



Feedstock and catalyst effects in fluid catalytic cracking – Comparative yields in bench scale and pilot plant reactors



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HIGHLIGHTS

- FCC reaction performance between a riser and a confined fluid bed reactor (CFBR).
- Performance of the CFBR at constant catalyst residence time and constant space time.
- CFBR correctly ranks feeds and catalysts but exaggerates relative differences.
- CFBR working at constant catalyst residence time simulates better the riser operation.
- Riser is the most reliable reactor to rank catalysts for commercial projections.

ARTICLE INFO

Article history:
Available online 26 November 2014

Keywords:
FCC
Feedstock
Bench scale units
Pilot plant
Reactors

ABSTRACT

Laboratory testing of fluid catalytic cracking (FCC) for feeds and catalysts in a confined fluid bed reactor (CFBR) is widely applied in industry as a standard evaluation tool. In this paper, comparative yields are presented from a circulating riser reactor (CRR) in an FCC pilot plant and in a standard CFBR unit. It is shown that, although a good agreement is obtained for comparative ranking of feedstock quality and catalyst activity, there are significant differences on the absolute yields obtained at constant conversion. These results are explained by differences in reactor operating parameters and their effect on catalyst performance and product selectivity.

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1. Introduction

Over the years different reactors and design configurations have been used for the evaluation of feeds and catalysts for fluid catalytic cracking (FCC) and for process studies as well. A recent article [1] reviews these units. However, three types of reactors have been mainly used that are described in details in the following paragraphs.

1.1. Microactivity unit (MAT)

In 1967, Atlantic Richfield and Davison Chemical published a microactivity test, which employed a fixed catalyst bed with small requirements for catalyst and feed [2]. Many companies modified the original test to provide shorter reaction times (less than 60 s) and higher space velocities [3]. All tests suffered from

heat and mass transfer limitations, non isothermal bed temperatures, feed reflux fractionation in cool zones above the catalyst bed and diffusional resistances stemming from the use of pelleted catalyst.

During the period 1969–1971, a new series of MAT tests evolved. In these tests, feed preheat and powdered catalyst were introduced. Reaction times were shortened to 50–75 s and typical operating conditions were: Temperature, °C: 485, Hydrocarbon Partial Pressure, bar: 0.34, Feed charge, g: 0.63, Catalyst charge, g: 3.0, Catalyst/Oil: 4.8, Weight Hourly Space Velocity (WHSV), h^{-1} : 16.8, Vapor residence time, s: 0.6, Run time, s: 50, Catalyst residence time, s: 50. Based on this test ASTM developed a Standard Testing Method [4] recommending the following changes: Catalyst charge, g: 4, Run time, s: 75.

Grace introduced major improvements in MAT testing [5–7] by recognizing that a catalyst contact time of 75 s is not representative of commercial operations, where contact times of 2–10 s are used. A new configuration (SCT-MAT) was adopted, by placing the catalyst mixed with glass beads in an annular catalyst bed created by a glass core of 1 cm diameter and 10 cm in length.

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The distance between reactor wall and glass core is 2.5 mm. The feed rate is kept constant at 1.5 g with run time 12 s. Catalyst-to-oil is varied by changing the mass of catalyst. The bed volume is always kept at 10 ml by diluting a varying catalyst weight with glass beads to ensure constant vapor velocities. The reaction temperature is maintained at 833 K.

Tests based on the use of a fixed bed catalyst have found wide application for the measurement of the relative catalyst activity and feed crackability in the 70's. As the use of the MAT unit was extended to carry out yield selectivity comparisons, many inconsistencies were noted in comparisons of MAT data with pilot plant data. These differences stem from the following reasons: (a) A large temperature drop during feed injection leading to higher coke yields, (b) Longer time on stream, which tends to overemphasize matrix effects, (c) Higher feed concentrations, which favors bimolecular reactions like hydrogen transfer reactions.

These problems were largely solved by Wallenstein et al. [6,7] with a clever redesign of the geometry of the catalyst bed, the injection system and the product recovery system. They demonstrated that the new SCT-MAT was correctly ranking catalysts in the same order as the continuous Davison Circulating Riser (DCR) unit. These conclusions were founded by a series of comparisons of high vs low rare earth catalysts and low vs high matrix catalysts.

1.2. Confined fluid bed reactors (CFBRs)

Units in this category extensively used for the evaluation of cracking catalysts for petroleum refineries include:

Fluid Bed Simulation Test (FST) introduced by Akzo Nobel [8], during which a gas oil feed at a fixed feed rate is processed over a fluid bed of cracking catalyst. Typical operating conditions are: Feed rate, g/min: 1.2, Catalyst load, g: 3–10, Injection time, s: 25–125, Catalyst to oil: 3–9, Vapor residence time, s: 0.5–2, Reaction temperature, °C: 500–600. The catalyst to oil changes by varying the catalyst load to the reactor.

Advanced Cracking Evaluation (ACE) introduced by Kayser [9]. This unit also utilizes a confined fluid bed reactor and it maintains a fixed feed rate together with a fixed rate of nitrogen to maintain a fluidized bed at bubbling conditions. Recommended operating conditions by Kayser are: Feed rate, g/min: 1.2, Catalyst charge, g: 9, Injection time, s: 50,60,75,90,120,150, Catalyst to oil: 3.75–9, Weight Hourly Space Velocity, h^{-1} : 8, Reaction temperature, °C: 538.

In trying to evaluate the relative use of the two fluid bed reactor systems, one quickly finds out that the ACE unit was widely accepted by the refining industry, because of its design feature and its unique capability to run multiple samples with a product recovery system securing reproducible results with acceptable mass balances. Although both tests can be used for relative ranking of feeds and catalysts, they have inherent drawbacks due to the following reasons: (a) The vapor superficial velocity (8–18 cm/s) exceeds the minimum fluidization velocity (0.12–0.48 cm/s) of the catalyst particles by a factor over 30. This implies that the majority of gas moves in plug flow through the bed and the catalyst is completely mixed. Part of the gas is backmixed and this results in secondary reactions producing high gas and coke yields at the expense of gasoline, (b) Since the catalyst time on stream is high, a large portion of the feed is cracked over a catalyst with high carbon on catalyst. This results in changes in catalyst activity and selectivity with time on stream [10]. In contrast the feed cracking in a commercial unit takes place over a catalyst with gradual carbon deposition and as a result the catalyst activity and hydrogen factor do not depend on time on stream of the catalyst to the same extent as in a confined fluid bed.

1.3. Pilot plant riser reactors

Two systems have found wide use by the petroleum industry. These are the ARCO pilot plant and the Grace Davison Riser reactor (DCR).

The ARCO pilot plant [11] was introduced in the 1970's and it is based on a unique design, where regenerated catalyst enters the bottom of a moving fluid bed reactor and it then discharges to a stripper, before it returns to the regenerator. Typical operating conditions are: Reactor temperature, °C: 482–540, Regenerator temperature, °C: 650, Feed rate, g/min: 8–15, Catalyst Circulation, g/min: 60–120, Catalyst/oil: 5–12, WHSV: 5–15. Although this unit correctly ranks catalyst and feeds it has two major limitations: Inability to simulate a modern commercial riser design and limited ability to process heavy resid feeds.

Grace Davison introduced a 12 feet riser based FCC pilot plant [12,13], which has found wide application in industry. Regenerated catalyst to the riser inlet is controlled with a slide valve. It offers many different modes of operation (isothermal, adiabatic, pseudo adiabatic) and it can simulate the operation of a commercial riser. Typical operating conditions are: Riser temperature, °C: 510–540, Regenerator temperature, °C: 690–750, Feed rate, g/h: 400–1500, Catalyst circulation, g/h: 4500–7500, Catalyst inventory, g: 3000. The wide acceptance of DCR by the industry implies that it satisfies most of the needs of the petroleum industry. However, it is not known whether DCR can run feedstocks with a high carbon residue.

Based on the literature search, it becomes evident that there is a continuous need to assess available laboratory reactors to offer support to petroleum refineries for both catalyst and feedstock selection. In this paper two systems available in Chemical Process and Energy Resources Institute (CPERI) will be compared: A riser pilot plant [14] and a CFBR (ACE) unit [9]. The methodology for developing conversion-selectivity plots will be presented for both feedstock and catalyst evaluation. Then a back to back comparison of the two systems will be performed at constant conversion for two cases: (a) feed comparison, (b) catalyst comparison. The goal is not to promote one system versus the other, but rather to offer the advantages and disadvantages for different applications.

2. Experimental

2.1. Units used

Experimental results from two reactor configurations are presented in this paper: a circulating riser reactor (CRR) and the ACE confined fluid bed reactor (CFBR). A brief description of each unit follows:

2.1.1. Confined fluid bed reactor

One of these systems with extensive use by the refining industry is the Advanced Cracking Evaluation (ACE) unit. Details on this unit are presented in reference [9]. Briefly, this unit consists of a 1.6 cm ID reactor containing 9–12 g of catalyst. This catalyst is fluidized with a constant stream of nitrogen (140 cc/min). During a test a feed flows, through a small diameter tube, at a distance of 1.1 inches from the bottom of the reactor. Results from two different modes of operation of the ACE unit are presented in this paper:

Constant catalyst weight, variable injection time (mode 1). This mode of operation will be designated as constant space time (τ), variable catalyst residence time (t_c). The operating conditions used for operation mode 1 are those recommended by Kayser Inc.:

Feed rate, g/min: 1.2.
Catalyst weight, g: 9.

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