Designation: D8393 – 21

Standard Guide for Determination of Pore Volume of Powdered Catalysts and Catalyst Carriers by Water Adsorption[1]

This standard is issued under the fixed designation D8393; 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 guide measures pore volume of powdered catalysts and catalyst carriers by titration with water. The water does not react with material. The range of pore volume is 0.25 mL/g to 0.46 mL/g.

1.2 This guide is suitable for fine catalysts such as fluid catalytic cracking (FCC) catalysts (fresh or equilibrium), catalyst additives and spray dried catalyst carriers or finished catalysts, or a combination thereof, and is typically applicable to powders with the majority of particles (above 90 %) in the distribution range between 20 and 150 µm equivalent spherical diameter (determined by Test Method D4464) and with an average particle size between 60 and 100 µm.

NOTE 1—This technique is capable of measuring particles below and above this range (for example, from 1 to 300 µm) but no precision data is available.

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]

D1193 Specification for Reagent Water

D4284 Test Method for Determining Pore Volume Distribution of Catalysts and Catalyst Carriers by Mercury Intrusion Porosimetry

D4464 Test Method for Particle Size Distribution of Catalytic Materials by Laser Light Scattering

E105 Guide for Probability Sampling of Materials

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E456 Terminology Relating to Quality and Statistics

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *capillary action, n*—the ability of a liquid to flow in narrow spaces as induced by the intermolecular forces between the liquid and surrounding solid surfaces.

3.1.2 *macropore, n*—pore with internal width greater than 50 nm.

3.1.3 *mesopore, n*—pore with internal width between 2 nm and 50 nm.

3.1.4 *surface tension, n*—the attractive force exerted upon the surface molecules of a liquid by the molecules beneath that tends to draw the surface molecules into the bulk of the liquid and makes the liquid assume the shape having the least surface area.

4. Summary of Guide

4.1 This guide is intended to provide mesopore and macropore volume information of powdered catalysts and catalyst carriers. It helps users to judge the end point during the titration of catalytic material with water.

4.2 The added water is drawn by capillarity action into the catalytic material's mesopores and macropores. When the end

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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.

point of the titration is reached, water overflows and forms a film on the surface of the water-saturated particles. The particles stick together by surface tension. They adhere to the internal surface of the conical flask upon tapping against a suitable object (for example, the operator's palm).

4.3 The pore volume of the catalytic materials is obtained based on the amount of water being adsorbed at the end point.

5. Significance and Use

5.1 This guide is intended to determine meso- and macropore volume which affects heavy oil cracking performance of a catalyst. The information is useful for materials specification, manufacturing control, and research and development in the evaluation of catalytic materials.

5.2 It has been reported in literature the existence of a correlation between the pore volume obtained from this guide and that from Test Method D4284.[3]

6. Apparatus

6.1 *Burette,* 25 mL with 0.1 mL graduations.

6.2 *Conical Flask With a Ground Stopper,* 100 mL.

6.3 *Balance,* analytical, capable of weighing to nearest 0.001 g.

6.4 *Muffle Furnace,* capable of at least 800 ± 25 °C.

6.5 *Desiccator.*

6.6 *Porcelain Evaporating Dish,* 100 mL.

6.7 *Thermostatic Water Bath,* capable of maintaining temperature of 20 °C stably.

6.8 *Glass Rod,* 8 mm diameter, 15-20 cm long.

6.9 *Cut Resistant Gloves.*

7. Reagents

7.1 *Deionized or Distilled Water,* conforming to Specification D1193.

8. Sampling

8.1 A sampling procedure is needed. Practice E105 is appropriate.

9. Sample Preparation

9.1 Heat a porcelain evaporating dish containing about 80 g of catalyst sample in a muffle furnace at 650 °C for 1 h. The hot evaporating dish is cooled to ambient temperature in a desiccator to prevent moisture pickup.

10. Procedure

10.1 Weigh out 20-30 g of sample (with precision of 0.001 g) and put in a 100 mL conical flask.

10.2 Drop deionized water from a 25 mL burette into the conical flask. For the first time, 4.0–4.5 mL of water (less than 80 % of the total amount) can be delivered.

10.3 Stir the sample with a glass rod quickly. Some sample particles may adhere to the internal surface of the conical flask due to the electrostatic force. The adsorption of water on catalyst is exothermic. During water addition, the sample temperature rises noticeably as felt by hand. Cool the flask to nearly room temperature by placing and shaking it, with constant stirring of sample, in a thermostatic water bath at 20 °C for 1 min.

10.4 Continue to add water. Each time after adding a few drops of water, stir the sample homogenously. Also, observe the fluidity of sample particles. The whole test should be completed within about 15 min. Avoid completing too fast or too slow.

10.5 As water continues to drop, sample particles stick together in clumps reducing fluidity gradually. One feels more resistance to stir. The end point is approaching.

10.6 Add 2–5 drops of water each time and stir the sample about 20 times. Keep the flask with a ground stopper in place horizontally and tap the corner of the flask forcefully 10–20 times against a suitable object, for example, the operator's palm. (**Warning—**Please be careful not to tap so forcefully as to break the glass or against any object that could break the glass, or vice versa.) Rotate slowly the flask for a complete turn (360°) along the horizontal central axis and observe the movement of the bulk sample. Use the following criteria to determine the end point.

10.7 *Before the End Point*—Before rotation, the bulk sample does not adhere to the internal surface of the flask in general, although minor particles may form a thin layer sticking to the wall. The bulk sample in the form of loose lumps moves freely following the rotation (see Fig. 1).

10.8 *Reaching the End Point*—Before rotation, the bulk sample appears as a dense lump adhering to the inner wall. The dense lump falls with or without a tap at the corner of the flask against the bench during rotation. After falling, the sample remains the same shape, but repeated fallings break the dense sample into big and firm lumps each with a noticeable boundary as the flask rotates (see Fig. 1).

10.9 *After the End Point*—Before rotation, the bulk sample appears as one whole dense lump adhering to the inner wall. In most cases, the dense sample falls only with a tap at the corner of the flask against the bench as the flask rotates. After repeated fallings, the dense lump remains the same shape without breaking into smaller lumps (see Fig. 1).

10.10 Record the final reading of the burette.

10.11 Videos demonstrating the procedure and determining the end point are available.[4,5]

[3] Ng, S., Zhu, Y., Humphries, A., Zheng, L., Ding, F., Gentzis, T., Charland, J.P., and Yui, S., "FCC Study of Canadian Oil Sands Derived Vacuum Gas Oils. 1. Feed and Catalyst Effects on Yield Structure," *Energy and Fuels*, Vol 16, 2002, pp. 1196–1208.

[4] "General Operation," 2019, https://youtu.be/Y0yajf0yhBg.

[5] "How to determine the end point," 2020, https://youtu.be/l7jxj9fjKXk.

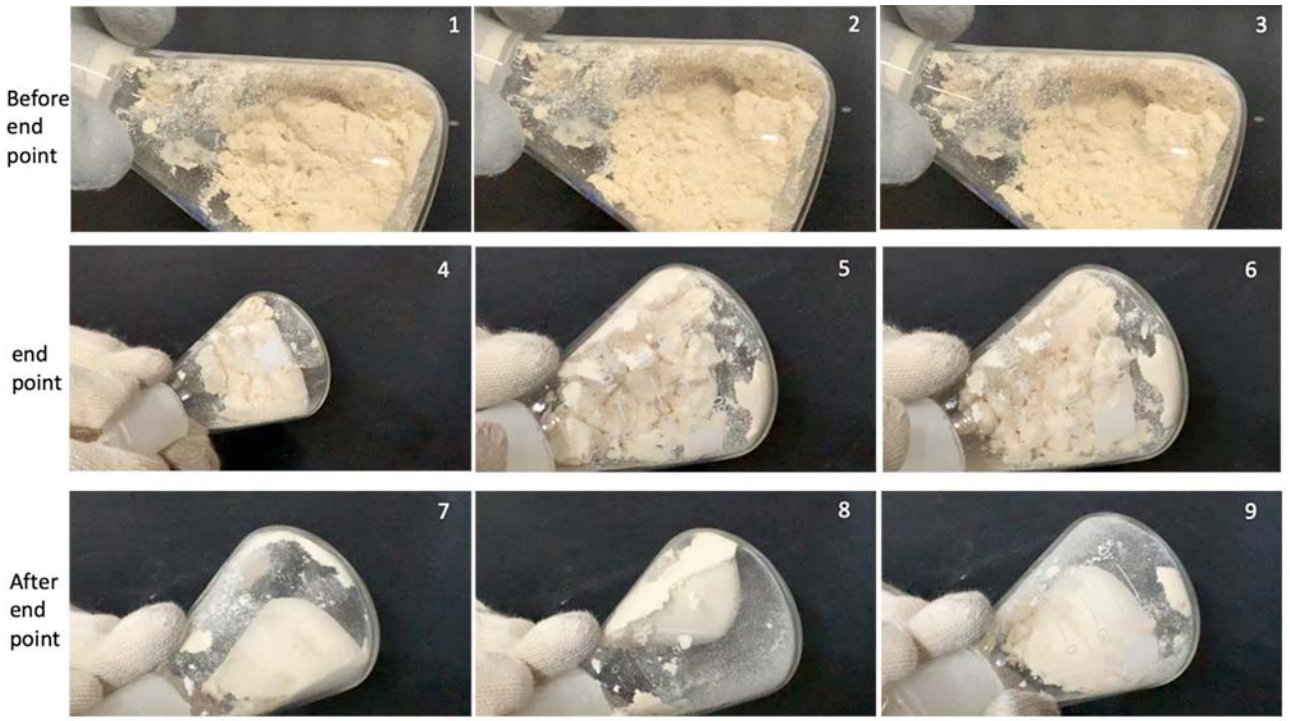

FIG. 1 Demonstration of Before End Point, at End Point and After End Point

11. Calculation

11.1 Calculate the pore volume of powdered catalytic material by water adsorption as follows:

$$V_p = V/M \quad (1)$$

where:

V_p = pore volume of powdered catalytic material, mL/g,
V = total volume of water added at end point, mL, and
M = mass of powdered catalytic material used, g.

12. Precision and Bias

12.1 *Test Program*—The precision of this guide is based on an interlaboratory study in which the named property was measured on four test materials by four separate laboratories. Practice E691, modified for nonuniform data sets, was followed for the data reduction.

12.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.77S, where 2.77S is the 95 % probability interval limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Practices E456 and E177, respectively. See Table 1.

12.3 *Bias*—The procedure in this guide for measuring pore volume has no known bias because there was no accepted reference material suitable for determining the bias for this guide.

13. Keywords

13.1 catalytic material; FCC; fluid catalytic cracking catalyst; pore volume; water adsorption

TABLE 1 Summary of Results From Analysis of Four FCC Catalysts

Sample	Average of pore volume, mL/g [A] M	Standard Deviation of Average Sx	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
A	0.282	0.00809	0.00477	0.0101	0.0132	0.0280
B	0.307	0.00787	0.00493	0.00891	0.0137	0.0247
C	0.378	0.00740	0.00498	0.00862	0.0138	0.0239
D	0.452	0.00705	0.00534	0.00825	0.0148	0.0229

[A] Each value represents the average of test results of each sample.