Designation: E3146 – 24

Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration[1]

This standard is issued under the fixed designation E3146; 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 carbonyl content of bio-oils derived from thermochemical decomposition of lignocellulosic biomass and their deoxygenated products. This method is used for determination of carbonyls between 0.5 and 8 mol/kg.

1.2 Review the current and appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions and proper personal protective equipment.

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration

D1193 Specification for Reagent Water

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

E1705 Terminology Relating to Bioenergy and Industrial Chemicals from Biomass

2.2 *Other Standards*

CEN/TR 17103:2017 Petroleum and Related Products - Fast Pyrolysis Bio-oils for Stationary Internal Combustion Engines - Quality Determination[3]

EN 16900:2017 Fast Pyrolysis Bio-oils for Industrial Boilers—Requirement and Test Methods[4]

3. Terminology

3.1 *Definitions of Terms:*

3.1.1 For definitions of terms used in this standard, refer to Terminology E1705.

NOTE 1—The user is advised that the definitions used by various industries, marketers, regulatory bodies, and other ASTM Committees can differ from those in this standard. When using this standard, it is critical to use terminology from Committee E48.

3.1.2 *bio-oil, n*—the crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.

3.1.3 *carbonyl, n*—the chemical functional group consisting of a carbon-oxygen double bond, C=O.

3.1.3.1 *Discussion*—For this method, this includes all aldehydes and ketones; carboxylic acids, esters, and lactone groups are not measured by this method.

3.1.4 *fast pyrolysis, n*—pyrolysis conducted with rapid heating and short residence time; typically less than 10 s.

3.1.4.1 *Discussion*—Other definitions for fast pyrolysis state residence times of typically less than 10 s (**1**, **2**),[5] 5 s (CEN/TR 17103:2017, EN 16900:2017), and 1 s (**3**, **4**).

[1] This test method is under the jurisdiction of ASTM Committee E48 on Bioenergy and Industrial Chemicals from Biomass and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion.

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

[3] Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, http://www.cen.eu.

[4] Available from British Standards Institution (BSI), 389 Chiswick High Rd., London W4 4AL, U.K., http://www.bsigroup.com.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

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

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

3.1.6 *oxime, n*—a group of compounds containing the chemical functional group >C=NOH, produced by the condensation of ketones or aldehydes with hydroxylamine.

3.1.7 *oximation reaction, n*—reaction with or conversion into an oxime.

4. Summary of Test Method

4.1 A bio-oil sample is dissolved in dimethylsulfoxide (DMSO) and solutions are added containing hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and triethanolamine (TEA). The mixture is sealed, stirred, and heated to 80 °C for 2 h. Carbonyl compounds (aldehydes and ketones) react with $NH_2OH{\cdot}HCl$ forming the corresponding oxime and liberating HCl. Liberated HCl is consumed by TEA, which drives the reaction forward. After the reaction, unconsumed TEA is titrated with a standardized HCl titrant to determine the molar concentration of carbonyls in the sample.

5. Significance and Use

5.1 While pyrolysis bio-oils are comprised of a large variety of compounds and chemical functional groups, quantification of carbonyl groups is especially important. Carbonyls are known to be responsible for the instability of bio-oil during both storage and processing. This method can be used to quantify the total carbonyl content of bio-oils.

6. Interferences

6.1 The selectivity of the method was tested by using 1-butanol, 1-pentanol, tertiary-butanol, 2-propanol, ethyl acetate, acetic acid, xylose, and glucose as model compounds, representing alcohol, ester, carboxylic acid, and carbohydrates in the bio-oil. No interferences were seen for ethyl acetate or acetic acid. Monosaccharides are measured using this method. Addition of alcohols causes interferences, but it is dependent on chain length. The reason is as yet undetermined but may be related to solvent properties of the alcohol rather than reaction with $NH_2OH{\cdot}HCl$ or TEA. Tests with primary, secondary, and tertiary butanol have shown the same effect.

7. Apparatus

7.1 *Analytical Balance,* accurate to 0.0001 g.

7.2 *Micro Reaction Vial,* borosilicate glass, cone shaped inside with at least 5 mL capacity and PTFE lined caps. See Fig. 1.

7.3 *Triangular Magnetic Stirring Bar,* PTFE lined and suitable size for use with micro reaction vessels.

7.4 *Dry Block Heater with Magnetic Stirrer,* capable of maintaining a temperature of 80 °C, for use with micro reaction vials. See Fig. 2.

7.4.1 A hot water bath with flat circular magnetic stirrer is also acceptable.

7.5 *Potentiometric Titrator*—Automatic titration systems capable of adding fixed increments of titrant at fixed time intervals (monotonic) or variable titrant increments with electrode stability between increment additions (dynamic) with endpoint seeking capabilities as prescribed in the method. At the very least, the automatic titration system shall meet the performance and specification requirements as warranted by the manufacturer.

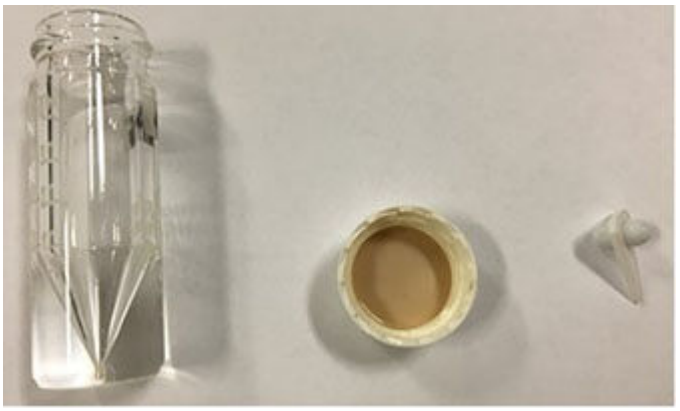

FIG. 1 Micro Reaction Vial with PTFE Lined Cap and Triangular Magnetic Stirring Bar

FIG. 2 Dry Block Heater

7.5.1 A monotonic or dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition may vary depending on the rate of change of the system. The recommended minimum volume increment is 0.05 mL, and the recommended maximum volume increment is 0.1 mL. A signal drift of 10 mV/min and endpoint recognition set to last is recommended to ensure endpoint detection. When using a monotonic titrant addition, the waiting time between increment additions shall be sufficient to allow for mixing and a stable electrode response. Wait at least 10 s between additions.

7.6 *Buret,* capable of delivering titrant in 0.02 mL or larger increments. The buret tip shall deliver titrant directly into the titration vessel (immersed about 25 mm in liquid) without exposure to the surrounding air.

7.7 *Titration Stand,* suitable for supporting the electrode, stirrer, and buret.

7.8 *Sensing Electrode,* standard pH, suitable for non-aqueous titrations.

7.9 *Reference Electrode*—Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M-3M LiCl in ethanol.