



## Standard Guide for Metals Free Steam Deactivation of Fresh Fluid Cracking Catalysts<sup>1</sup>

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### 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 or operating conditions, or both, 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 performances 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, but is addressed in Guide [D7206/D7206M](#).

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 [D3907](#)) or activities plus selectivities (Test Method [D5154](#)).

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 either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

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.*

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<sup>1</sup> This guide is under the jurisdiction of ASTM Committee [D32](#) on Catalysts and is the direct responsibility of Subcommittee [D32.04](#) on Catalytic Properties.

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## 2. Referenced Documents

### 2.1 *ASTM Standards:*<sup>2</sup>

- D3663** Test Method for Surface Area of Catalysts and Catalyst Carriers  
**D3907** Test Method for Testing Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test  
**D3942** Test Method for Determination of the Unit Cell Dimension of a Faujasite-Type Zeolite  
**D4365** Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst  
**D5154** Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test  
**D7206/D7206M** Guide for Cyclic Deactivation of Fluid Catalytic Cracking (FCC) Catalysts with Metals  
**E105** Practice 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. Summary of Guide

3.1 A sample of fresh fluid cracking catalyst is placed in a reactor, either fixed bed or preferably 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 activity plus selectivity determination, by using the microactivity test (Test Methods **D3907** or **D5154**).

## 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]  $\pm 2^\circ\text{C}$  [ $\pm 3.6^\circ\text{F}$ ] during the steam treatment.

5.3 Temperature control during steam treatment is critical, as temperature variations of  $\pm 2^\circ\text{C}$  [ $\pm 3.6^\circ\text{F}$ ] 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 **E105** 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]  $\pm 2^\circ\text{C}$  [ $\pm 3.6^\circ\text{F}$ ].

8.1.6 Stop the nitrogen flow and start a flow of undiluted steam at atmospheric pressure and at constant temperature of 760, 788 or 800°C [1400, 1450 or 1472°F]. Continue this steam flow for 5 hours. For fixed bed operation, keep the steam flow velocity at  $5 \pm 1$  cm/s [ $0.16 \pm 0.03$  ft/s] at the desired deactivation temperature. For fluid bed operation, keep the steam velocity at  $3 \pm 1$  cm/s [ $0.10 \pm 0.03$  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 *Testing of Steamed Catalyst*—The steamed catalyst may be tested for gas oil cracking activity or activity plus selectivity, using Test Methods **D3907** or **D5154**, respectively.

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

## 9. Precision and Bias<sup>3</sup>

**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 **E691** 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  $2.772 \cdot S$ , where  $2.772 \cdot S$  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 **E456** and Practice **E177**, respectively.

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  $C_1$  to  $C_3$  hydrocarbons which are sensitive to the relative activities of the zeolite and matrix components of contemporary cracking

catalysts.<sup>4</sup> Also the ratio of isobutane/( $C_3$  olefins +  $C_4$  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 particularly 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 **D3663** and **D4365** and zeolite unit cell size of the zeolite from Test Method **D3942**.

**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.<sup>5</sup> 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.<sup>6</sup> Also mixtures of fresh and uniformly steamed catalyst portions can simulate the selectivity properties of equilibrium catalysts.<sup>7</sup>

## 11. Keywords

11.1 catalytic activity; fresh fluid cracking catalyst; hydrothermal treatment; microactivity test; steam deactivation

<sup>3</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1012.

<sup>4</sup> Campagna, R. J., Wick, J. P., Brady, M. E., and Fort, D. L., "Fresh FCC Catalyst Tests Predict Performance," *Oil and Gas Journal*, March 24, 1986, pp. 85–96.

<sup>5</sup> Chester, Arthur W. and Stover, William A., "Steam Deactivation Kinetics of Zeolite Cracking Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, Vol 16, No. 4, 1977, pp. 285–290.

<sup>6</sup> Keyworth, D. A., Turner, W. J., and Reid, T. A., "Catalyst Aging Procedure Simulates FCC Conditions," *Oil and Gas Journal*, March 14, 1988, pp. 65–68.

<sup>7</sup> Moorehead, E. L., McLean, J. B., and Witoshkin, A., "New Approach for the Laboratory Evaluation of FCC Catalysts," *National Petroleum Refiners Association*, 1990 Annual Meeting, March 25–27, 1990.

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