



Designation: **D7964/D7964M – 14** **D7964/D7964M – 19**

Standard Test Method for Determining Activity of Fluid Catalytic Cracking (FCC) Catalysts in a Fluidized Bed¹

This standard is issued under the fixed designation D7964/D7964M; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers determining the activity and coke selectivity of either equilibrium or laboratory deactivated fluid catalytic cracking (FCC) catalysts. The activity is evaluated on the basis of mass percent conversion of gas oil feed in a fluidized bed reactor. The coke yield is defined as the mass of carbon laid down on the catalyst, also expressed as a percent of the gas oil feed. The scope of the round robin will be limited to the determination of activity and coke. All other analyses are thus beyond this scope and should be noted as “optional.”

1.2 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~~ are not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other. Combining other, and values from the two systems may result in non-conformance with the standard; shall not be combined.

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

1.4 *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

[D2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography](#)

[D4463 Guide for Metals Free Steam Deactivation of Fresh Fluid Cracking Catalysts](#)

[D5154/D5154M Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking \(FCC\) Catalysts by Microactivity Test](#)

[E105 Practice for Probability Sampling of Materials](#)

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[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 ~~activity~~—*activity, n*—a measure of the rate of a specific catalytic reaction, calculated in the present case by dividing conversion by the difference of 100 minus conversion.

3.1.2 ~~catalyst/oil (C/O) ratio~~—*ratio, n*—the mass of catalyst used in the test divided by the mass of feed fed to the reactor.

3.1.3 ~~coke~~—*coke, n*—mass of carbon laid down on the catalyst during the FCC reaction times 1.083.

3.1.4 ~~conversion~~—*conversion, n*—the starting mass of reactant feed minus the mass of the liquid product that boils above 221°C [430°F]; Δ 221 °C [430 °F]; this delta is then reported as a percentage of the starting mass of feed.

3.1.5 ~~delivery time~~—*time, n*—this is the time, in seconds, during which feed is introduced to the reactor.

¹ This test method 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 Nov. 1, 2014/April 1, 2019. Published January 2015/May 2019. Originally approved in 2014. Last previous edition approved in 2014 as D7964/D7964M – 14. DOI: 10.1520/D7964-14.10.1520/D7964-19.

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.

3.1.6 ~~FCC~~—FCC, *n*—fluid catalytic cracking.

3.1.7 ~~gasoline~~—gasoline, *n*—C₅ compounds through compounds boiling at 221°C [430°F]; 221 °C [430 °F].

3.1.8 ~~HCO~~—HCO, *n*—the heavy cycle oil product, which is defined to have a minimum boiling point of 343°C [650°F]; 343 °C [650 °F].

3.1.9 ~~LCO~~—LCO, *n*—the light cycle oil product, which is defined to have a boiling point range of 221 to 343°C [430 to 650°F]; 650 °F].

3.1.10 ~~liquid product~~—product, *n*—all products formed in the catalytic reaction that can be condensed in the chiller bath afterward, usually a combination of gasoline, LCO, and HCO, but can contain a trace of C₄ and C₄ minus compounds.

3.1.11 ~~normalized product yield~~—yield, *n*—the result obtained when each product yield has been corrected for non-perfect mass balances.

3.1.11.1 *Discussion*—

For a run to be judged acceptable, the total recovery, mass % of feed, should be in the range of 96 to 102 % prior to normalization. If the recovery is outside this range the test data should be discarded.

3.1.12 ~~product yield~~—yield, *n*—one hundred times the mass of a specific product divided by the mass of feed used in the test.

3.1.13 ~~selectivity~~—selectivity, *n*—same as yield. ~~Selectivity generally refers to how much of a particular product, such as coke, is formed during a chemical reaction; selectivity is related to, but different from, conversion, which is the total amount of all products formed during the reaction.~~

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4. Summary of Test Method

4.1 A sample of FCC catalyst is contacted with gas oil in a fluidized bed reactor using a specified reaction temperature, a specified mass of catalyst and oil, and specified oil feed rate. Reaction products (liquid product, gas, and coke on catalyst) are analyzed. Conversion, coke, and individual product yields are calculated for each experiment.

4.2 Following analysis of the products, the total recovery (that is, mass balance) of the feed as converted and unconverted products is determined. If the recovery is less than 96 % or greater than 102 %, then the test is rejected as unsatisfactory (an outlier).

4.3 For each catalyst tested, a normalized conversion or activity and a coke mass are determined.

4.4 Further to this test method, a video has appeared in the literature along with a detailed protocol and a table of specific materials/equipment³ to guide users in obtaining materials for the tests.

5. Significance and Use

5.1 The fluidized bed test provides data to assess the relative performances of FCC catalysts. Because results are affected by catalyst pretreatment, feedstock characteristics, and operating parameters, this test method is written specifically to address the accuracy and precision when a common catalyst and oil are tested under the same conditions but at different sites, using Kayser Technologies Advanced Catalytic Evaluation (ACE) unit.^{4,5} Analytical procedures may vary among the sites. However, significant variations are not expected.

NOTE 1—ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

5.2 The standard reaction temperature for purposes of the accuracy and precision statement is 532°C [990°F]; 532 °C [990 °F]. Other reaction temperatures can be used in practice; however, yield data developed at temperatures other than 532°C [990°F]; 532 °C [990 °F] will not be the same. Also, test precision may be different at other reaction temperatures.

³ Ng, S. H., Heshka, N. E., Zhang, Y., and Little, E., "Laboratory Production of Biofuels and Biochemicals from a Rapeseed Oil through Catalytic Cracking Conversion," *J. Vis. Exp.*, e54390, doi:10.3791/54390.

⁴ The fluidized bed reactor described herein is covered by US Patent 6,069,012. Interested parties are invited to identify an alternative(s) to this patented reactor system. Alternative(s) should be submitted to the ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁵ Trademarked, ACE Technology.

6. Apparatus

6.1 The fluidized bed reactor of this test method is shown in Fig. 1. The full ACE apparatus also includes a feed delivery system and both a gas and a liquid collection system. In a typical gas collection system, water is displaced by the collected gas and the volume of displaced water provides a quantitative measurement of the amount of gas collected. Other gas collection systems can be used, such as the water-free gasometer (consisting of two gas chambers in series, each with a piston inside) which is more ideal for H₂S quantification.³ However, it can be a challenge to operate this system in auto mode. Committee D32 can only suggest and will not recommend nor certify any specific vendor. However, significant variations from the test apparatus of this method most likely will result in significantly different activity and selectivity data from identical catalyst samples.

6.2 Chromatographic Equipment:

6.2.1 Liquid product analyses should be performed using Test Method D2887 on a gas chromatograph (GC) equipped with a flame ionization detector.

6.2.2 Gas product analyses may be accomplished in two parts. First, a GC equipped with a thermal conductivity detector is needed for quantitative identification of H₂ and N₂. H₂S can optionally be detected, but will not be quantitative in units that collect gas by water displacement. The second part of the analysis requires a GC equipped with either FID or TCD, for the separation and quantitative identification of hydrocarbon species. Typically, the following compounds are individually quantified: methane, ethane, ethylene, propane, propylene, n-butane, iso-butane, ~~1-butene and 1-butene~~, iso-butene, cis-2-butene, trans-2-butene, iso-pentane, n-pentane, ~~and the unsaturated C₅ isomers (C₅ olefins).~~ For purposes of this test method and round robin the higher boiling gaseous compounds will be lumped into a olefins, and an unresolved C₆⁺ fraction group. If C₅ olefins are not separately identified, then they are included with the C₆⁺ lump as well. The mass of the C₅'s (C₅ and saturates, that is, iso-pentane and n-pentane, and C₅ the olefins, that is, iso-pentenes and n-pentenes, if the latter can be separately identified) and the C₆⁺ group (C₅ olefins, if they cannot be separately identified, and C₆-C₉) are mathematically added to the gasoline liquid fraction.

6.3 Carbon analysis of a representative sample of the spent catalyst (that is, after the cracking reaction has been completed) may be accomplished using a commercially available carbon analyzer if the ACE unit being used does not have catalyst regeneration capability. If the ACE is a model that does have regeneration capability, then the carbon on catalyst is back calculated from the CO₂ evolved in the flue gas during the regeneration cycle.

7. Sampling

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

8. Sample Preparation

8.1 *Equilibrium Catalysts*—Dry samples and remove coke by heating a shallow (less than 10 mm thick) bed of catalyst in a porcelain crucible at 590 ± 20°C [1094 ± 36°F] [36°F] for a length of time sufficient to remove any coke. This typically

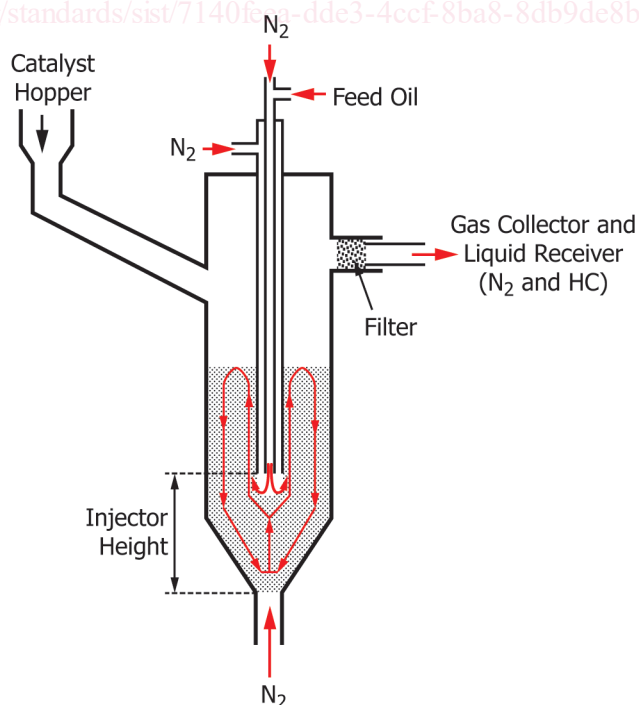


FIG. 1 Fluidized Bed Reactor

requires approximately 3 h. Sufficient air should be available in the furnace to burn the sample free of coke. Insufficient coke removal is indicated by a difference in color of the top and bottom layers. The hot crucible is cooled in a desiccator to prevent moisture pickup. Only equilibrium catalyst will be used in the precision and bias statement of this test method.

NOTE 2—Heavily coked samples may be damaged by sintering or deactivation if oxidation is allowed to occur too rapidly, leading to artificially low catalytic activity and surface area.

8.2 *Fresh Catalysts*—Fresh catalyst samples should be steam treated prior to ACE testing. Steaming procedures such as those specified in Guide D4463 may be used. However, specific conditions (temperature, partial pressure of steam, and time) should be chosen such that the steamed catalyst properties (activity, zeolite and matrix surface areas, and unit cell size) approximate those found in equilibrium FCC catalysts of the same type.

9. Procedure

9.1 Reactor Preparation:

9.1.1 The oil feed line on the ACE unit is meant to be changed with some regularity. Whenever the oil feed line pressure exceeds 1.5 psig, the feed line should be changed. For purpose of this round robin, install a feed line that yields a 1.125 in. injector height. Injector height is defined as the distance from the lowest point of the conical reactor bottom to the bottom end of the feed injector.

9.1.2 The drier tube and humidifier should be serviced as described in the ACE Operating Manual.

9.1.3 The ACE CO₂ analyzer should be calibrated as described in the ACE Operating Manual.

9.2 Preparation of Syringe and Liquid Product Receiver:

9.2.1 Preheat the gas oil feedstock to $170 \pm 5^\circ\text{C}$ [$338 \pm 9^\circ\text{F}$], at which temperature a typical Gulf Coast gas oil will flow easily into the syringe and can be accurately delivered to the reactor. Set the oil feed pump to deliver feed at the prescribed rate for this testing. Calibration of the feed rate is a manual process consisting of changing the speed setting on the pump and performing a feed test. The oil feed line is opened so that oil can be delivered into a tared beaker. The amount per minute is recorded and the test repeated until the oil mass collected is on target.

NOTE 3—If heavier feedstocks are used, the measured rate may be inconsistent. The syringe temperature can be increased to $220 \pm 5^\circ\text{C}$ [$428 \pm 9^\circ\text{F}$] as long as this does not exceed the initial boiling point of the oil.

9.2.2 A small plug of glass wool should be placed in the outlet of the receiver to reduce the carryover of C₅⁺ aerosol into the gas collection vessel. Obtain the initial mass of the liquid product receiver(s) including the glass wool. Weigh each receiver in an analytical balance the top window of which is covered by a cubic plastic shield³ to ensure a draft-free environment.

9.2.3 Install receiver(s) and connect the gas line to the gas collection system. Open the gas vent valve to prevent premature collection of purge gas.

9.2.4 Prepare ethylene glycol bath(s) for the receiver(s) if needed. Immerse the receiver(s) to the level of the gas outlet line(s). Maintain the bath temperature at -15°C [$+10^\circ\text{F}$], -15°C [$+10^\circ\text{F}$].

9.2.5 *Pressure Test*—Pressurize the reactor to 20 kPa [$+150\text{ mm Hg}$] [$+150\text{ mm Hg}$] nitrogen and close the gas vent and nitrogen supply valves. Watch the pressure gauges for 2 min to determine if any significant leaks occur. If no leaks are apparent using the criteria specified in the ACE Operating Manual, then open the gas vent valve carefully to release pressure.

9.3 Performing the Run:

9.3.1 Set up the run conditions in the ACE control interface. Up to six runs can be programmed to run automatically on the ACE unit.

9.3.2 Once the reaction is complete and the gas has been collected, record the volume of displaced water (V_B), the gas temperature (T_R), and atmospheric pressure (P_R). Typically this is done through the ACE control interface. After being mixed, the collected gases may then be analyzed immediately by syringe sampling or by forcing from the gas collection system into a gas sampling loop or a sealable gas sample bag for storage and later analysis.

9.3.3 If using a Model R or R+ unit, then the carbon mass determined by IR must be recorded for later analysis of products. If using an ACE unit that is not equipped with catalyst regeneration capability (Model AP or P), then alternatively the catalyst can be removed from the reactor for carbon analysis as described in 9.4.89.4.9.

9.4 Analyses of Products:

9.4.1 Remove the liquid product receiver(s) and immediately cork the top. After removing the liquid receiver from the bath, the outside is rinsed with water and then with acetone. It is allowed to dry on a rack for 20 min. The contents will warm up a bit during this time so the cork remains in the receiver until final weighing.

9.4.2 Collect the liquid holdup in the reactor exit line and around the reactor-receiver joint with a tared cotton wool swab or other suitable material. Determine the mass of this liquid and record (WQ). Experience indicates this liquid material is predominantly unconverted feed.

9.4.3 ~~The receiver is weighed for mass balance purposes and the mass recorded.~~ Open the liquid product receiver to atmosphere in a vented fume hood for pressure equalization by momentarily removing the stopper on the top outlet of the receiver.

9.4.4 Put the stopper back on and obtain the receiver mass for mass balance purposes.

9.4.5 The vial containing the liquid product is removed and placed in the autoinjector tray of the simulated distillation analyzer, typically an Agilent gas chromatograph equipped with appropriate software for boiling point analysis.