



Standard Guide for Metals Free Steam Deactivation of Fresh Fluid Cracking Catalysts¹

This standard is issued under the fixed designation D 4463; 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 covers the deactivation of fresh fluid catalytic cracking (FCC) catalyst by hydrothermal treatment prior to the determination of the catalytic cracking activity in the microactivity test (MAT).

1.2 The hydrothermal treatment of fresh FCC catalyst, prior to the MAT, is important because the catalytic activity of the catalyst in its fresh state is an inadequate measure of its true commercial performance. During operation in a commercial cracking unit, the catalyst is deactivated by thermal, hydrothermal and chemical degradation. Therefore, to maintain catalytic activity, fresh catalyst is added (semi) continuously to the cracking unit, to replace catalyst lost through the stack or by withdrawal, or both. Under steady state conditions, the catalyst inventory of the unit is called “equilibrium catalyst;” this catalyst has an activity level substantially below that of fresh catalyst. Therefore, artificially deactivating a fresh catalyst prior to determination of its cracking activity should provide more meaningful catalyst performance data.

1.3 Due to the large variations in properties among fresh FCC catalyst types as well as between commercial cracking unit designs and/or operating conditions, no single set of steam deactivation conditions is adequate to artificially simulate the equilibrium catalyst for all purposes.

1.3.1 In addition, there are many other factors that will influence the properties and performance of the equilibrium catalyst. These include, but are not limited to: deposition of heavy metals such as Ni, V, Cu; deposition of light metals such as Na; contamination from attrited refractory linings of vessel walls. Furthermore, commercially derived equilibrium catalyst represents a distribution of catalysts of different ages (from fresh to > 300 days). Despite these apparent problems, it is possible to obtain reasonably close agreement between the performance of steam deactivated and equilibrium catalysts. It is also recognized that it is possible to steam deactivate a catalyst so that its properties and performance poorly represent the equilibrium. It is therefore recommended that when assessing the performance of different catalyst types, a common

steaming condition be used. Catalyst deactivation by metals deposition is not addressed in this guide.

1.4 This guide offers two approaches to steam deactivate fresh catalysts. The first part provides specific sets of conditions (time, temperature and steam pressure) that can be used as general pre-treatments prior to comparison of fresh FCC catalyst MAT activities (Test Method D 3907) and selectivities.

1.4.1 The second part provides guidance on how to pretreat catalysts to simulate their deactivation in a specific FCCU and suggests catalyst properties which can be used to judge adequacy of the simulation. This technique is especially useful when examining how different types of catalyst may perform in a specific FCCU, provided no other changes (catalyst addition rate, regenerator temperature, contaminant metals levels, etc.) occur. This approach covers catalyst physical properties that can be used as monitors to indicate the closeness to equilibrium catalyst properties.

1.5 The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information only.

1.6 *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:

- D 3663 Test Method for Surface Area of Catalysts²
- D 3907 Test Method for Testing Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test²
- D 3942 Test Method for Determination of the Unit Cell Dimension of a Faujasite-Type Zeolite²
- D 4365 Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst²
- D 5154 Test Method for Determining the Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test²
- E 105 Practice for Probability Sampling of Materials³
- E 177 Practice for Use of the Terms Precision and Bias in

¹ This guide is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.04 on Catalytic Properties.

Current edition approved March 10, 1996. Published May 1996. Originally published as D 4463 – 85. Last previous edition D 4463 – 91.

² *Annual Book of ASTM Standards*, Vol 05.03.

³ *Annual Book of ASTM Standards*, Vol 14.02.

ASTM Test Methods³
 E 456 Terminology Relating to Quality and Statistics³
 E 691 Practice for Conducting an Interlaboratory Study to
 Determine the Precision of a Test Method³

3. Summary of Guide

3.1 A sample of fresh fluid cracking catalyst is placed in a reactor, either fixed bed or preferably in a fluid bed, and is contacted with steam at elevated temperature. This treatment causes partial deactivation of the catalyst.

NOTE 1—In a fixed bed reactor, material containing sulfates, chlorides, etc. can result in significant additional chemical deactivation.

3.2 The catalyst is withdrawn from the reactor and may be subjected to an activity or selectivity determination, or both, by using the microactivity test. (Test Methods D 3907 or D 5154, or both.)

4. Significance and Use

4.1 In general, steam treatment of FCC catalyst can be used either to compare a series of cracking catalysts at a simulated equilibrium condition or conditions, or to simulate the equilibrium condition of a specific cracking unit and a specific catalyst. This guide gives an example for the first purpose and an approach for the latter purpose.

5. Apparatus

5.1 Fixed bed or fluid bed steaming reactors can be used for the hydrothermal treatment of FCC catalyst.

5.2 In the steaming reactor, temperatures of the catalyst can be maintained at selected constant mean levels between 700°C (1292°F) and 850°C (1562°F) \pm 2°C (\pm 3.6°F) during the steam treatment.

5.3 Temperature control during steam treatment is critical, as temperature variations of \pm 2°C (\pm 3.6°F) can lead to \pm 1 wt. % conversion changes or more, especially at higher temperatures.

5.4 In fixed bed steaming, the temperature gradient through the catalyst bed should be kept as small as possible and should not exceed 4°C (7.2°F). In fluid bed steaming the bed temperature must be homogeneous.

5.5 Heating and cooling of the catalyst must be performed in the reactor under a flow of dry nitrogen.

5.6 Precautions must be taken to achieve uniform contact of the steam with the bed.

6. Sampling

6.1 A suitable sampling procedure is needed. Practice E 105 is appropriate

7. Sample Preparation

7.1 No sample preparation is necessary if the catalyst is heated slowly during preheating (non-shock steaming).

7.2 If the sample is introduced directly into a preheated steaming reactor, (shock-steaming) it is desirable to predry the sample for about one hour at about 550°C (1022°F) to prevent excessive catalyst loss.

8. Procedure

8.1 Procedure for fluid bed and fixed bed steam treatment (non-shock steaming):

8.1.1 With the reactor heated to 300°C (572°F) or lower, load the reactor with catalyst.

8.1.2 Start nitrogen flow to the reactor at a flow velocity of 3 cm/s (0.1 ft/s).

8.1.3 Heat the reactor at the maximum rate until a temperature of 600°C (1112°F) is reached.

8.1.4 Keep the temperature constant at 600°C (1112°F) for 30 min in order to remove volatile material from the catalyst.

8.1.5 Heat the reactor at the maximum rate until the desired steaming temperature is reached; for example, at 760, 788 or 800°C (1400, 1450 or 1472°F) \pm 2°C (\pm 3.6°F).

8.1.6 Stop the nitrogen flow and start a flow of undiluted steam at atmospheric pressure and at constant temperature (760, 788 or 800°C). Continue this steam flow for 5 hours. For fixed bed operation, keep the steam flow velocity at 5 ± 1 cm/s (0.16 ± 0.03 ft/s) at the desired deactivation temperature. For fluid bed operation, keep the steam velocity at 3 ± 1 cm/s (0.10 ± 0.03 ft/s).

8.1.7 After 5 h, stop the steam flow and start nitrogen flowing at 3 cm/s (0.10 ft/s) through the reactor.

8.1.8 Cool down the reactor to less than 300°C (572°F). The rate of cooling is not critical.

8.1.9 Remove the catalyst from the reactor and store in a sealed bottle.

8.2 Variations in this procedure in which predried catalyst is added to a steaming reactor preheated to the desired steaming temperature (shock steaming) are also permissible provided a consistent procedure is used.

8.3 *Analysis of Steamed Catalyst*—The steamed catalyst may be analyzed by cracking activity or selectivity determination, or both, using the micro-activity test to measure gas-oil conversion and selectivities as described in Test Methods D 3907 and D 5154, respectively.

9. Precision and Bias ⁴

9.1 *Test Program*—An interlaboratory study was conducted in which the wt. % MAT Conversion was measured in two test materials steamed at three temperatures each in fixed or fluid bed steaming reactors in ten separate laboratories. Multiple sample portions were steamed only by some laboratories, and not all temperatures were used by all the laboratories. Practice E 691 was followed to the extent practicable for the data set. Analysis details are in the research report.

9.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in relative value by less than $2.772 * S$, where $2.772 * S$ is the 95 % probability interval limit on the difference between two test results, and S is the appropriate estimate of relative standard deviation. Definitions and usage are given in Terminology E 456 and Practice E 177, respectively.

⁴ Supporting data are available from ASTM Headquarters. Request RR:D-32-1012.

| | |
|-------------------------------------------------------------------------------|------------------------------------------------------------|
| Mean Within-Lab Relative Standard Deviation in Wt. % MAT Conversion | 95 % Repeatability Interval (Within Laboratory) |
| S = 2.6 % | 7.2 % |
| Mean Between-Lab Relative Standard Deviation in Wt. % MAT Conversion | 95 % Reproducibility Interval (Between Laboratories) |
| S = 4.8 % | 13.3 % |

The within-lab repeatability is of the same order as that found for the wt. % MAT conversion itself.

9.3 *Bias*—This procedure is without known bias, since there is by definition no absolute standard for comparison.

10. Approach to Simulate a Certain Equilibrium Catalyst

10.1 It is frequently desirable to find steaming conditions which give as close a match as possible to the properties of an equilibrium catalyst from a particular FCC unit. These conditions can then be used with other catalysts to be evaluated for that unit with some assurance that the steaming conditions are appropriate to simulate the severity of that particular catalyst addition rate and the regenerator severity. Due to differences in hydrothermal stability of various zeolite and matrix components currently in use in FCC catalysts, a perfect match cannot be obtained with all catalysts under the same steaming conditions.

10.2 Critical steamed catalyst properties to be matched to the equilibrium catalyst include MAT conversion (activity) and selectivity to products such as coke, hydrogen and C₁ to C₃ hydrocarbons which are sensitive to the relative activities of the zeolite and matrix components of contemporary cracking catalysts.⁵ Also the ratio of isobutane/(C₃ + C₄) olefins can be used as an indicator for the ratio of zeolite cracking/matrix cracking. Another critical parameter is the zeolite unit cell size which is, for many catalysts, related to gasoline octane quality. Physical measurements which have been found to be particu-

larly useful in evaluating the match between steamed and equilibrium catalysts are total, matrix (mesopore) and (by difference) zeolite (micropore) surface areas as defined by Test Methods D 3663 and D 4365 and zeolite unit cell size of the zeolite from Test Method D 3942.

10.3 A major problem in steaming fresh catalysts to match equilibrium catalyst is that the zeolite and matrix components deactivate at different rates relative to each other under accelerated hydrothermal conditions than they do at the lower temperatures and steam partial pressures in the FCC unit regenerator.⁶ This rate difference is most pronounced with high matrix activity catalysts having hydrothermally stable matrices and results in steamed catalysts having excessive matrix activity at the same overall activity as the equilibrium catalyst. Relatively higher matrix activity shows up as higher coke, hydrogen and light hydrocarbon yields in the MAT relative to the equilibrium catalyst and as a higher matrix (mesopore) surface area. This problem can be alleviated somewhat by using longer steaming times at lower temperature, but cannot be eliminated by any practical experimental conditions.

10.4 Steaming conditions which have proven to be useful and practical for simulating various FCC units are times of 4 to 6 h at temperatures from about 780°C (1436°F) to 810°C (1490°F). Alternatively, longer times of 16 to 24 h at about 25°C (45°F) lower temperatures may be used. Another technique to simulate equilibrium catalyst properties is to mix portions of catalyst, each steamed under different conditions of time, temperature and steam partial pressure, in order to better match the presence of different catalyst ages in an actual equilibrium catalyst.⁷ Also mixtures of fresh and uniformly steamed catalyst portions can simulate the selectivity properties of equilibrium catalysts.⁸

⁶ Arthur W. Chester and William A. Stover, "Steam Deactivation Kinetics of Zeolite Cracking Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, Vol 16, No. 4, 1977, pp. 285–290.

⁷ D. A. Keyworth, W. J. Turner, and T. A. Reid, "Catalyst Aging Procedure Simulates FCC Conditions," *Oil and Gas Journal*, March 14, 1988, pp. 65–68.

⁸ E. L. Moorehead, J. B. McLean, and A. Witoshkin, "New Approach for the Laboratory Evaluation of FCC Catalysts," *National Petroleum Refiners Association*, 1990 Annual Meeting, March 25–27, 1990.

⁵ R. J. Campagna, J. P. Wick, M. E. Brady, and D. L. Fort, "Fresh FCC Catalyst Tests Predict Performance." *Oil and Gas Journal*, March 24, 1986, pp. 85–96.

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