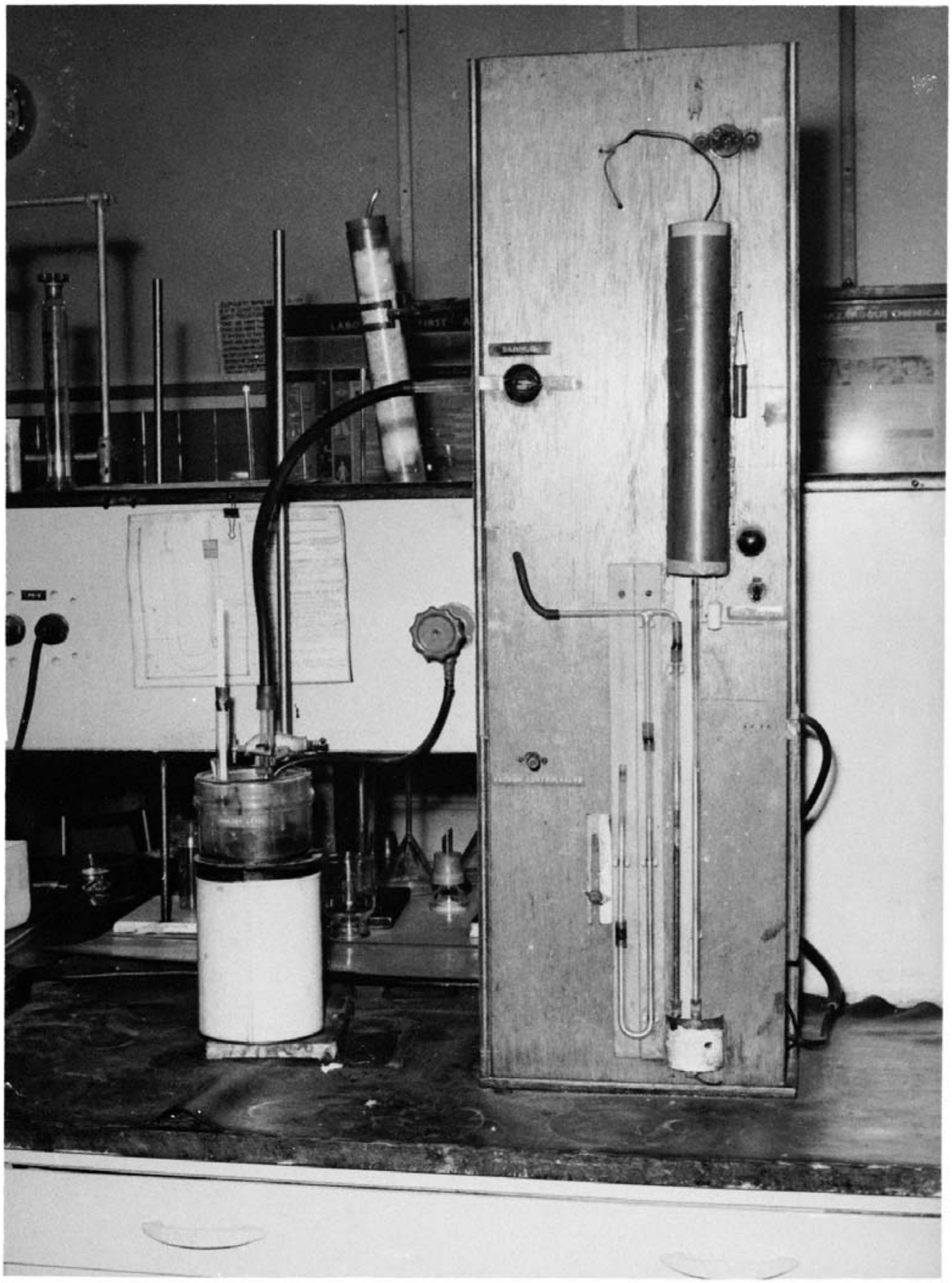

FIG. X1.2 Fluidity Temperature Apparatus

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

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

X1.7 Preparation of Apparatus

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

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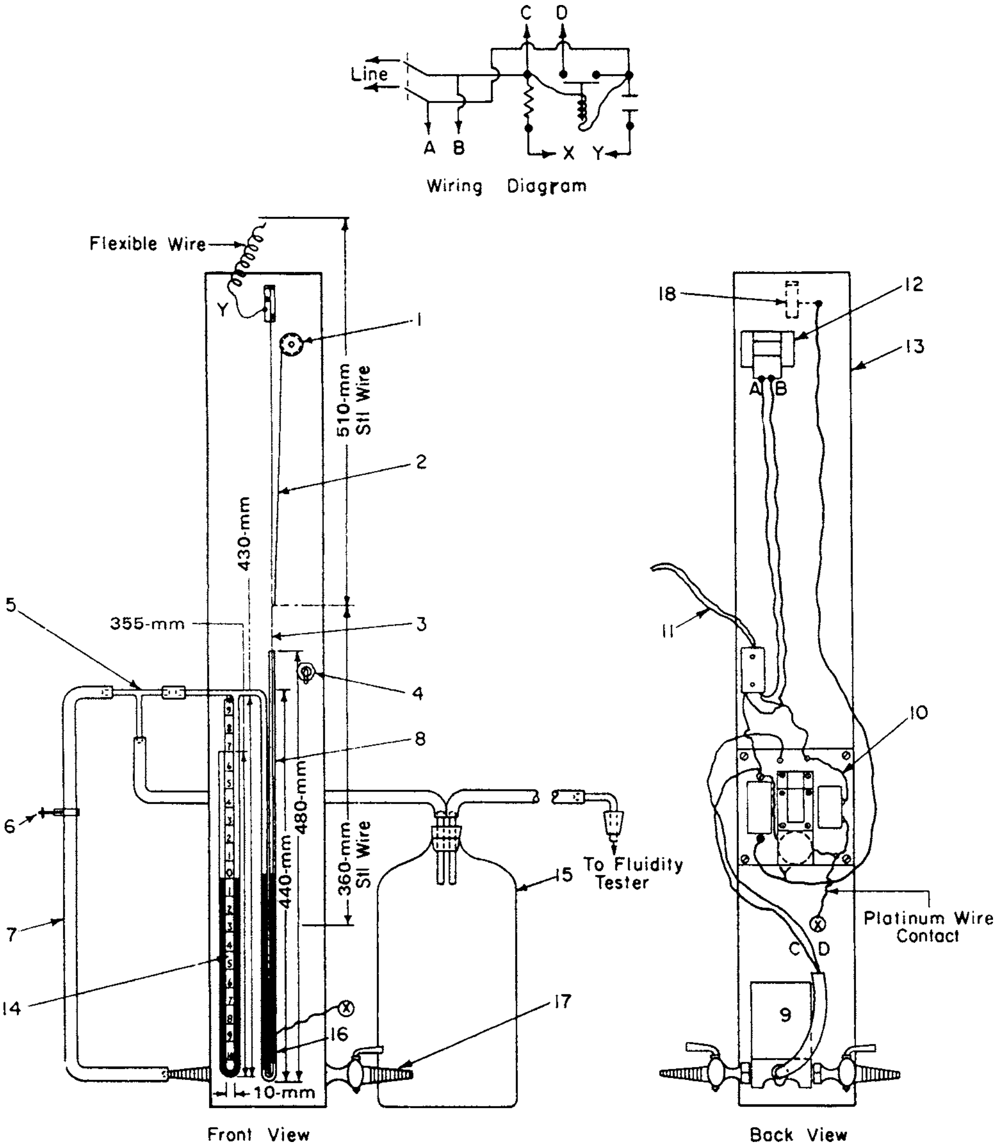
[9] This apparatus may be shop fabricated. Details of special parts are indicated in Figs. X1.3 and X1.4. Alternatively the apparatus can be purchased.



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

FIG. X1.3 Assembly Automatic Vacuum Controller Apparatus

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

X1.8 Procedure

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

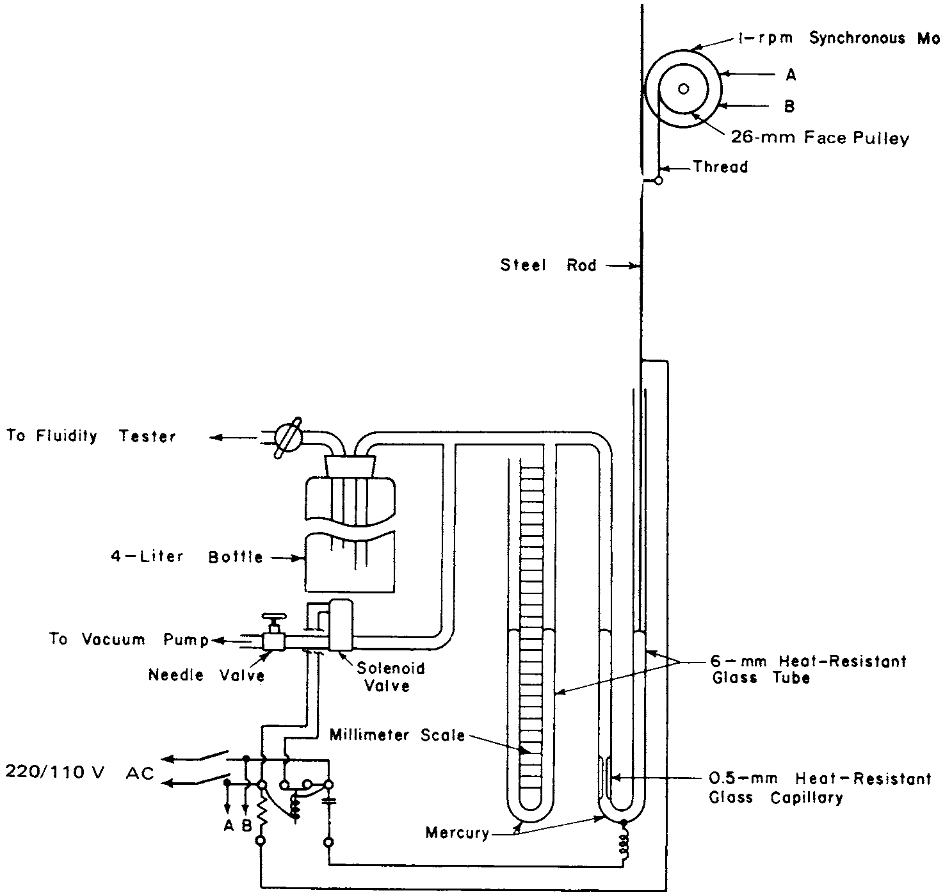


FIG. X1.4 Detail of Automatic Vacuum Controller

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

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

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

X1.9 Report

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

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

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

X1.10 Precision and Bias

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

SUMMARY OF CHANGES

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

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

APPENDIX 6

ASTM D 6371-05

Designation: D 6371 – 05

An American National Standard

Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels[1]

This standard is issued under the fixed designation D 6371; 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.

1. Scope*

1.1 This test method covers the determination of the cold filter plugging point (CFPP) temperature of diesel and domestic heating fuels using either manual or automated apparatus.

NOTE 1—This test method is technically equivalent to test methods IP 309 and EN 116.

1.2 The manual apparatus and automated apparatus are both suitable for referee purposes.

1.3 This test method is applicable to distillate fuels, including those containing a flow-improving or other additive, intended for use in diesel engines and domestic heating installations.

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

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

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 2500 Test Method for Cloud Point of Petroleum Products

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 5771 Test Method for Cloud Point of Petroleum Products (Optical Detection Stepped Cooling Method)

D 5772 Test Method for Cloud Point of Petroleum Products (Linear Cooling Rate Method)

D 5773 Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *IP Standards:*[3]

IP 309 Diesel and domestic heating fuels - Determination of cold filter plugging point

Specifications for IP Standard Thermometers

2.3 *ISO Standards:*[4]

IP 3310 Test sieves - Technical requirements and testing - Part 1: Metal cloth

2.4 *European Standards:*[5]

EN 116 Diesel and domestic heating fuels - Determination of cold filter plugging point

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *certified reference material, n*—a stable petroleum product with a method-specific nominal CFPP value established by a method-specific interlaboratory study following RR:D02-1007[6] guidelines or ISO Guides 34 and 35.[4]

3.1.2 *cold filter plugging point, n*—highest temperature, expressed in multiples of 1°C, at which a given volume of fuel fails to pass through a standardized filtration device in a specified time when cooled under the conditions prescribed in this test method.

4. Summary of Test Method

4.1 A specimen of the sample is cooled under specified conditions and, at intervals of 1°C, is drawn into a pipet under a controlled vacuum through a standardized wire mesh filter. The procedure is repeated, as the specimen continues to cool, for each 1°C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipet exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C.

4.2 The indicated temperature at which the last filtration was commenced is recorded as the CFPP.

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

Current edition approved May 1, 2005. Published May 2005. Originally approved in 1999. Last previous edition approved in 1999 as D 6371–99.

[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.

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

[5] Available from European Committee for Standardization, Central Secretariat, Rue Bréderode 2, B-1000, Brussels, Belgium.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007.

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

5. Significance and Use

5.1 The CFPP of a fuel is suitable for estimating the lowest temperature at which a fuel will give trouble-free flow in certain fuel systems.

5.2 In the case of diesel fuel used in European light duty trucks, the results are usually close to the temperature of failure in service except when the fuel system contains, for example, a paper filter installed in a location exposed to the weather or if the filter plugging temperature is more than 12°C below the cloud point value in accordance with Test Method D 2500, D 5771, D 5772, or D 5773. Domestic heating installations are usually less critical and often operate satisfactorily at temperatures somewhat lower than those indicated by the test results.

5.3 The difference in results obtained from the sample *as received* and after heat treatment at 45°C for 30 min can be used to investigate complaints of unsatisfactory performance under low temperature conditions.

6. Apparatus

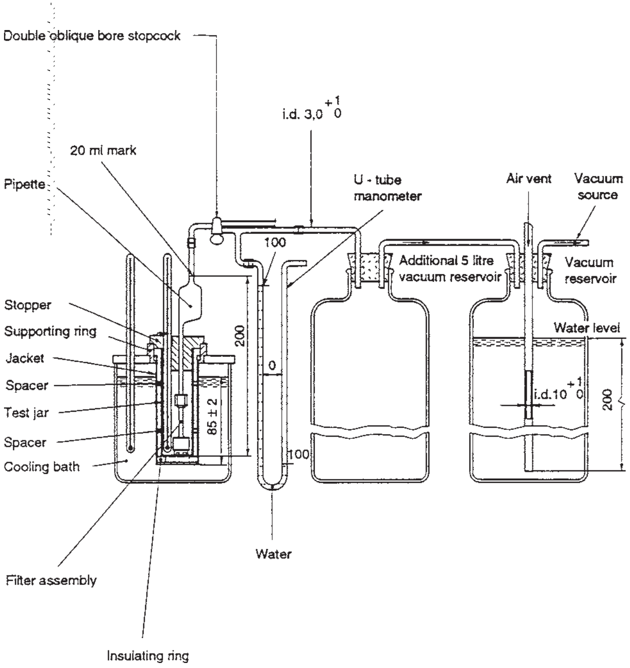
6.1 *Manual Apparatus*:

6.1.1 The apparatus, as detailed in 6.1.2-6.1.13, shall be arranged as shown in Fig. 1.

6.1.2 *Test Jar*, cylindrical, of clear glass, flat bottomed, with an internal diameter of 31.5 ± 0.5 mm, a wall thickness of 1.25 ±0.25 mm and a height of 120 ± 5 mm. The jar shall have a permanent mark at the 45 ± 1 mL level.

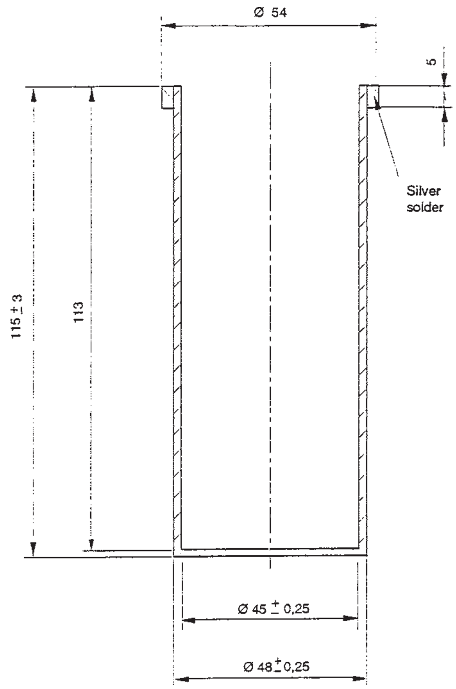
NOTE 2—Test jars of the required dimensions may be obtained by selection from jars conforming to Test Method D 2500, which specifies a wider diameter tolerance.

6.1.3 *Jacket*, brass, watertight, cylindrical, flat bottomed, to be used as an air bath. It shall have an inside diameter of 45 ±0.25 mm, outside diameter of 48 ± 0.25 mm, and a height of 115 ± 3 mm (see Fig. 2).



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 1 Arrangement of Manual CFPP Apparatus



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

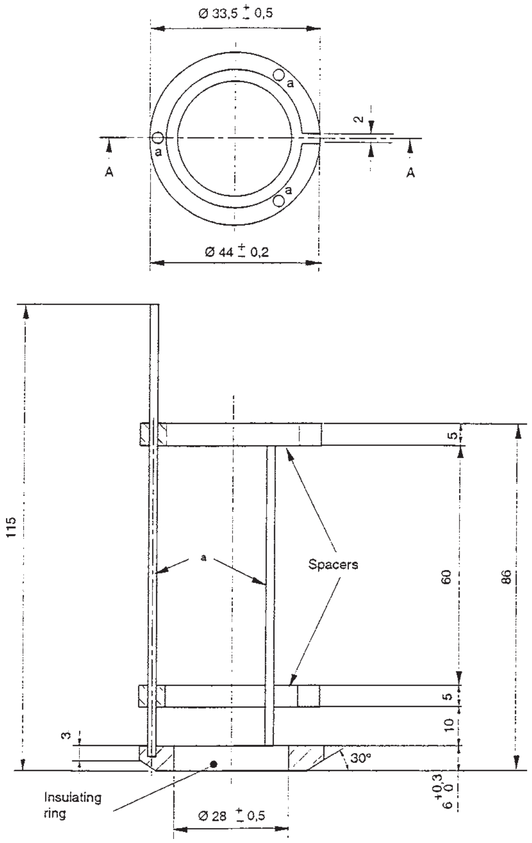
FIG. 2 Watertight Brass Jacket

6.1.4 *Insulating Ring*, made from oil-resistant plastics or other suitable material, to be placed in the bottom of the jacket (see 6.1.3) to provide insulation for the bottom of the test jar. It shall fit closely inside the jacket and have a thickness of 6 + 0.3 - 0.0 mm.

6.1.5 *Spacers (two)*, approximately 5-mm thick, made of oil-resistant plastics or other suitable material, to be placed as shown in Fig. 1 around the test jar (see 6.1.2) to provide insulation for the test jar from the sides of the jacket. The spacers shall fit closely to the test jar and closely inside the jacket. The use of incomplete rings, each with a 2-mm circumferential gap, will accommodate variations in test jar diameter. The spacers and insulating ring may be made as a single part as shown in Fig. 3.

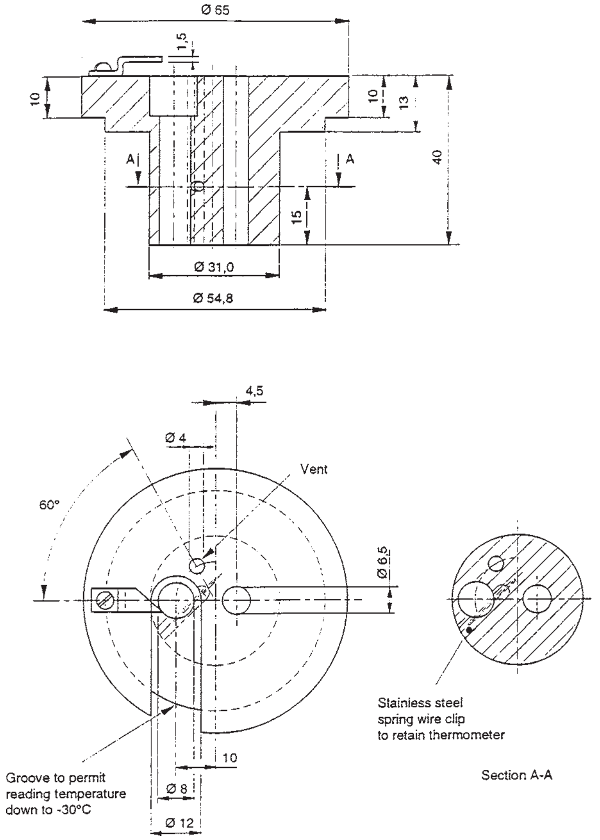
6.1.6 *Supporting Ring*, of oil resistant plastics or other suitable non-metallic, non-absorbent, oil-resistant material, used to suspend the jacket (see 6.1.3) in a stable and upright position in the cooling bath and to provide a concentric location for the stopper (see 6.1.7). A design is shown in Fig. 4 for guidance, but this design may be modified to suit the cooling bath.

6.1.7 *Stopper*, of oil-resistant plastics or other suitable nonmetallic, nonabsorbent, oil-resistant material, to fit the test jar and the support ring as shown in Fig. 5. It shall have three holes to accommodate the pipet (see 6.1.8) and the thermometer (see 6.1.9) and to allow venting of the system. If necessary, when using the high-range thermometer (see 6.1.9), the upper part of the stopper shall have an indentation to permit the thermometer (see 6.1.9) to be read down to a temperature of -30°C. A pointer shall be fitted to the upper surface of the stopper to facilitate location of the thermometer in relation to



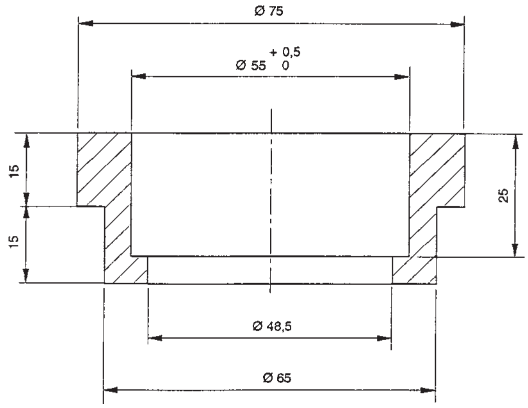
NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 3 Spacers


Ø 65
1,5
10
10
13
A
A
40
15
Ø 31,0
Ø 54,8
4,5
Ø 4
Vent
60°
Ø 6,5
Stainless steel spring wire clip to retain thermometer
Section A-A
10
Groove to permit reading temperature down to -30°C
Ø 8
Ø 12

NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 5 Stopper with Holes for Thermometer, Pipet, and Vent



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 4 Supporting Ring

the bottom of the test jar. A spring wire clip shall be used to retain the thermometer in the correct position.

6.1.8 *Pipet with Filter Unit*:

6.1.8.1 *Pipet*, of clear glass with a calibration mark corresponding to a contained volume of 20 ± 0.2 mL at a point 149 ± 0.5 mm from the bottom of the pipet (see Fig. 6). It shall be connected to the filter unit (see 6.1.8.2).

6.1.8.2 *Filter Unit (see* Fig. 7*)*, containing the following elements:

(1) Brass Body, with a threaded cavity that houses the wire mesh holder. The cavity shall be fitted with an O-ring of oil-resistant plastics. The internal diameter of the central tube shall be 4 ± 0.1 mm.

(2) Brass Screw Cap, to connect the upper part of the body of the filter unit (see 6.1.8.2) to the lower part of the pipet (see 6.1.8.1) to ensure a leak-free joint. An example of satisfactory connection is shown in Fig. 7.

(3) Disc, 15 ± 0.1-mm diameter, of plain weave stainless steel wire mesh gauze with a nominal aperture size of 45 µm. The nominal diameter of the wire shall be 32 µm, and the tolerance for the size of an individual aperture shall be as follows:

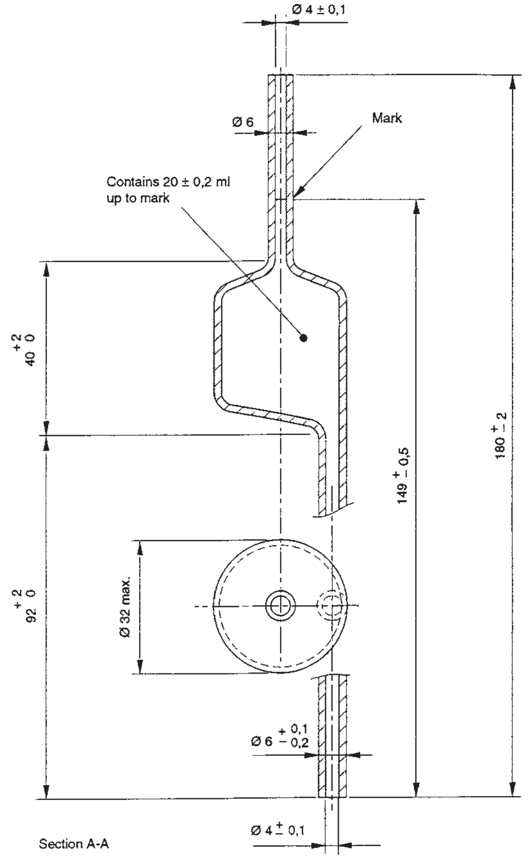
No aperture size shall exceed the nominal size by more than 22 µm.

The average aperture size shall be within ± 3.1 µm of the nominal size.

Not more than 6 % of the apertures shall be above the nominal size by more than 13 µm.

(4) Filter Holder of Brass, in which the disc of wire mesh gauze (see 6.1.8.2 (*3*)) is firmly clamped by a retaining ring pressed into the filter holder. The diameter of the exposed part of the gauze shall be 12 + 0.1 - 0.0 mm (see Fig. 8).

(5) Brass Cylinder, threaded on the outside, that can be screwed into the cavity of the body (see 6.1.8.2 (*1*)) to clamp the filter holder (see 6.1.8.2 (*4*)) against the O-ring (6.1.8.2



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 6 Pipet

(*1*)), The lower end shall have four slots to allow the specimen to flow into the filter unit.

NOTE 3—The requirements for the wire mesh are taken from ISO 3310, to which reference may be made for methods for testing the gauze.

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

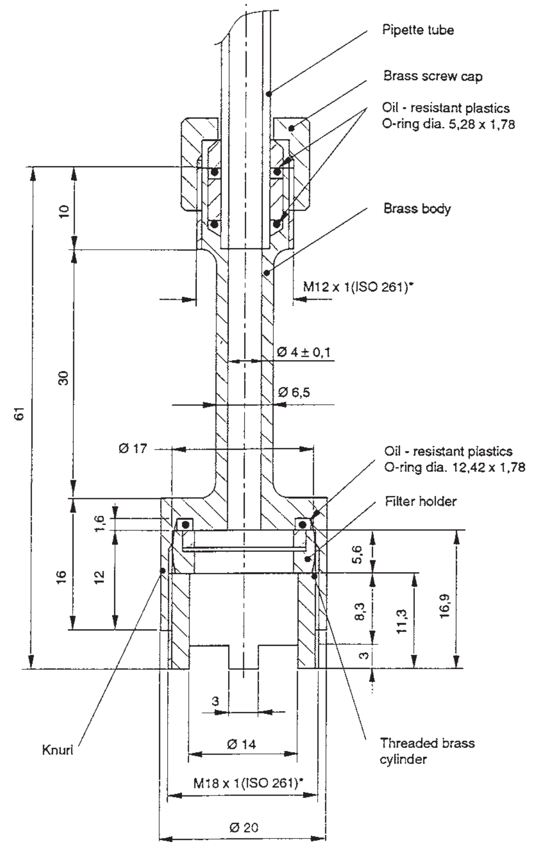
Thermometer	Temperature Range	Thermometer Number ASTM	IP
High-range for CFPP down to −30°C	−38°C to +50°C	5C	1C
Low-range from CFPP below −30°C	−80°C to +20°C	6C	2C
Cooling bath	−80°C to +20°C	6C	2C

6.1.10 *Cooling Bath*:

6.1.10.1 The type of cooling bath is optional, but it shall be of a shape and size suitable for containing the jacket (see 6.1.3) in a stable and upright position at the required depth.

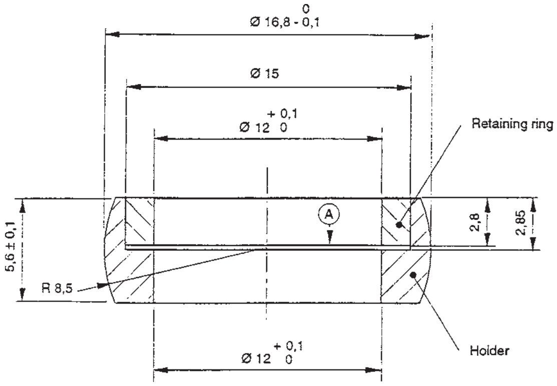
6.1.10.2 The bath shall be fitted with a cover with one or more holes in it to accommodate the supporting ring (see 6.1.6). The jacket (see 6.1.3) may be permanently mounted in the cover.

6.1.10.3 The bath temperature shall be maintained at the required value and tolerance by a refrigeration unit or by the use of suitable freezing mixtures, ensuring a homogenous temperature in the bath by stirring or other means of agitation.



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 7 Filter Unit



NOTE—All dimensions are in millimetres, and the comma (,) is used as the decimal point.

FIG. 8 Brass Filter Holder

Table 1 lists the bath temperature set-points required in the CFPP procedure. If only one bath is utilized, it must have the

TABLE 1 Cooling Bath Temperatures

Expected CFPP	Required Cooling Bath Temperature(s)
Down to −20°C	−34 ± 0.5°C
Between −20°C and −35°C	−34 ± 0.5°C then −51 ± 1°C
Below −35°C	−34 ± 0.5°C then −51 ± 1°C then −67 ± 2°C

ability to change down to the next lower set-point temperature in a time period not exceeding 2 min 30 s.

6.1.11 *Stopcock*, glass, with double oblique bore of 3-mm diameter.

6.1.12 *Vacuum Source*, vacuum pump or water pump powerful enough to ensure an air flow rate in the vacuum regulator of 15 ± 1 L/h for the duration of the test.

6.1.13 *Vacuum Regulator*, consisting of a glass bottle, at least 350-mm high, not less than 5 L capacity, partially filled with water. It shall be closed by a stopper with three holes of convenient diameters for glass tubes. Two tubes shall be short and shall not go below the water level. The third tube, with an internal diameter of 10 ± 1 mm, shall be long enough for one end to be approximately 200 mm beneath the surface of the water while the other end reaches a few centimetres above the stopper. The depth of the immersed part shall then be adjusted to obtain a depression of 200 ± 1 mm of water (2 ± 0.05 kPa) on the manometer, which shall contain water. A second empty 5 L bottle shall be fitted in the line to serve as a vacuum reservoir to ensure a constant depression. The arrangement is shown in Fig. 1.

6.1.14 *Stopwatch*, with a graduation or reading of 0.2 s or lower, with an accuracy of 0.1 % over a period of 10 min.

6.2 *Automated Apparatus*:

6.2.1 The automated apparatus shall include elements conforming to 6.1.1-6.1.8, platinum resistance thermometers, cooling bath(s), vacuum pump, and suitable electronic control and measurement devices.

6.2.2 *Cooling Bath*, a refrigeration unit capable of maintaining the cooling bath at the required temperature and also of automatically changing the bath temperature within 2 min 30 s at the appropriate stage (see 12.2.5).

6.2.3 *Vacuum Pump*, powerful enough to ensure an air flow rate in the vacuum regulator of a minimum of 15 ± 1 L/h, and to maintain a constant vacuum of 200 ± 1 mm (2 ± 0.05 kPa) for the duration of the test. For multi-position testers using the same vacuum pump, the flow rate shall be checked when several positions are operating simultaneously.

7. Reagents and Materials

7.1 *Heptane*, clean commercial or reagent grade. (**Warning—**Flammable. Harmful if inhaled.)

7.2 *Acetone*, clean commercial or reagent grade. (**Warning—**Extremely flammable.)

7.3 *Filter Paper*, (approximately 4 to 6 µm retention).

7.4 *Certified Reference Materials*.

8. Sampling

8.1 Unless otherwise specified in the commodity specification, samples shall be taken as described in Practice D 4057 or D 4177 in accordance with the requirements of national standards or regulation for the sampling of the product under test, or both.

9. Preparation of Test Specimen

9.1 Filter approximately 50 mL of the sample (see 8.1) at laboratory ambient temperature, but in any case not at a temperature less than 15°C, through dry filter paper (see 7.3).

10. Preparation of Apparatus

10.1 Prepare the manual apparatus or the automated apparatus for operation in accordance with the manufacturer's instructions for calibrating, checking, and operating the equipment. See Fig. 1 for manual apparatus.

10.2 Before each test, dismantle the filter unit (see 6.1.8.2) and wash the pieces and the test jar (see 6.1.2), the pipet (see 6.1.8.1) and the thermometer (see 6.1.9 for manual apparatus and 6.2 for platinum resistance used in automated equipment) with heptane (see 7.1), then rinse with acetone (see 7.2) and dry in a stream of filtered air. Check the cleanliness and dryness of all elements, including the jacket (see 6.1.3). Examine the wire mesh (see 6.1.8.2(*3*)) and the joints (see 6.1.8.2(*1*) and 6.1.8.2(*2*) for damage; if necessary renew them.

10.3 Check that the screw cap (see 6.1.8.2(*2*) is tight enough to prevent leakage.

11. Calibration and Standardization

11.1 Adjust the automated CFPP apparatus (when used) in accordance with the manufacturer's instructions.

11.2 Calibrate the temperature measuring device in accordance with the manufacturer's instructions.

11.3 Periodically verify the correct functioning of manual and automated apparatus using a certified reference material or in-house secondary reference material, such as fuel of known CFPP value.

NOTE 4—It is preferable that verification be carried out at least two times a year, where possible, using certified reference materials. The apparatus should be checked more frequently (for example, weekly) using a secondary verification material.

11.4 When the CFPP values obtained using a verification material deviate by more than the test repeatability (see 15.2), or an unacceptable statistical quality control bias is observed, check the condition and operation of the apparatus to ensure conformity with the specification as stated in this test method. The manufacturer's instruction manual should provide guidance on ensuring that the apparatus is correctly set up and calibrated.

12. Procedure

12.1 *Manual Apparatus*:

12.1.1 Establish the cooling bath temperature at –34 ± 0.5°C

12.1.2 Place the insulating ring (see 6.1.4) on the bottom of the jacket (see 6.1.3). If spacers (see 6.1.5) are not mounted on the insulating ring (see 6.1.4), position them approximately 15 and 75 mm above the bottom of the test jar (see 6.1.2).

12.1.3 Pour the filtered specimen (see Section 9) into the clean and dry test jar to the mark (45 mL).

12.1.4 Close the test jar with the stopper (see 6.1.7) carrying the pipet with filter unit (see 6.1.8) and the appropriate thermometer (see 6.1.9). Use a low-range thermometer if the expected CFPP is below –30°C. Thermometers shall not be changed during the test. Adjust the apparatus in such a way that the bottom of the filter unit (see 6.1.8.2(*5*)) rests on the bottom of the test jar, and position the thermometer so that its lower end is 1.5 ± 0.2 mm above the bottom of the test jar. Take care to ensure that no part of the thermometer is not in contact with the side of the test jar or the filter body.

NOTE 5—The precise positioning of the thermometer in the test jar is a critical parameter of this test method. The position of the lower end of the thermometer above the bottom of the test jar can be indirectly measured by marking the stem of the thermometer flush with the stopper (see 6.1.7) when the lower end of the thermometer is just touching the bottom of the test jar, and then pulling the thermometer up such that the reference line is 1.5 ± 0.2 mm above the top of the stopper.

12.1.5 If the jacket is not an integral part of the cooling bath, place the jacket vertically to a depth of 85 ± 2 mm in the cooling bath (see 6.1.10), which is maintained at the temperature of –34 ± 0.5°C.

12.1.6 Insert the test jar assembly in a stable vertical position into the jacket.

12.1.7 With the stopcock (see 6.1.11) open to atmosphere, connect the pipet to the vacuum system (see 6.1.12 and 6.1.13) by means of flexible tubing attached to the stopcock (see Fig. 1). Switch on the vacuum source and regulate to ensure an air flow rate of 15 L/h in the vacuum regulator (see 6.1.13). Before starting a test, check that the U-tube manometer indicates a 200 ± 1 mm of water depression (2 ± 0.05 kPa).

12.1.8 Start the test immediately after inserting the test jar assembly into the jacket, but if the cloud point of the sample is known, it is permitted to wait until the specimen has cooled to a temperature of not less than 5°C above its cloud point.

12.1.9 When the specimen temperature reaches a suitable integer value, turn the stopcock (see 6.1.11) so that the filter assembly is connected to the vacuum source, causing the specimen to be drawn through the wire mesh into the pipet; simultaneously start the stopwatch.

12.1.10 When the specimen reaches the mark on the pipet, stop the stopwatch and turn the stopcock to its initial position to vent the pipet and so allow the specimen to return to the test jar.

12.1.11 If the time taken to reach the mark exceeds 60 s on the first filtration, abandon the test and repeat it on a fresh portion, starting at a higher temperature.

12.1.12 Repeat the operations (see 12.1.9 to 12.1.10) for each 1°C decrease of the specimen temperature until the temperature is reached at which the pipet is not filled to the 20 mL mark within 60 s. Record the temperature at which this last filtration was commenced as CFPP (see Section 13).

NOTE 6—A small minority of samples may exhibit anomalous aspiration behavior, which can be detected by examining the observed aspiration times. This behavior is marked by an unexpected reduction in the time taken to fill the pipet, after which aspiration time again continues to increase progressively, until the failure limit of 60 s is reached.

12.1.13 If the filter has not plugged when the temperature of the specimen reaches –20°C, continue the test by using a second cooling bath maintained at –51 ± 1°C, quickly transferring the test jar and filtration assembly to a new jacket placed on the second cooling bath. Alternatively, for single bath apparatus, adjust the refrigeration unit to –51 ± 1°C. The new temperature must be reached within 2 min 30 s of the adjustment. Repeat the operations 12.1.9 to 12.1.10 to each 1°C decrease of the specimen temperature.

12.1.14 If the filter has not plugged when the temperature of the specimen reaches –35°C, continue the test by using a third cooling bath maintained at –67 ± 2°C by quickly transferring the test jar and filtration assembly to a new jacket placed on the second cooling bath. Alternatively, for single bath apparatus, adjust the refrigeration unit to –67 ± 2°C. The new temperature must be reached within 2 min 30 s of the adjustment. Repeat the operations 12.1.9 to 12.1.10 at each 1°C decrease of the specimen temperature.

12.1.15 If the filter has not plugged when the temperature of the specimen reaches –51°C, discontinue the test (see Section 13).

12.1.16 If, after cooling in accordance with 12.1.12, 12.1.13, and 12.1.14, the specimen fills the pipet to the mark in less than 60 s, but does not flow back completely into the test jar when the pipet is vented to atmosphere through the stopcock (see 6.1.11) before the start of the next aspiration, record the temperature at the commencement of the filtration as the CFPP (see Section 13).

12.2 *Automated Apparatus*:

12.2.1 Check that the cooling bath is operating and has reached the temperature required as specified in the manufacturer's instructions.

12.2.2 Pour the filtered specimen (see Section 9) into the clean and dry test jar to the 45 mL mark.

12.2.3 Close the test jar with the stopper (see 6.1.7) carrying the pipet with filter unit (see 6.1.8) and the platinum resistance thermometer. Adjust the apparatus in such a way that the bottom of the filter unit (see 6.1.8.2(*5*)) rests on the bottom of the test jar, and position the thermometer so that its lower end is 1.5 ± 0.2 mm above the bottom of the test jar. Take care to ensure that no part of the thermometer is in contact with the side of the test jar or the filter body.

NOTE 7—The precise positioning of the thermometer in the test jar is a critical parameter of this test method. The position of the lower end of the thermometer above the bottom of the test jar can be indirectly measured by marking the stem of the thermometer flush with the stopper (see 6.1.7) when the lower end of the thermometer is just touching the bottom of the test jar, and then pulling the thermometer up such that the reference line is 1.5 ± 0.2 mm above the top of the stopper.

12.2.4 If necessary, reconnect the pipet to the vacuum system. Switch on the vacuum source and regulate to ensure an air flow rate of 15 L/h in the vacuum regulator. Check that the U-tube manometer (if used) indicates a 200 ± 1 mm depression (2 ± 0.05 kPa) or that the electronic vacuum regulator indicates a pressure of 2 ± 0.05 kPa.

12.2.5 Press the start button immediately after insertion of the test jar assembly. If the cloud point is known, aspiration of the specimen through the filter may be set to start when it has cooled to a temperature not less than 5°C above the cloud point. The apparatus will carry out the test procedure filtering the specimen at each 1°C decrease if temperature and measuring the filtering time. If the time to reach the 20 mL mark exceeds 60 s on the first filtration, the test is to be abandoned and repeated on a fresh specimen starting at a higher temperature. The apparatus will record the first temperature at which the specimen fails to reach the 20 mL mark in less than 60 s or fails to flow back into the test jar when the vacuum is cut off as CFPP (see Section 13). The test will be discontinued if the specimen reaches −51°C without plugging (see Section 13). During the procedure, the apparatus will automatically change the cooling bath temperature as indicated below.

	Bath Temperature
Start of test	−34 ± 0.5°C
When (if) specimen reaches −20°C	−51 ± 1°C
When (if) specimen reaches −35°C	−67 ± 2°C

NOTE 8—A small minority of samples may exhibit anomalous aspiration behavior, which can be detected by examining the aspiration times recorded in the test printout for signs of an unexpected reduction in the time taken to fill the pipet, after which aspiration time again continues to increase progressively until the failure limit of 60 s is reached.

12.2.6 If the automated CFPP apparatus used does not incorporate a lower light sensor, it shall only be used if the test sequence is observed as in the manual procedure (see 12.1.16), so that any fuels not flowing back into the test jar as described are detected and reported accordingly.

13. Report

13.1 Report the temperature read or indicated at the beginning of the last filtration to the nearest 1°C (see 12.1.12, 12.1.16, and 12.2.5) as the CFPP.

13.2 If the specimen has reached −51°C without plugging (see 12.1.15 and 12.2.5) report as "Not plugged at −51°C."

13.3 The report shall contain at least the following information:

13.3.1 The type and identification of the product under test;

13.3.2 A reference to this test method;

13.3.3 The sampling procedure used (see Section 8);

13.3.4 The result of the test (13.1 or 13.2);

13.3.5 Any deviation from the procedure described (see Note 6 and Note 8); and

13.3.6 the date of the test.

14. Precision and Bias

14.1 The precision of this procedure as determined by the statistical examination of the interlaboratory test results is as follows:

14.2 *Repeatability*—The difference between results obtained on the same day by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, with normal and correct operation of the test method, exceed 1.76°C only in one case in twenty.

14.3 *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 the values indicated by the formula:

$$0.102\ (25-X)°\mathrm{C}$$

where: X is the average of the two results being compared, only in one case in twenty.

NOTE 9—The interlaboratory test program used to determine the precision of this test method was carried out in 1988 by the IP. The program involved 46 laboratories and 5 samples, ranging in CFPP values from 0°C to −33°C. Extrapolations to measurements more than a few degrees outside this range are unsupported by the data. The raw data from the 1988 program was reanalyzed in 1997 using the ASTM D2PP program. The report of the reevaluation is available from ASTM Headquarters.[7]

14.4 *Bias*—The procedure in this test method has no bias because the value of CFPP can be defined only in terms of a test method.

14.5 *Relative Bias*—The current interlaboratory tests confirm that there is no relative bias between the manual and automated apparatuses. Both apparatuses are suitable for reference purposes.

15. Keywords

15.1 automated cold filter plugging point; cold filter plugging point (CFPP); diesel; domestic heating fuels; filterability; manual cold filter plugging point

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1452.

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 6371–99) that may impact the use of this standard.

(*1*) Modified 7.3 to remove the reference to "lintless."

APPENDIX 7

ASTM D 664-04

Designation: D 664 – 04$^{\epsilon 1}$

An American National Standard
British Standard 4457

Designation 177/96

Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration[1]

This standard is issued under the fixed designation D 664; 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.

ϵ^1 NOTE—Variable *C* in 12.3.1 was corrected editorially in September 2004.

1. Scope*

1.1 This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9}; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9}. The range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH.

NOTE 1—In new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents.

1.2 The test method may be used to indicate relative changes that occur in oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil. Although the titration is made under definite equilibrium conditions, the test method is not intended to measure an absolute acidic property that can be used to predict performance of oil under service conditions. No general relationship between bearing corrosion and acid number is known.

NOTE 2—The acid number obtained by this standard may or may not be numerically the same as that obtained in accordance with Test Methods D 974 and D 3339. There has not been any attempt to correlate this method with other non-titration methods.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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

2. Referenced Documents [2]

2.1 *ASTM Standards:*

D 974 Test Method for Acid and Base Number by Color-Indicator Titration
D 1193 Specification for Reagent Water
D 3339 Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

3.1.1 *acid number, n*—the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified end point.

3.1.1.1 *Discussion*—This test method expresses the quantity of base as milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in a mixture of toluene and propan-2-ol to which a small amount of water has

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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 D02.06 on Analysis of Lubricants.

Current edition approved Feb. 1, 2004. Published March 2004. Originally approved in 1942. Last previous edition approved in 2001 as D 664–01.

This test method was adopted as a joint ASTM-IP standard in 1964. ASTM Test Method D 4739 has been developed as an alternative to the base number portion of D 664.

[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.

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

been added from its initial meter reading in millivolts to a meter reading in millivolts corresponding to an aqueous basic buffer solution or a well-defined inflection point as specified in the test method.

3.1.1.2 *Discussion*—This test method provides additional information. The quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading in millivolts to a meter reading in millivolts corresponding to a freshly prepared aqueous acidic buffer solution or a well-defined inflection point as specified in the test method shall be reported as the *strong acid number.*

3.1.1.3 *Discussion*—The causes and effects of the so-called strong acids and the causes and effects of the other acids can be very significantly different. Therefore, the user of this test method shall differentiate and report the two, when they are found.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions.

5. Significance and Use

5.1 New and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount of acidic substance in the oil, always under the conditions of the test. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

5.2 Since a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosion properties, the test method cannot be used to predict corrosiveness of oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals.

6. Apparatus

6.1 *Manual Titration Apparatus*:

6.1.1 *Meter*, a voltmeter or a potentiometer that will operate with an accuracy of ±0.005 V and a sensitivity of ±0.002 V over a range of at least ±0.5 V when the meter is used with the electrodes specified in 6.1.2 and 6.1.3 and when the resistance between the electrodes falls within the range from 0.2 to 20 MΩ. The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching, with a grounded lead, any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter.

NOTE 3—A suitable apparatus could consist of a continuous-reading electronic voltmeter designed to operate on an input of less than 5×10^{-12} A, when an electrode system having 1000-MΩ resistance is connected across the meter terminals and provided with a metal shield connected to the ground, as well as a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from any external electrostatic field.

6.1.2 *Sensing Electrode*, Standard pH, suitable for nonaqueous titrations.

6.1.3 *Reference Electrode*, Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M–3M LiCl in ethanol.

6.1.3.1 *Combination Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. The combination electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, for example, 1M–3M LiCl in ethanol. These combination electrodes shall have the same response or better response than a dual electrode system. They shall have removable sleeves for easy rinsing and addition of electrolyte.

NOTE 4—A third electrode, such as a platinum electrode, may be used to increase the electrode stability in certain systems.

6.1.4 *Variable-Speed Mechanical Stirrer*, a suitable type, equipped with a propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution. A propeller with blades 6 mm in radius and set at a pitch of 30 to 45° is satisfactory. A magnetic stirrer is also satisfactory.

6.1.4.1 If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the meter reading during the course of the titration.

6.1.5 *Burette*, 10-mL capacity, graduated in 0.05-mL divisions and calibrated with an accuracy of ±0.02 mL. The burette shall have a tip that extends 100 to 130 mm beyond the stopcock and shall be able to deliver titrant directly into the titration vessel without exposure to the surrounding air or vapors. The burette for KOH shall have a guard tube containing soda lime or other CO_2-absorbing substance.

6.1.6 *Titration Beaker*, 250 mL capacity, made of borosilicate glass or other suitable material.

6.1.7 *Titration Stand*, suitable for supporting the electrodes, stirrer, and burette.

NOTE 5—An arrangement that allows the removal of the beaker without disturbing the electrodes and stirrer is desirable.

6.2 *Automatic Titration Apparatus*:

6.2.1 Automatic titration systems shall be able to carry out the necessary analyses as prescribed in the method. As a minimum, the automatic titration system shall meet the performance and specification requirements listed in 6.1 as warranted.

6.2.2 A dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition shall vary depending on the rate of change of the system. The recommended maximum volume increment is 0.5 mL and the recommended minimum volume increment is 0.05 mL.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as being equivalent.

7.1.2 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water at least at the level of Type III of Specification D 1193.

7.3 *Ethanol*, (**Warning**—Flammable and toxic, especially when denatured.)

7.4 *Hydrochloric Acid (HCl)*—Relative density 1.19. (**Warning**—Corrosive, causes burns.)

7.5 *Lithium Chloride*, LiCl.

7.6 *Lithium Chloride Electrolyte*, Prepare a 1M–3M solution of lithium chloride (LiCl) in ethanol.

7.7 *Methanol*, (**Warning**—Flammable. Toxic if swallowed.)

7.8 *Potassium Hydroxide*, (**Warning**—Causes severe burns.)

7.9 *Propan-2-ol, Anhydrous*, (less than 0.1 % H_2O). (**Warning**—Flammable.) If adequately dry reagent cannot be procured, it can be dried by distillation through a multiple plate column, discarding the first 5 % of material distilling overhead and using the 95 % remaining. Drying can also be accomplished using molecular sieves such as Linde Type 4A, by passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent.

NOTE 6—It has been reported that, if not originally inhibited against it, propan-2-ol can contain peroxides. When this occurs, an explosion is possible when the storage of the vessel or other equipment such as a dispensing bottle, is near empty and approaching dryness.

7.10 *Toluene*, (**Warning**—Flammable.)

7.11 *Hydrochloric Acid Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 7.4 and 7.9.) Mix 9 mL of hydrochloric (HCl, relative density 1.19) acid with 1 L of anhydrous propan-2-ol. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of approximately 8 mL (accurately measured) of the 0.1-mol/L alcoholic KOH solution diluted with 125 mL of CO_2-free water.

7.12 *Commercial Aqueous pH 4, pH 7 and pH 11 Buffer Solutions*—These solutions shall be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

7.13 *Potassium Hydroxide Solution, Standard Alcoholic*, (0.1 mol//L). (**Warning**—See 7.8 and 7.9.) Add 6 g of potassium hydroxide (KOH) to approximately 1 L of propan-2-ol. Boil gently for 10 min to effect solution. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO_2) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbents and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO_2-free water.

7.14 *Titration Solvent*—Add 5 ± 0.2 mL of water to 495 ± 5 mL of anhydrous propan-2-ol and mix well. Add 500 ± 5 mL of toluene. (**Warning**—Flammable.) The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

7.15 *Chloroform*, (**Warning**—Flammable. Hazardous material.)

8. Electrode System

8.1 *Preparation of Electrodes*:

8.1.1 When a Ag/AgCl reference electrode is used for the titration and it contains an electrolyte which is not 1M–3M LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

8.2 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent then with water. Dip them into a pH 4 aqueous buffer solution. Read the mV value after stirring one minute. Remove the electrodes and rinse with water. Dip the electrodes into a pH 7 aqueous buffer. Read the mV value after stirring one minute. Calculate the mV difference. A good electrode system will have a difference of at least 158 mV (20 to 25°C). If the difference is less than 158 mV, lift the sleeve of the electrode and insure electrolyte flow. Repeat the measurements. If the difference is still less than 158 mV, clean or replace the electrode(s).

8.2.1 When the sensing electrode and the reference electrode are separate, one pair of electrodes shall be considered as

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

one unit. If one or the other is changed, it shall be considered as different pair and shall be re-tested.

8.3 *Maintenance and Storage of Electrodes*—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining repeatable potentials, since contamination may introduce uncertain erratic and unnoticeable liquid contact potentials. While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be quite serious when end points are chosen at arbitrarily fixed cell potentials.

8.3.1 Clean the glass electrode at frequent intervals based on use and type of samples being analyzed (not less than once every week during continual use) by immersing in non-chromium containing, strongly oxidizing cleaning solution. The reference electrode shall be cleaned periodically when in use or when a new electrode is installed. Drain the reference electrode at least once each week and refill with the fresh LiCl electrolyte as far as the filling hole. Ensure that there are no air bubbles in the electrode liquid. If air bubbles are observed, hold the electrode in a vertical position and gently tap it to release the bubbles. Maintain the electrolyte level in the reference electrode above that of the liquid in the titration beaker or vessel at all times.

8.3.2 Prior to each titration soak the prepared electrodes in water (pH 4.5 to 5.5) for at least 5 minutes. Rinse the electrodes with propan-2-ol immediately before use, and then with the titration solvent.

8.3.3 When not in use, immerse the lower half of the reference electrode in LiCl electrolyte. When the glass electrode is used, store it in water that has been acidified with HCl to a pH of 4.5 to 5.5. Do not allow electrodes to remain immersed in titration solvent for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

NOTE 7—*Electrode Life*—Typically, electrode usage is limited to 3 to 6 months depending, upon usage. Electrodes have a limited shelf life and shall be tested before use (see 8.2).

9. Standardization of Apparatus

9.1 *Determination of Meter Readings for the Aqueous Buffer Solutions*—To ensure comparable selection of end points when definite inflection points are not obtained in the titration curve, determine daily, for each electrode pair, the meter readings obtained with aqueous acidic and basic buffer solutions.

NOTE 8—The response of different glass electrodes to hydrogen ion activity is not the same. Therefore, it is necessary to establish regularly for each electrode system the meter readings corresponding to the buffer solutions arbitrarily selected to represent acidic or basic end points.

9.2 Immerse the electrodes in the pH 4 and the pH 11 aqueous buffers and stir each of them for approximately 5 min, maintaining the temperature of the buffer solution at a temperature within 2°C of that at which the titrations are to be made. Read the cell voltage for each of them. The readings so obtained are taken as the end points in titration curves having no inflection points.

10. Preparation of Sample of Used Oil

10.1 Strict observance of the sampling procedure is necessary since the sediment itself is acidic or basic or has absorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

10.1.1 When applicable, refer to Practice D 4057 (Manual Sampling) or Practice D 4177 (Automatic Sampling) for proper sampling techniques.

10.1.2 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources.

NOTE 9—As used oil can change appreciably in storage, test samples as soon as possible after removal from the lubricating system; and note the dates of sampling and testing.

10.2 Heat the sample (see Note 10) of used oil to 60 ± 5°C in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can or if it is glass and more than three-fourths full, transfer the entire sample to a clear-glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by vigorous agitation of portions of the sample in the original container.

NOTE 10—When samples are visibly free of sediment, the heating procedure described can be omitted.

10.3 After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100-mesh screen for removal of large contaminating particles.

NOTE 11—When samples are visibly free of sediment, the straining procedure described can be omitted.

11. Procedure for Acid Number and Strong Acid Number

11.1 Into a 250-mL beaker or a suitable titration vessel, introduce a weighed quantity of sample as recommended in Table 1 (see Note 12) and add 125 mL of titration solvent (see Note 13). Prepare the electrodes as directed in 8.2. Place the beaker or titration vessel on the titration stand and adjust its position so that the electrodes are about half immersed. Start the stirrer, and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

NOTE 12—If it suspected that the recommended sample size will foul the electrodes, a smaller sample size can be taken. Results using smaller sample size may not be equivalent to results obtained with the recommended sample size. The precision statement does not include results when using a smaller sample size.

NOTE 13—A titration solvent that contains chloroform (**Warning**—

TABLE 1 Recommended Size of Test Portion

Acid Number	Mass of Test Portion, g	Accuracy of Weighing, g
0.05 – < 1.0	20.0 ± 2.0	0.10
1.0 – < 5.0	5.0 ± 0.5	0.02
5 – < 20	1.0 ± 0.1	0.005
20 – < 100	0.25 ± 0.02	0.001
100 – < 260	0.1 ± 0.01	0.0005

May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned) can be used in place of toluene to completely dissolve certain heavy residues of asphaltic materials. Results using chloroform may not be equivalent to results obtained using toluene. The precision statement does not include results when using chloroform.

11.2 Select the right burette, fill with the 0.1-mol/L alcoholic KOH solution, and place the burette in position on the titration assembly, ensuring that the tip is immersed about 25 mm in titration vessel liquid. Record the initial burette and meter (cell potential) readings.

11.3 *Manual Titration Method*:

11.3.1 Add suitable small portions of 0.1-mol/L alcoholic KOH solution and wait until a constant potential has been established, record the burette and meter readings.

11.3.2 At the start of the titration and in any subsequent regions (inflections) where 0.1 mL of the 0.1-mol/L KOH solution consistently produces a total change of more than 30 mV in the cell potential, add 0.05-mL portions.

11.3.3 In the intermediate regions (plateau) where 0.1 mL of 0.1-mol/L alcoholic KOH changes the cell potential less than 30 mV, add larger portions sufficient to produce a total potential change approximately equal to, but not greater than 30 mV.

11.3.4 Titrate in this manner until the potential changes less than 5 mV/0.1 mL of KOH and the cell potential indicates that the solution is more basic than the aqueous basic buffer.

11.3.5 Remove the titration solution, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol and finally with reagent grade water. Immerse the electrodes in water for at least 5 min before starting another titration to restore the aqueous gel layer of the glass electrode. After 5 min in the water, rinse the electrodes with propan-2-ol then the titration solvent before proceeding to the next titration. If the electrodes are found to be dirty and contaminated, proceed as in 8.1. Store electrodes according to 8.3.3.

11.4 *Automatic Titration Method*:

11.4.1 Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titrant addition.

11.4.2 Verify that the instrument will determine the amount of strong acid when the initial mV of the test sample, relative to the mV reading of the aqueous acidic buffer, indicates the presence of such acids. Record the volume of KOH added to reach the mV of the pH 4 aqueous buffer. This value is used to calculate the strong acid number. Proceed with the automatic titration and record potentiometric curves or derivative curves as the case may be.

11.4.3 Titrate with the 0.1-mol/L alcoholic KOH solution. The apparatus shall be adjusted or programmed such that, when an inflection point, suitable for use in the calculation is approached, the rate of addition of titrant and volume of titrant added are based on the change in slope of the titration curve. The titrant shall be added in increments of a suitable size to achieve a potential difference of 5 to 15 mV per increment. Increment volume shall vary between 0.05 and 0.5 mL. The next increment shall be added if the signal does not change more than 10 mV in 10 seconds. The maximum waiting time in between increments shall not exceed 60 seconds.

11.4.4 The titration can be terminated when the signal reaches the pH 11 buffer potential past 200 mV. An equivalence point is recognizable if the first derivative of the titration curve produces a maximum, which is significantly higher than the noise produced by electrostatic effects. See also 12.1.1.

11.4.5 On completion of the titration, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol, and finally with reagent grade water. Immerse the electrodes in water for at least 5 min before starting another titration to restore the aqueous gel layer of the glass electrode. Rinse the electrodes with propan-2-ol and finally with the titration solvent prior to running the next sample. If electrodes are found dirty and contaminated, proceed as in 8.1. Store electrodes according to 8.3.3.

NOTE 14—When acid numbers about or below 0.1 are expected, better precision can be obtained by modifying the method in one or more ways, such as by substituting a 0.01 or 0.05 M alcoholic KOH solution; increasing the sample size above 20 g; or switching from a manual operated burette (that is, graduated in 0.05 mL divisions) to an automated burette that can dispense smaller increments of the KOH solution, if samples are being analyzed by manual titration.

11.5 *Blanks*:

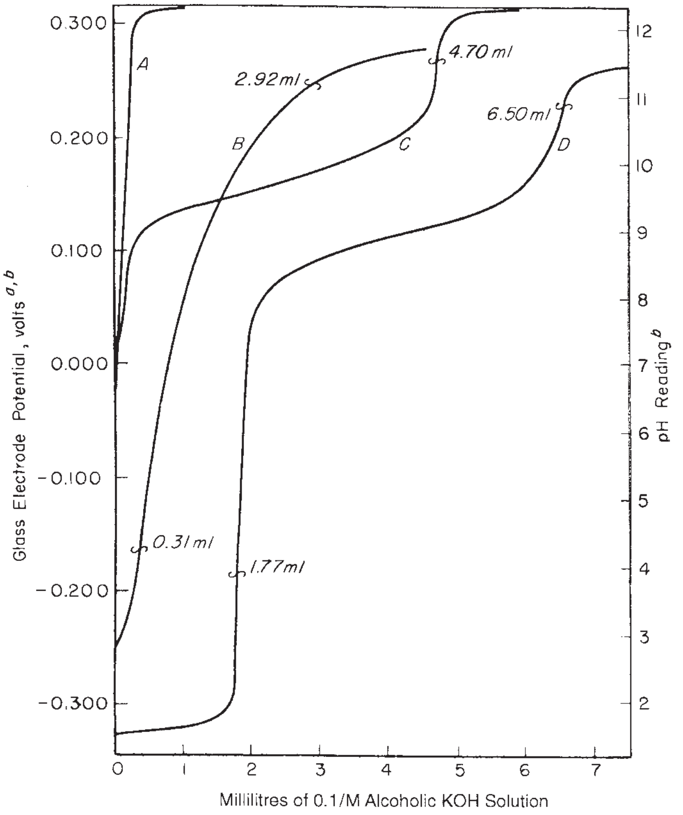
11.5.1 For each set of samples and for every new batch of titration solvent, perform a blank titration of 125 mL of the solvent. For manual titration, add 0.1-mol/L alcoholic KOH solution in 0.01 to 0.05-mL increments, waiting between each addition until a constant cell potential is reached. Record the meter and readings when the former becomes constant after each increment. For automatic titration, use the same mode of titration as for the determination of the acidic property of the sample but use smaller increments of titrant addition, 0.01 to 0.05-mL. Recheck the blank periodically based on the sample load.

11.5.2 When strong acids are present and a strong acid number is to be determined, perform a blank titration of 125 mL of the titration solvent, adding 0.1 mol/L alcoholic HCl solution in 0.01 to 0.05-mL increments in a manner comparable to that specified in 11.5.1.

12. Calculation

12.1 *Manual Titration*—Plot the volumes of the 0.1-mol/L alcoholic KOH solution added against the corresponding meter readings (see Fig. 1). Mark as an end point only a well-defined inflection point (see Note 15) that is closest to the cell voltage corresponding to that obtained with the aqueous acidic or basic buffer. If inflections are ill defined or no inflection appears (see Fig. 1, Curve B), mark the end point at the meter reading corresponding to that obtained with the appropriate aqueous buffer.

NOTE 15—One inflection point is generally recognizable by inspection whenever several successive 0.05-mL increments each produce a cell potential change greater than 15 mV at least 30 % greater than those produced by previous or subsequent increments of the same size. Generally, definite inflection points may be discerned only in regions where increments of the same size are used.



Key:

Curve A—Blank on 125 mL of titration solvent.

Curve B—10.00 g of used crankcase oil plus 125 mL of titration solvent. Since no sharp inflections are apparent, the end points are chosen at the meter readings obtained with the two aqueous buffer solutions.

Curve C—10.00 g of oil containing a weak acid plus 125 mL of titration solvent. The end point is chosen as the point at which the curve is most nearly vertical.

Curve D—10.00 g of oil containing weak and strong acids plus 125 mL of titration solvent. The end points are chosen as the points at which the curve is most nearly vertical.

FIG. 1 Illustrative Titration Curves

12.1.1 Some additive chemistry may produce an inflection point beyond the buffer endpoint. For additives, take the last inflection point for calculation. **Precaution**—If using an automatic titrator, a change in the instrument parameters may be required to detect this type of endpoint.

12.1.2 For all acid titrations on used oils, mark as an end point, the point on the curve that corresponds to the meter reading for an aqueous basic buffer (pH 11) and the meter reading for the aqueous acid buffer (pH 4) when strong acids are indicated.

NOTE 16—The cooperative work done on acid number determinations on fresh oils, additive concentrates, and used oils indicated well-defined inflection points for fresh oils and additive concentrates, and generally ill-defined inflections, or no inflection points at all, for used oils.

12.2 *Automatic Titration Method*—Mark the end points on the curves obtained in 11.4, in the same way as for the manual titration method.

12.3 *Method of Calculation*—The method of calculation in 12.3.1 is applicable to both manual and automatic methods.

12.3.1 Calculate the acid number and strong acid number as follows:

$$\text{Acid number, mg KOH/g} = (A - B) \times M \times 56.1/W \quad (1)$$

$$\text{Strong acid number, mg KOH/g} = (CM - Dm) \times 56.1/W \quad (2)$$

where:

A = volume of alcoholic KOH solution used to titrate sample to end point that occurs at the meter reading of the inflection point closest to the meter reading corresponding to the pH 11 aqueous buffer, or in case of ill-defined or no inflection point, to the meter reading corresponding to the pH 11 aqueous buffer, mL. For additives, A is the volume of alcoholic KOH at the last inflection point,
B = volume corresponding to A for blank titration, mL,
M = concentration of alcoholic KOH solution, mol/L,
m = concentration of alcoholic HCl solution, mol/L,
W = sample, mass, g,
C = alcoholic KOH solution used to titrate the sample to end point that occurs at a meter reading corresponding to the pH 4 aqueous buffer, mL, and
D = alcoholic HCl solution used to titrate solvent blank to end point corresponding to C, mL.

13. Quality Control Checks

13.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

NOTE 17—Because used oils, particularly used engine oils, are known to change during storage, such samples may not be suitable for this purpose.

13.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.[4]

13.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the total testing process.[4] Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

13.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC precision should be periodically checked against the precision listed in the Precision and Bias Section of this method to ensure data quality.

13.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. Because the base number can vary while the QC sample is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

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[4] See *ASTM MNL 7, Manual on Presentation of Data Control Chart Analysis*, 6th edition, ASTM International, W. Conshohocken, PA.

14. Report

14.1 Given there are two different ways to determine the endpoint, report the type of endpoint used: inflection point or buffer endpoint. Report sample size used if differs from the recommended sample size. Also, report if chloroform was used as solvent. Report the results as acid number or strong acid number as follows:

$$\text{Acid number (Test Method D 664)} = \text{(result)} \tag{3}$$

$$\text{Strong acid number (Test Method D 664)} = \text{(result)} \tag{4}$$

14.2 For used oil samples report also the date of testing and, when available, the date the sample was taken (see 10.2).

15. Precision and Bias

15.1 *Acid Number*:

15.1.1 *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 the following values only in one case in twenty.

$$\text{Fresh Oils} = 0.044(X + 1) \tag{5}$$

$$\text{Used Oils Buffer end point} = 0.117\ X \tag{6}$$

where:

X = the average of the two test results.

15.1.2 *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 the following values only in one case in twenty.

$$\text{Fresh Oils} = 0.141(X + 1) \tag{7}$$

$$\text{Used Oils Buffer end point} = 0.44X \tag{8}$$

where:

X = the average of the two test results.

15.2 *Strong Acid Number*:

15.2.1 Precision data have not been developed for strong acid number because of its rare occurrence in sample analysis.

15.3 *Bias*—The procedures in this test method have no bias because the acid values can be defined only in terms of the test method.

16. Keywords

16.1 acid number; lubricants; petroleum products; potentiometric; strong acid number; titration

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D 664–01) that may impact the use of this standard.

(1) The majority of this standard was rewritten and differs significantly from previous versions.

(2) Added information on the use of Ag/AgCl reference electrodes.

(3) Added more specifications for using automatic titration equipment.

(4) Replaced non-aqueous buffers with aqueous buffers throughout.

(5) Removed calomel electrodes, which are difficult to obtain.

(6) Added a Quality Control section.

APPENDIX 8

EN 15751

BRITISH STANDARD

BS EN 15751:2009
BS 2000-574:2009

Automotive fuels — Fatty acid methyl ester (FAME) fuel and blends with diesel fuel — Determination of oxidation stability by accelerated oxidation method

ICS 75.160.20

British Standards

National foreword

This British Standard is the UK implementation of EN 15751:2009.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

Energy Institute, under the brand of IP, publishes and sells all Parts of BS 2000, and all BS EN petroleum test methods that would be Part of BS 2000, both in its annual publication “Standard methods for analysis and testing of petroleum and related products and British Standard 2000 Parts” and individually.

Further information is available from:
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Automotive fuels - Fatty acid methyl ester (FAME) fuel and blends with diesel fuel - Determination of oxidation stability by accelerated oxidation method

Carburants pour automobiles - Esters méthyliques d'acides gras (EMAG) et mélanges avec gazole - Détermination de la stabilité à l'oxydation par méthode d'oxydation accélérée

Kraftstoffe für Kraftfahrzeuge - Kraftstoff Fettsäuremethylester (FAME) und Mischungen mit Dieselkraftstoff - Bestimmung der Oxidationsstabilität (beschleunigtes Oxidationsverfahren)

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Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 15751:2009: E

Contents

Foreword

This document (EN 15751:2009) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by December 2009, and conflicting national standards shall be withdrawn at the latest by December 2009.

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Introduction

This document is based on EN 14112:2003 [1], which was specifically adapted for the determination of oxidation stability of fatty acid methyl esters (FAME). This method had been developed under CEN/TC 307 (Fats and oils). At the time of development the method was applicable for FAME fuel according to EN 14214 [2], but questions remained on the accuracy towards blends of FAME and diesel fuel.

The modifications to EN 14112 as given in this document, allow application of this test method for oxidation stability for pure FAME and diesel/FAME blends at various levels.

The goal was to have one single test method for FAME fuel, diesel/FAME blends and pure diesel fuels. Although the modifications cover FAME fuel and diesel/FAME blends, CEN/TC 307 decided that it was better to retain EN 14112 for methyl esters and publish a separate Standard for all automotive fuel and heating oil applications, as the use of 'diesel and diesel blends' falls out the scope of CEN/TC 307.

The modifications required a new validation covering pure FAME, diesel/FAME blends and pure diesel fuels, which resulted in the fact that the method is not suitable for pure petroleum-based diesel fuels.

1 Scope

This European Standard specifies a test method for determining the oxidation stability of fuels for diesel engines. The method is applicable to fatty acid methyl esters (FAME) intended for use as pure biofuel or as a blending component for diesel fuels, and to blends of FAME and petroleum-based diesel containing 2 volume percentage of FAME at minimum.

NOTE EN 14112 [1] describes a similar test method for oxidation stability determination of pure fatty acid methyl esters (see the Introduction to this European Standard). EN ISO 12205 [3] describes a test method that is applicable to pure petroleum-based diesel.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3170, *Petroleum liquids – Manual sampling (ISO 3170:2004)*

EN ISO 3171, *Petroleum liquids – Automatic pipeline sampling (ISO 3171:1988)*

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply.

3.1
induction period
time which passes between the moment when the measurement is started and the moment when the formation of oxidation products rapidly begins to increase

3.2
oxidation stability
induction period determined according to the procedure specified in this European Standard, expressed in hours

4 Principle

A stream of purified air is passed through the sample which has been brought to a specified temperature. The vapours released during the oxidation process, together with the air, are passed into a flask containing water which has been demineralised or distilled and contains an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of the induction period when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. For more details on the background of the method see Annex A.

5 Reagents and materials

Use only reagents of recognised analytical grade, and distilled or demineralised water [4].

5.1 Ternary solvent mixture, consisting of methanol/toluene/acetone 1:1:1 (by volume)

5.2 Alkaline laboratory glass cleaning solution

5.3 2-Propanol

6 Apparatus

Usual laboratory equipment and glassware, together with the following:

6.1 Appliance for the determination of oxidation stability, consisting of the following (see Figures 1 and 2 for diagrammatic representations):

NOTE An apparatus for determining oxidation stability can be obtained commercially under the trade name Rancimat®, (model 743 or higher, from Metrohm AG, Herisau, Switzerland) or OSI® Instrument (from Omnion Inc., Rockland, Massachusetts, USA). These are examples of suitable equipment and are given for the convenience of users of this document. It does not constitute an endorsement by CEN of this equipment.

6.1.1 Air filter, comprising a tube fitted with filter paper at the ends and filled with a molecular sieve (6.6), connected to the suction end of a pump.

6.1.2 Gas diaphragm pump, with an adjustable flow rate of 10 l/h in combination with an apparatus to control the flow rate manually or automatically with a maximum deviation of ± 1,0 l/h from the set value.

6.1.3 Reaction vessels of borosilicate glass, provided with a sealing cap.

The length of the reaction vessel depends on the measuring equipment and shall stick out of the oven at least for 130 mm. Condensing volatile fuel components at the cold vessel walls outside the oven reduces evaporation losses to a minimum.

EXAMPLE Total length of the test tube for the Metrohm Rancimat 743 L = 250 mm, for the Omnion OSI Instrument L = 300 mm.

The sealing cap shall be fitted with a gas inlet and outlet tube. The cylindrical part of the vessel shall preferably be narrower a few centimetres below the top in order to break any emerging foam. An artificial foam blocker (e.g. glass ring) may also be used for this purpose.

6.1.4 Closed measurement cells, of approximately 150 ml capacity, with a gas inlet tube extending to the bottom inside of the vessel. The cell shall be provided at the top with ventilation holes.

6.1.5 Electrodes, for measuring conductivity with a measuring range of 0 µS/cm to 300 µS/cm aligned with the dimensions of the measurement cell (6.1.4).

6.1.6 Measuring and recording apparatus, comprising of:

a) an amplifier, and

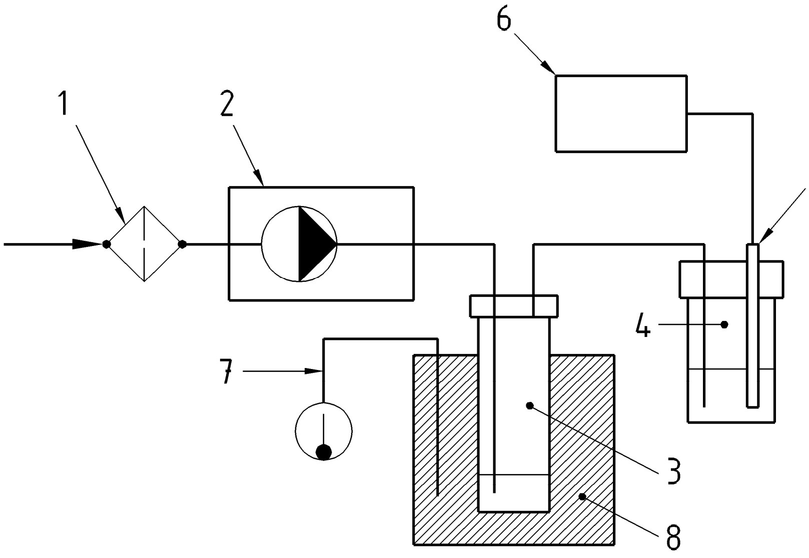
b) a recorder for registering the measuring signal of each of the electrodes (6.1.5).

6.1.7 Thyristor and contact thermometer graduated in 0,1 °C **or Pt 100 element** to measure the block temperature, with attachments for relay connection and an adjustable heating element; temperature scale 0 °C to 150 °C.

6.1.8 Heating block, made of cast aluminium, adjustable to a temperature up to (150 ± 0,1) °C. The block shall be provided with holes for the reaction vessels (6.1.3), and an aperture for the contact thermometer (6.1.7).

Alternatively, a **heating bath** may be used, filled with oil suitable for temperatures up to 150 °C and adjustable to the nearest 0,1 °C.

6.2 Certified and calibrated thermometer or Pt100 element, with a temperature range up to 150 °C, graduated in 0,1 °C.



Key

1	Air filter (6.1.1)	5	Electrode (6.1.5)
2	Gas diaphragm pump with flow rate control (6.1.2)	6	Measuring and recording apparatus (6.1.6)
3	Reaction vessel (6.1.3)	7	Thyristor and contact thermometer (6.1.7)
4	Measurement cell (6.1.4)	8	Heating block (6.1.8)

Figure 1 — Diagrammatic representation of the apparatus

6.3 Measuring pipettes and/or measuring cylinders

6.4 Oven, capable of being maintained up to (150 ± 3) °C.

6.5 Connecting hoses, flexible and made of inert material [polytetrafluoroethylene (PTFE) or silicone].

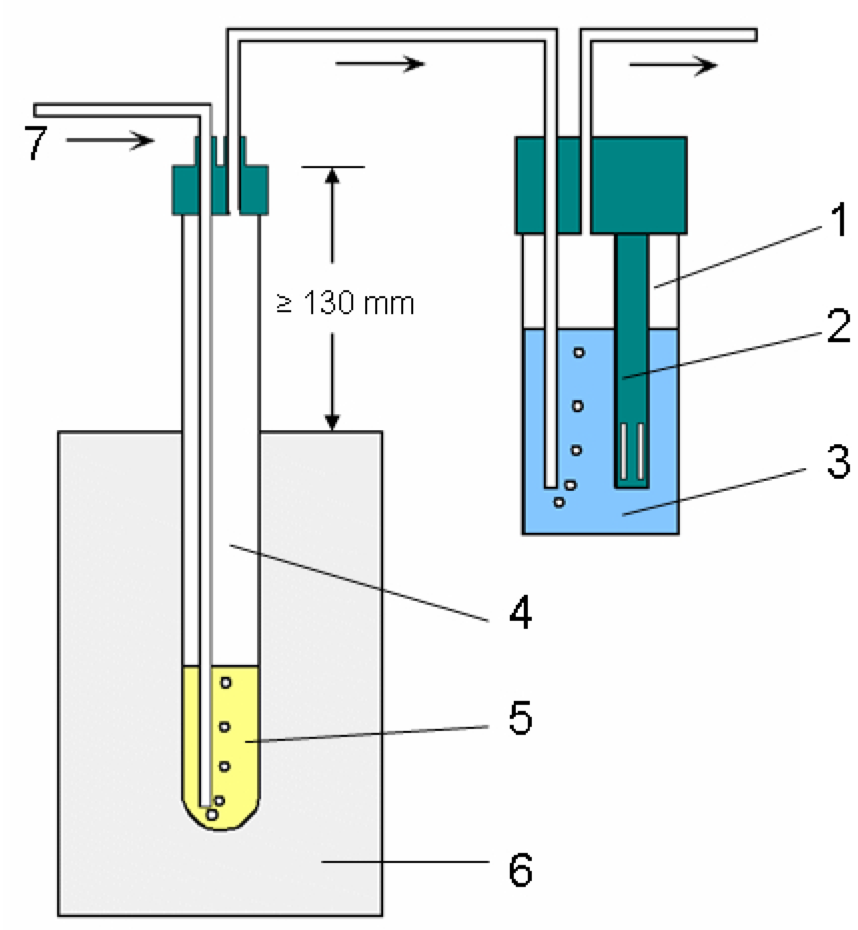
6.6 Molecular sieve, with moisture indicator, pore size 0,3 nm, dried in an oven set at 150 °C and cooled down to room temperature in a desiccator before use.

7 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

It is important that the laboratory receive a sample which is truly representative and has not been damaged or changed during transport and storage.

Store the sample in the dark at about 4 °C and measure it as soon as possible after receipt.



Key

1	Measuring vessel	5	Sample
2	Electrode	6	Heating block
3	Measuring solution	7	Air inlet
4	Reaction vessel		

Figure 2 — Diagrammatic representation of heating block, reaction vessel and measurement cell

8 Preparation of measurement

8.1 Preparation of test sample

In order to prevent the preparation of the test sample from influencing the test result, all handling of the laboratory sample shall be restricted to the steps given below.

Remove the required quantity from the centre of the carefully homogenised sample using a pipette.

Samples shall be analysed immediately after the test sample preparation.

8.2 Preparation of apparatus

8.2.1 Cleaning procedure

NOTE 1 The use of new disposable reaction vessels, air inlet tubes and connecting hoses is recommended in order to save the cleaning procedure.

Always wash the sealing caps, measuring cells and electrodes with 2-Propanol in order to remove organic residues. The connecting hoses should also be washed in the same manner if not replaced.

Rinse with tap water and finally with demineralised or distilled water. Dry them in an oven for at least 2 h at 80 °C. The temperature may not exceed 80 °C due to elastomer stability.

NOTE 2 The drying time of at least 2 h assures that material absorbed by the elastomers is heated off completely.

If not replaced, wash the emptied reaction vessels and the air inlet tubes at least three times with ternary solvent mixture (5.1) in order to remove residual fuel and adherent ageing organic residues. The last solvent portion should be colourless.

Rinse with 2-Propanol and tap water. Put the inlet tube into the reaction vessel and fill completely with an aqueous alkaline laboratory cleaning solution.

Store the vessels at room temperature over night.

Rinse the purified vessels and their inlet tubes thoroughly with tap water and finally with demineralised or distilled water. Dry them in an oven for at least 2 h at 80 °C.

In case of doubt, the cleanliness of the sealing caps and connecting hoses can be checked by running the clean test equipment without sample under the standard experimental conditions. Clean equipment shall not produce a conductivity increase exceeding 10 µS/cm within 5 hours.

8.2.2 Determination of temperature correction

The difference between the actual temperature of the sample and the temperature of the heating block is called **temperature correction** ΔT. For the determination of ΔT an external calibrated temperature sensor is used.

Before starting the determination of ΔT, the heating block has to be switched on and the target temperature has to be reached.

Fill one reaction vessel with 5 g thermo-stable oil. Insert the temperature sensor through the cap into the reaction vessel. Use distance clips to keep the sensor away from the air inlet. The sensor should touch the bottom of the vessel.

Insert the complete vessel into the heating block and connect the air supply.

If the value of the measured temperature is constant, calculate ΔT :

$$\Delta T = T_{\text{Block}} - T_{\text{sensor}} \tag{1}$$

where

ΔT is the delta T "temperature correction“;

T_{Block} is the temperature of the heating block;

T_{sensor} is the measured temperature in the reaction vessel.

Correct the block temperature:

$$T_{\text{Block}} = T_{\text{Target}} + \Delta T \qquad (2)$$

where

T_{target} is the temperature which the sensor is expected to measure

EXAMPLE T_{target} may be chosen at 110 °C, which is usually the test temperature.

After this temperature correction the measured temperature in the reaction vessel should be equal to the target temperature.

9 Procedure

9.1 Set up the apparatus as shown in Figure 1. If the apparatus is available commercially, follow the manufacturer's instructions.

9.2 Attach the gas diaphragm pump (6.1.2) and adjust the flow to exactly 10 l/h. Then switch the pump off again. Commercially available apparatus may control the set flow automatically.

9.3 Bring the heating block (6.1.8) up to the desired temperature (usually 110 °C, but see 8.2.2) using the thyristor and contact thermometer (6.1.7) or by using an electronic controller. The temperature shall be maintained constant to within ± 0,1°C during the test period.

If a heating bath (6.1.8) is used, bring it to the desired temperature and check in the manner described.

9.4 Fill the measurement cells (6.1.4) with 60 ml of distilled or demineralised water using a measuring pipette (6.3).

NOTE At temperatures above about 25 °C, volatile carboxylic acids may evaporate from the water in the measurement cell. This can lead to a decrease in the conductivity of the aqueous solution. The rapidly rising part of the conductivity curve will therefore produce a deviant shape so it becomes impossible to determine the tangent on this part of the curve (see reference [5]).

9.5 Check the electrodes (6.1.5) and adjust their signals using a calibration potentiometer so that they are on the zero axis of the recorder paper.

Set the paper rate at 10 mm/h and the measuring frequency at one measuring point per 30 s. Set the measuring value of 200 µS/cm at the maximum result of 100 %.

If it is not possible to adjust the paper rate to 10 mm/h, one should use 20 mm/h. This shall be reported on the recorder paper.

NOTE Commercially available apparatuses may acquire the data via PC.

9.6 Weigh (7,5 ± 0.1) g of the conditioned sample (see 8.1) into a reaction vessel using a pipette (6.3).

9.7 Switch on the gas diaphragm pump (6.1.2) and set the flow again at exactly 10 l/h. Connect the air inlet tube and outlet tube with the reaction vessels and the measurement cells, using the connecting hoses (6.5).

9.8 Place the reaction vessel with the sealing cap (6.1.3) into the hole intended for it in the heating block or into the heating bath (6.1.8), both of which shall have reached the required temperature.

The preparation steps 9.7 and 9.8 should be done as quickly as possible. Then immediately start the automatically data recording or note the time that measurements were begun on the recorder paper.

9.9 The measurement may be terminated:

— when the signal has reached 100 % of the recorded scale, usually 200 µS/cm (see Figure 3, left diagram), or

— when the conductivity curve flattens again after exceeding the induction period (see Figure 3, right diagram). Care should be taken to ensure that the test is not terminated before the curve has flattened sufficiently to fit an accurate second tangent.

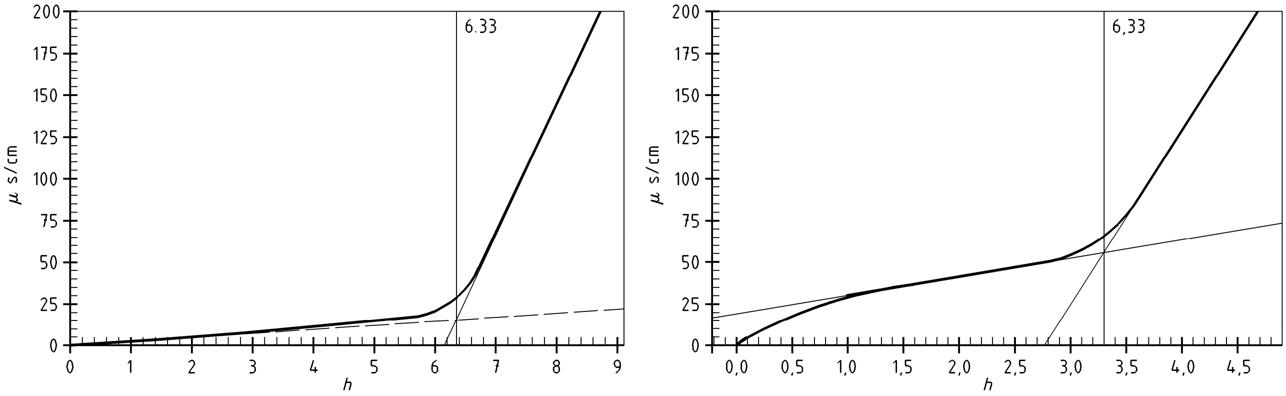


Figure 3 — Measurement termination indications

9.10 During the determination, carry out the following precautions:

a) check the setting of the flow meter and adjust where necessary in order to ensure a constant flow;

b) check the colour of the molecular sieve (6.6) of the air filter and repeat measurements when the molecular sieve turns colour during the test. It is recommended to exchange the molecular sieve prior to each run.

10 Calculation and evaluation

10.1 Automatic evaluation

The automatic evaluation as given by the equipment manufacturers may be used if the second derivative of the conductivity curve shows a clear maximum. This is generally the case if pure FAME and diesel/FAME blends with a FAME content equals or higher than 10 percent are investigated (see Figure 4, left diagram).

If the second derivative of the conductivity curve is noisy, and no clear maximum can be recognised, the manual evaluation (10.2) of the conductivity curve itself shall be applied (see Figure 4, right diagram).

NOTE Software settings are recommended that permit simultaneous display of the conductivity curve and its second derivative in order to enable the operator to check the automatically calculated value for the induction period.

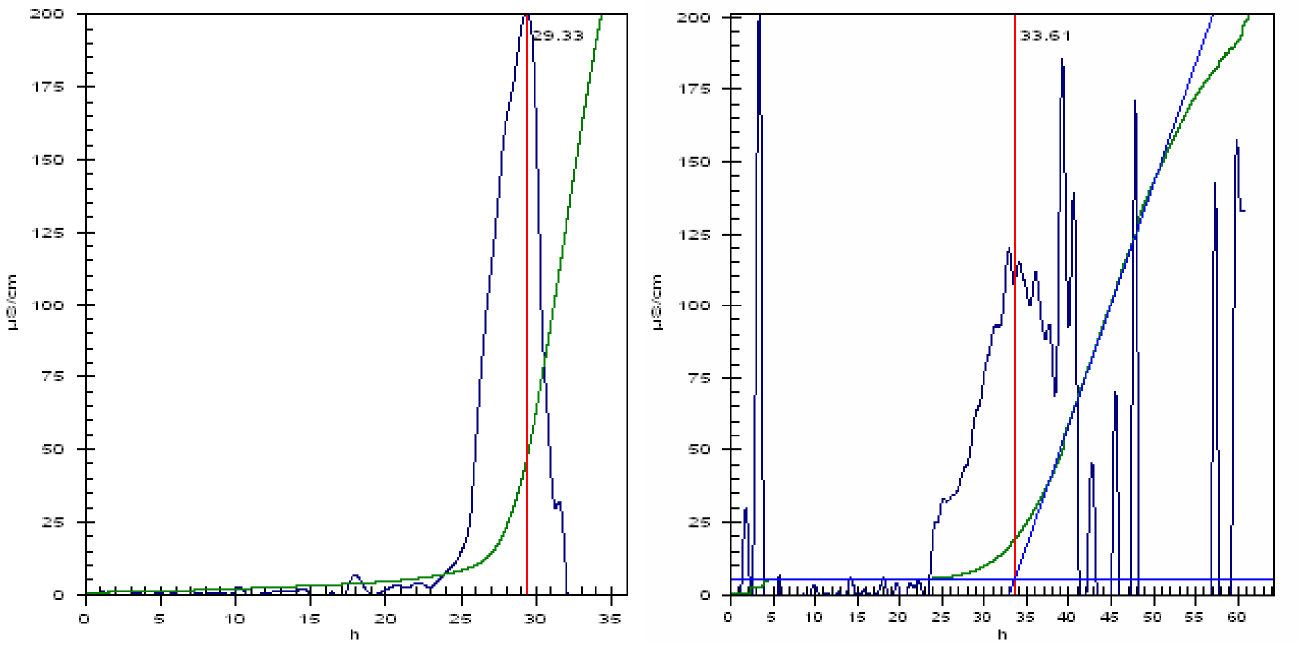


Figure 4 — Evaluation indications

10.2 Manual evaluation

Set the first tangent to the flattest part of the slowly increasing conductivity curve. Great care should be taken to fit the best possible tangent line, e.g. by using an enlarged presentation of the original graph. Some instruments supply a zoom-function to accomplish this. The second tangent is set after exceeding the inflection point at the steepest part of the conductivity curve (see Figure 3).

The induction period is obtained from the intersection point of both tangents.

NOTE A rapid conductivity increase immediately after starting the test and before reaching the induction period may indicate insufficient cleaning of the sealing caps or connecting hoses (evaporation of residual volatile compounds out of the elastomers) (see Figure 5). The cleanliness can be validated according to the procedure given in Note 1 in 8.2.1. Also, fuels that contain volatile acids can unexpectedly show a rapid initial conductivity increase (see Figure 6).

11 Expression of results

Report the induction period, obtained from 10.1 or 10.2, in hours and rounded to the nearest 0,1 h.

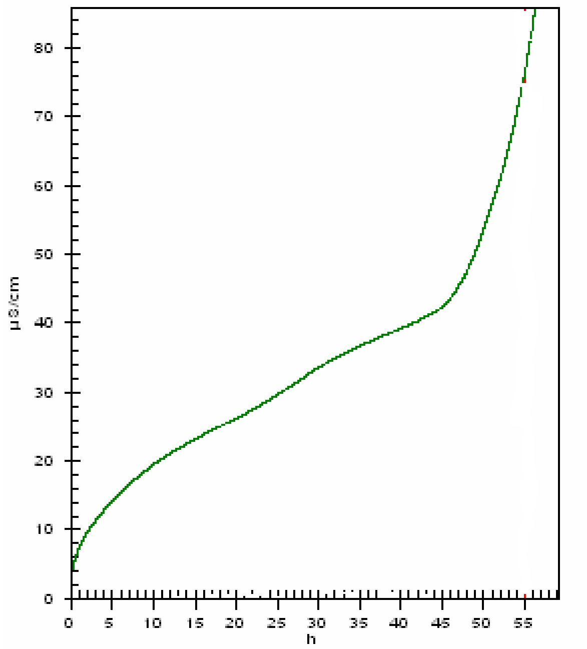


Figure 5 — Insufficient cleaning indication

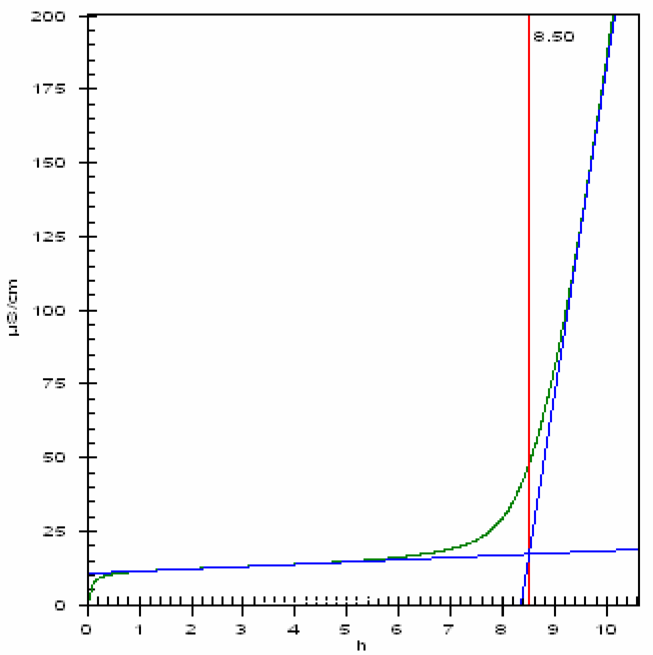


Figure 6 — Rapid initial conductivity increase indication

12 Precision

12.1 General

An interlaboratory test organised in 2007 at European level with the participation of 12 laboratories was carried out on 10 samples and gave the precision, derived from statistical analysis by EN ISO 4259 [6].

Results from the calculation of precision estimates used shall be rounded to the nearest 0,1 h.

12.2 Repeatability, *r*

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 the test method, exceed the values calculated from the following equation in absolute value only in one case in twenty, where X represents the mean of the two results:

$$r = 0{,}220\ 27 + 0{,}043\ 44\ X \quad (3)$$

12.3 Reproducibility, *R*

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 the test method, exceed the values calculated from the following equation in absolute value only in one case in twenty, where X represents the mean of the two results:

$$R = 0{,}372\ 69 + 0{,}190\ 38\ X \quad (4)$$

13 Test report

The test report shall specify:

a) a reference to this European standard (i.e. EN 15751:2009);

b) the type and complete identification of the product tested;

c) the sampling method used if known (see 7);

d) the temperature at which the determination was carried out;

e) the test result(s) obtained (see 11), or if the repeatability has been checked, the final quoted result obtained;

f) all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

g) any deviation, by agreement or otherwise, from the procedure specified;

h) the date of test.

Annex A
(informative)

Background of the method

Over the years, a number of methods have been developed for the determination of the oxidation stability of oils and fats. These methods are based on the rate of oxygen absorption by oils and fats (in a liquid state) which have been placed in contact with air.

Oxygen absorption may be measured directly using the Warburg apparatus or indirectly by determination of peroxides or the products dissociated from them during oxidation.

Of the indirect methods of determination, the Active Oxygen Method (AOM) is the oldest. This is based on the determination of the peroxide value in line with the progress of the aeration of the sample at 98,7 °C and specifies the time which elapses until a peroxide value of 100 mmol (active oxygen per 2 kg) has been reached. The Swift Stability Test has been derived from this method. These determinations are very time-consuming and cannot be automated.

In the method described in this European Standard, the oxidation process is split in two phases.

a) The first phase (the induction period) is characterised by slow reaction of oxygen during which peroxides are formed;

b) The second phase (tainted odour and flavour phase) is characterised by rapid reaction in which peroxides are not only formed but these peroxides are then dissociated under the influence of the high temperature. During this, products such as aldehydes, ketones and low fatty acids are formed. These products give rise to deviant odour and flavour.

The method described in this European Standard is a conductimetric determination of volatile acid dissociation products (mainly formic acid and acetic acid) produced during oxidation. The procedure was published in 1974 [7].

An automated potentiometric determination method was published in 1972 [8], and the method was standardized by ISO/TC 34/SC 11 as ISO 6886 in 1996 (later revised in 2006, [9]).

From the conductivity curve, an induction time is determined in line with the induction time obtained using the AOM, provided that the determinations are carried out at the same temperature. The curves can have very different shapes (see Figures 3 to 6 and reference [10]).

Bibliography

[1] EN 14112:2003, *Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of oxidation stability (accelerated oxidation test)*

[2] EN 14214:2003, *Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods*

[3] EN ISO 12205, *Petroleum products – Determination of the oxidation stability of middle-distillate fuels (ISO 12205:1995)*

[4] EN ISO 3696, *Water for analytical laboratory use – Specification and test methods* (ISO 3696:1987)

[5] DE MAN, J. M., FAN TIE and DE MAN, L. J., Am. Oil Chem. Soc., **64**, 1987, p. 993

[6] EN ISO 4259, *Petroleum products – Determination and application of precision data in relation to methods of test (ISO 4259:2006)*

[7] HADORN, H. and ZÜRCHNER, K. Deutsche Lebens. Rundschau, **70**, 1974, p. 57

[8] PARDUN, H. and KROLL, E. Fette, Seifen, Anstrichmittel, **74**, 1972, p. 366

[9] ISO 6886, *Animal and vegetable fats and oils – Determination of oxidative stability (accelerated oxidation test)*

[10] VAN OOSTEN, C. W., POOT, C. and HENSEN, A. C. Fette, Seifen, Anstrichmittel, 83, 1981, p. 133

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APPENDIX 9

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Traduction de la version allemande légale.

MANUFACTURER'S CERTIFICATE FOR CAPILLARY VISCOMETER

(Manufacturer's certificate M according to DIN 55 350, Part 18)

Subject: Ubbelohde viscometer with suspending ball-level for the determination of the kinematic viscosity according to ISO/DIS 3105 and ASTM D 2515/D 446

Manufacturer: SI Analytics GmbH, Mainz

Viscometer: Type and capillary no.: 525 13 / Ic
Apparatus no.: 1075844

This viscometer is suitable to determine the kinematic viscosity of newtonian liquids according to ISO/DIS 3105, Annex B. The instrument constant **K** refers to the timing marks during the visual survey of the meniscus passage. It comes to

CERTIFICAT DU FABRICANT DE TUBE VISCOSIMETRIQUE CAPILLAIRE

(Certificat du fabricant M selon DIN 55 350, Partie 18)

Objet: Viscosimètre selon Ubbelohde avec un niveau sphérique pendant pour la détermination de la viscosité cinématique selon ISO/DIS 3105 et ASTM D 2515/D 446.

Fabricant: SI Analytics GmbH, Mainz

Viscosimètre: No. de type et de capillaire: 525 13 / Ic
No. d'appareil: 1075844

Ce viscosimètre est approprié pour la détermination de la viscosité cinématique de liquides newtoniens selon ISO/DIS 3105, Annex B. La constante **K** de l'instrument est valable pour des index rotatifs avec une saisie visuelle du passage du ménisque. Elle est de

$$\mathbf{K = 0{,}02944\ mm^2/s^2.}$$

It was determined by using comparative measurements with reference viscometers, of which the constants were determined at the Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig.

The instrument constant **K** is valid for liquids with a surface tension of 20 to 30 mN/m and an acceleration of the fall of 9.8105 m/s^2. For temperatures up to 100 °C it is not required to pay attention to the heat expansion of the viscometer. The kinematic viscosity ν within mm^2/s of liquids can be calculated using the instrument constant in the equation:

Elle a été déterminée par des mesures de comparaison avec des viscosimètres étalons dont les constantes ont été déterminées auprès de la Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig.

La constante **K** de l'instrument est valable pour des liquides avec une tension de surface de 20 à 30 mN/m et avec une accélération de la pesanteur de 9,8105 m/s^2. Dans le cas de températures jusqu'à 100 °C, il n'est pas nécessaire de tenir compte de la dilatation thermique du viscosimètre. La viscosité cinématique ν en mm^2/s de liquides peut être calculée à l'aide de la constante de l'instrument selon l'équation:

$$\nu = K \cdot t,$$

whereby **t** is the flow time in seconds which was corrected -if necessary- according to ISO/DIS 3105, Part 6.2

The relative uncertainty of the mentioned numerical value of **K** comes to 0.7 % at a confidence level of 95 %.

It is required to check the instrument constant in regular intervals. In particular any change to the viscometer, for example when using liquids that corrode glass or a glass blowing repair took place, makes a new determination of the instrument constant necessary.

t est le temps d'écoulement en secondes qui a été corrigé -si nécessaire- selon ISO/DIS 3105, Partie 6,2.

L'insécurité relative de la valeur numérique de **K** indiquée est de 0,7 % dans le cas d'un niveau de confiance de 95 %.

Il est nécessaire de contrôler la constante de l'instrument en intervalles réguliers. Une nouvelle détermination de la constante de l'instrument devient absolument nécessaire lors de toute modification du viscosimètre, par exemple, en raison de l'utilisation de liquides qui attaquent le verre, ou dans le cas de réparations par un souffleur de verre.

SI Analytics GmbH, Hattenbergstraße 10, D-55122Mainz

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Traduction de la version allemande légale.

MANUFACTURER'S CERTIFICATE FOR CAPILLARY VISCOMETER

(Manufacturer's certificate M according to DIN 55 350, Part 18)

CERTIFICAT DU FABRICANT DE TUBE VISCOSIMETRIQUE CAPILLAIRE

(Certificat du fabricant M selon DIN 55 350, Partie 18)

Subject: Ubbelohde viscometer with suspending ball-level for the determination of the kinematic viscosity according to ISO/DIS 3105 and ASTM D 2515/D 446

Manufacturer: SI Analytics GmbH, Mainz

Viscometer: Type and capillary no.: 525 10 / I
Apparatus no.: 1075930

Objet: Viscosimètre selon Ubbelohde avec un niveau sphérique pendant pour la détermination de la viscosité cinématique selon ISO/DIS 3105 et ASTM D 2515/D 446.

Fabricant: SI Analytics GmbH, Mainz

Viscosimètre: No. de type et de capillaire: 525 10 / I
No. d'appareil: 1075930

This viscometer is suitable to determine the kinematic viscosity of newtonian liquids according to ISO/DIS 3105, Annex B. The instrument constant **K** refers to the timing marks during the visual survey of the meniscus passage. It comes to

Ce viscosimètre est approprié pour la détermination de la viscosité cinématique de liquides newtoniens selon ISO/DIS 3105, Annex B. La constante **K** de l'instrument est valable pour des index rotatifs avec une saisie visuelle du passage du ménisque. Elle est de

$$\mathbf{K = 0{,}009820\ mm^2/s^2.}$$

It was determined by using comparative measurements with reference viscometers, of which the constants were determined at the Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig.

The instrument constant **K** is valid for liquids with a surface tension of 20 to 30 mN/m and an acceleration of the fall of 9.8105 m/s^2. For temperatures up to 100 °C it is not required to pay attention to the heat expansion of the viscometer. The kinematic viscosity ν within mm^2/s of liquids can be calculated using the instrument constant in the equation:

Elle a été déterminée par des mesures de comparaison avec des viscosimètres étalons dont les constantes ont été déterminées auprès de la Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig.

La constante **K** de l'instrument est valable pour des liquides avec une tension de surface de 20 à 30 mN/m et avec une accélération de la pesanteur de 9,8105 m/s^2. Dans le cas de températures jusqu'à 100 °C, il n'est pas nécessaire de tenir compte de la dilatation thermique du viscosimètre. La viscosité cinématique ν en mm^2/s de liquides peut être calculée à l'aide de la constante de l'instrument selon l'équation:

$$\nu = \mathbf{K} \cdot \mathbf{t},$$

whereby **t** is the flow time in seconds which was corrected -if necessary- according to ISO/DIS 3105, Part 6.2

The relative uncertainty of the mentioned numerical value of **K** comes to 0.7 % at a confidence level of 95 %.

It is required to check the instrument constant in regular intervals. In particular any change to the viscometer, for example when using liquids that corrode glass or a glass blowing repair took place, makes a new determination of the instrument constant necessary.

t est le temps d'écoulement en secondes qui a été corrigé -si nécessaire- selon ISO/DIS 3105, Partie 6,2.

L'insécurité relative de la valeur numérique de **K** indiquée est de 0,7 % dans le cas d'un niveau de confiance de 95 %.

Il est nécessaire de contrôler la constante de l'instrument en intervalles réguliers. Une nouvelle détermination de la constante de l'instrument devient absolument nécessaire lors de toute modification du viscosimètre, par exemple, en raison de l'utilisation de liquides qui attaquent le verre, ou dans le cas de réparations par un souffleur de verre.

SI Analytics GmbH, Hattenbergstraße 10, D-55122Mainz

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