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Standard Specification for Pyrolysis Liquid Biofuel[1]

This standard is issued under the fixed designation D7544; 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 a pyrolysis liquid biofuel produced from biomass intended for use in industrial burners equipped to handle these types of fuels. This type of biofuel is not intended for use in residential heaters, small commercial boilers, engines, or marine applications.

NOTE 1—For information on the significance of the physical, chemical, and performance properties identified in this specification, see Appendix X1.

1.2 This specification is for use in contracts for the purchase of pyrolysis liquid biofuel and for guidance of consumers of this type of fuel.

1.3 Nothing in this specification should preclude observance of national or local regulations, which may be more restrictive.

NOTE 2—The generation and dissipation of static electricity may create problems in the handling of pyrolysis liquid biofuel. 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*—BTU units are included for information only in 3.5.1.

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]

D93 Test Methods for Flash Point by Pensky-Martens Closed Cup Tester
D97 Test Method for Pour Point of Petroleum Products
D240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter
D396 Specification for Fuel Oils
D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
D482 Test Method for Ash from Petroleum Products
D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
~~D4057 Practice for Manual Sampling of Petroleum and Petroleum Products~~
~~D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products~~
D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
D4865 Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D6469 Guide for Microbial Contamination in Fuels and Fuel Systems
D7579 Test Method for Pyrolysis Solids Content in Pyrolysis Liquids by Filtration of Solids in Methanol
E70 Test Method for pH of Aqueous Solutions With the Glass Electrode
E203 Test Method for Water Using Volumetric Karl Fischer Titration

[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.

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

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

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.2 *bulk fuel*, *n*—fuel in the storage facility in quantities over 190 L.

3.3 *char*, *n*—fine carbonaceous powder that is separated from the vapors of biomass during pyrolysis.

3.3.1 *Discussion*—Pyrolysis liquid biofuel contains uniformly suspended char.

3.4 *fuel degradation products*, *n*—those materials that are formed in fuel during extended storage or exposure to high temperatures.

3.4.1 *Discussion*—During storage, reactive organic compounds in pyrolysis liquid can act together to form larger molecules (fuel degradation products), which can become insoluble or increase the fuel viscosity, or both.

3.5 *industrial burner*, *n*—device which produces heat for industrial use through the combustion of liquid fuels.

3.5.1 *Discussion*—Industrial burners are typically designed for one of two applications: (*1*) industrial furnaces—integral components of manufacturing processes that provide direct heating; for example, in aggregate, cement, lime, or phosphate kilns; coke ovens; or blast, smelting, melting, refining, or drying ovens and (*2*) industrial boilers—large indirect heating units which transfer thermal energy to water or other fluids or gases for use in heating in industrial settings, power generation and in manufacturing processes. These boilers can be classified as utility/large industrial boilers with a heat input greater than 105 GJ/h (100 × 106 BTU/h) or small industrial boilers with a heat input of between 10.5 to 105 GJ/h (10 to 100 × 106 BTU/h).

3.6 *long-term storage*—storage of fuel for longer than 3 months after it is received by the user.

3.7 *medium-term storage*—storage of fuel for up to 3 months after it is received by the user.

3.7.1 *Discussion*—It is recommended that fuel be consumed within 6 months of receipt.

3.8 *pyrolysis*, *n*—chemical decomposition of organic materials by heating in the absence of oxygen.

3.9 *pyrolysis liquid biofuel*, *n*—liquid product from the pyrolysis of biomass.

3.9.1 *Discussion*—Pyrolysis liquid biofuel is comprised of a complex mixture of the decomposition products of ligno-cellulosic biomass including highly oxygenated organic compounds. It is produced from the pyrolysis of biomass, followed by the rapid condensation of its vapors.

3.10 *pyrolysis solids*, *n*—solid particles contained within the pyrolysis liquid biofuel.

3.10.1 *Discussion*—Pyrolysis solids is comprised of ash and char.

4. General Requirements

4.1 The pyrolysis liquid biofuel specified in this specification shall remain uniform in medium-term storage and not separate by gravity into layers.

NOTE 3—Long-term storage or equipment down time can necessitate circulation of pyrolysis liquid biofuel in-tank to prevent such separation. The buyer and seller should agree on any requirements for long-term storage. If minor separation occurs during medium-term storage, mild agitation or product circulation should reverse such separation.

5. Detailed Requirements

5.1 The pyrolysis liquid biofuel specified shall conform to the detailed requirements shown in Table 1.

5.2 The properties selected for limitation are those that are believed to be of the greatest significance in obtaining acceptable performance of the burner.

6. Sampling

6.1 Review all intended test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method. See Table 2.

6.2 As indicated in 4.1, during medium-term storage, pyrolysis liquid biofuel shall remain uniform and not separate into layers. Note, however, that separation may occur during long-term storage. Therefore, samples should be well mixed when transferring from the primary sampling process or container, or both, to another container or analytical apparatus, or both. Sampling from an active circulation loop or a well mixed or agitated tank is preferred. Refer to Practice D5854 for more guidance on mixing and handling samples.

TABLE 1 Detailed Requirements for Pyrolysis Liquid Biofuels

Property	Test Method	Specification	Units
Gross Heat of Combustion	D240	15 min	MJ/kg
Water Content	E203	30 max	mass %
~~Pyrolysis Solids Content~~	~~Annex A1~~	~~2.5 max~~	~~mass %~~
Pyrolysis Solids Content	D7579	2.5 max	mass %
Kinematic Viscosity at 40°C	D445[A]	125 max	mm^2/s
Density at 20°C	D4052	1.1–1.3	kg/dm^3
Sulfur Content	D4294	0.05 max	mass %
Ash Content	D482	0.25 max	mass %
pH	E70	Report	...
Flash Point	D93, Procedure B	45 min	°C
Pour Point	D97	–9 max	°C

[A] Without filtering.

TABLE 2 Typical Sampling Procedures for Containers

Type of Container	Procedure
Storage tanks that are well-mixed by circulation or agitation	Automatic or Manual Pipeline Sampling
Tank cars, tank trucks, or ship tanks	Dipper Sampling *or* All-Level Sampling

6.3 *Sample Size*—A minimum of 1 L is recommended.

7. Test Methods

7.1 The requirements enumerated in this specification shall be determined in accordance with the following test methods:

7.1.1 *Gross Heat of Combustion*—Test Method D240.

7.1.2 *Water Content*—Test Method E203.

7.1.3 *Pyrolysis Solids Content*~~—See Annex A1~~—See Test Method D7579.

7.1.4 *Kinematic Viscosity*—Test Method D445.

7.1.5 *Density*—Test Method D4052.

7.1.6 *Sulfur*—Test Method D4294.

7.1.7 *Ash Content*—Test Method D482.

7.1.8 *pH*—Test Method E70.

7.1.9 *Flash Point*—Test Method D93.

7.1.10 *Pour Point*—Test Method D97.

8. Keywords

~~8.1pyrolysis liquid biofuel; bio-oil; pyrolysis oil; pyoil; py-oil; bio-crude-oil; bio-fuel-oil; wood liquids; burner fuel; renewable energy; alternative energy; fuel oils; furnace oils~~

~~**ANNEX**~~

~~**(Mandatory Information)**~~

~~**A1.TEST METHOD FOR PYROLYSIS SOLIDS CONTENT IN PYROLYSIS LIQUIDS BY FILTRATION OF SOLIDS IN METHANOL**~~

~~**A1.1Scope**~~

~~A1.1.1This test method describes a filtration procedure for determining the pyrolysis solids content of pyrolysis liquid. It is intended for the analysis of pyrolysis liquid with all ranges of pyrolysis solids concentrations.~~

~~A1.1.2The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.~~

~~A1.1.3*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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.~~

~~A1.1.4For Referenced Documents, see Section 2.~~

~~A1.1.5For Terminology, see Section 3.~~

~~**A1.2Summary of Test Method**~~

~~A1.2.1A pyrolysis liquid sample is dissolved in a methanol and dichloromethane solution (1:1), which is then filtered through a vacuum filter system. After filtering, the filtrand is washed with the solvent until the filtrate is clear. The filter is removed, dried and weighed. The pyrolysis solids content is calculated based on the original pyrolysis liquid sample.~~

~~**A1.3Significance and Use**~~

~~A1.3.1Pyrolysis liquid can be produced to various char concentrations. Increasing pyrolysis solids content can affect the pyrolysis liquid biofuel handling, atomization, and storage stability in a negative manner.~~

~~**A1.4Apparatus (see Fig. A1.1)**~~

~~A1.4.1*Smooth-tip Forceps*.~~

~~A1.4.2*Beaker*, 400 mL.~~

~~A1.4.3*Glass Stirring Rod*.~~

~~A1.4.4*Oven*, explosion-proof, capable of maintaining a temperature of 105 ± 3°C.~~

~~A1.4.5*Filtering Flask*, 1 L.~~

~~A1.4.6*Filter Holders*, borosilicate glass.~~

A1.4.7 *Filter Membrane*, binder free glass microfiber, 1 µm.
A1.4.8 *Weighing Dish*, aluminum.
A1.4.9 *Balance*, capable of weighing to the nearest 0.0001g (0.1 mg) with a range of 300 g.
A1.4.10 *Vacuum*.

A1.5 Reagents and Solvents

A1.5.1 *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. 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. If an industrial grade reagent is used, it shall be filtered using 0.45 µm filter paper prior to use.

A1.5.2 *Ethanol*, reagent grade (**Warning—**Flammable. Toxic. Can be harmful or fatal if ingested or inhaled. Avoid skin contact.)

A1.5.3 *Methanol (MeOH)*, reagent grade (**Warning—**Flammable. Toxic. Can be harmful or fatal if ingested or inhaled. Avoid skin contact.)

A1.5.4 *Dichloromethane (DCM)*, reagent grade (**Warning—**Flammable. Toxic. Can be harmful or fatal if ingested or inhaled. Avoid skin contact.)

A1.5.5 *Filter Paper*, 1 µm pore size, binder free glass microfiber.

A1.6 Sampling

A1.6.1 Obtain a sample using either Practice D4057 or D4177.

A1.6.2 Obtain a representative sample of the pyrolysis liquid from a well-mixed container. The sample should be well mixed to ensure homogeneity.

A1.7 Procedure

A1.7.1 Dry a clean filter membrane for 15 min in a desiccator, place in a labeled aluminum weighing dish, and weigh to the nearest 0.1 mg.

A1.7.2 Place a 400 mL beaker on the balance, and tare it.

A1.7.3 Vigorously shake the sample by hand for a minimum of 15 s.

A1.7.4 Using a disposable pipette, weigh approximately 15 g of pyrolysis liquid sample into the beaker. Record the weight to the nearest 0.1 mg.

A1.7.5 Add approximately 100 to 200 mL MeOH-DCM solution (1:1) into the beaker and stir the mixture vigorously to dissolve the pyrolysis liquid in the solvent.

A1.7.6 Mount the filter on a dry holder and apply a vacuum. Mount and securely clamp the filter funnel to the filter holder.

A1.7.7 Use methanol to wash the filter paper to properly seal the latter to the bottom of the funnel.

A1.7.8 Filter the solution through the vacuum filter system on 1 µm filter paper. Quickly but carefully poor the solution into the center of the funnel. Thoroughly wash the beaker with MeOH-DCM solution and return the contents to the funnel. Wash the filtrand with methanol until the filtrate runs clear.

A1.7.9 Remove the filter funnel from the filter holder and ensure the edges of the filter funnel are clean of any pyrolysis solids. If required, rinse any pyrolysis solids on the filter funnel onto the filter paper with methanol, ensuring no pyrolysis solids are lost.

A1.7.10 Release the vacuum, and using the smooth-tip forceps transfer the filter membrane and filtrand to its original weighing dish, and dry in the oven at 105 ± 3°C for 30 min.

A1.7.11 Remove the weighing dish and filter membrane and cool to room temperature in a dessicator for a minimum of 1 h.

A1.7.12 Weigh the filter membrane and weighing dish and record the stabilized weight to the nearest 0.1 mg.

A1.8 Calculation

A1.8.1 Calculate the pyrolysis solids content of the pyrolysis liquid sample in accordance with Eq A1.1.

$$\text{pyrolysis solids}(\text{wt\%}) = \frac{PS_1}{PL} \times 100\% \qquad (A1.1)$$

pyrolysis solids	=	pyrolysis solids content, wt%,
PS_1	=	pyrolysis solids retained on 1 µm filter paper (g), and
PL	=	pyrolysis liquid sample taken for analysis (g).

A1.9 Report

A1.9.1 Report the pyrolysis oil solids content to two significant figures.

A1.10 Precision and Bias

A1.10.1 This interim precision statement represents replicate analyses performed in two laboratories over ten successive days by the same analyst on the same day on the same instrument.