

Design Engineering, Implementation And Control Of A Flexible Cyclic Deactivation Unit

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In commercial Fluid Catalytic Cracking (FCC) units the catalyst that circulates around the unit, is progressively deactivated even during the first few cycles. Cyclic deactivation (CD) procedure mimics the deactivation that happens in the industrial FCC unit by exposing the catalyst to process conditions at cycles of cracking, stripping and regeneration respectively. The objective of the present work is to investigate the challenges that arise from the automated operation of a deactivation process unit using a novel control scheme, based on a distributed control system (DCS). Experiments showed that the unit runs effectively showing stability under a wide range of experimental conditions. The obtained results revealed the ability of the system to accurately operate according to the predefined procedure and providing with deactivated catalyst according to specified requirements by the deactivation protocol.

1. Introduction

Fluid catalytic cracking (FCC) is responsible for the conversion of heavy feedstocks (gas oils streaming out from vacuum distillation towers or residues from atmospheric and vacuum distillation towers) into lighter, more valuable products such as liquefied petroleum gas (LPG) and cracked naphtha, the major constituent of the gasoline pool. Together with the desired cracking reactions, coke formation (highly condensed hydrocarbons and/or lighter compounds dragged or retained in the pore structure of the catalyst after stripping) also occurs in these systems. The typical FCC catalyst consists of a mixture of an inert matrix (kaolin), an active matrix (alumina), a binder (silica or silica–alumina) and a Y-zeolite. During the FCC process, a small but significant portion of the feedstock is converted into coke. This coke temporarily deactivates the active sites of the catalyst by poisoning, pore blockage or both, resulting in an important activity loss (Cerqueira et al, 2008). In order to recover the activity, the FCC catalyst continuously circulates between the riser (FCC reactor) and the regenerator vessel. In the regenerator, coke is converted into CO, CO₂, H₂O, SO_x and NO_x compounds. The new discoveries of heavy oil deposits have favored many FCC units to begin processing feedstocks with a higher tendency to form coke. This is particularly true for residue fluid catalytic cracking (RFCC) units, which are designed to convert 100% residue from the atmospheric distillation tower. Due to the fluidized bed nature of the process, the

catalyst particles may break, producing fines that will result in particulate emissions. In order to cope with the loss of catalyst in the form of fines due to catalyst attrition and also in order to maintain catalyst activity, fresh catalyst make-up is frequently needed. For some FCC units processing feedstocks with a high level of metals, it is also common to remove a portion of the inventory and increase the catalyst make-up to accelerate the replacement of catalyst by fresh portions and, thus, keep contaminant metals at an acceptable level. The fresh catalyst addition needed to maintain the activity of the inventory (1400 t/d for 350 FCC units worldwide) is responsible for making the FCC process the most important market for catalysts (Rawlence et al, 1991). As a consequence, the catalyst that effectively participates in the cracking reactions has an age distribution (Lin et al, 2007) i.e., it is composed of a mixture of young (low metal concentration, high activity) and old (high metal concentration, low activity) particles. This mixture of young and old catalyst from an industrial FCC unit is called *equilibrium catalyst* (e-cat).

Due to the complexity of the deactivation mechanisms, the prediction of the commercial catalysts' performance is one of the most important research activities in the oil refining industry. As a result, one of the biggest challenges in FCC research field is to first simulate how the fluid cracking catalyst is deactivated in a commercial FCC unit and then evaluate its performance in laboratory/pilot-scale testing. It should be underlined here that selecting the proper catalyst deactivation method is just as important as the pilot testing of FCC catalyst. Thus, there is a need for the development of a realistic deactivation technique that would simulate in the laboratory the deactivation of catalysts that happens in a commercial FCC unit, under the combined action of metals, steam, temperature, thermal shock, etc. The pilot cyclic deactivation unit (CDU) was engineered in CPERI. The objective of the present work is to investigate the challenges that arise from the automated operation of a deactivation process unit using a novel control scheme, based on a distributed control system (DCS). The main emphasis was given to the design and development a control scheme, which is based on a state of the art control system.

2. Cyclic deactivation (CD)

Cyclic deactivation procedure mimics the deactivation that happens in the industrial FCC unit by exposing the catalyst to process conditions at cycles of cracking, stripping and regeneration respectively. Psarras et al (2007) with the study of the accessibility effect on the irreversible deactivation of FCC catalyst from contaminant metals, using CPERI's cyclic deactivation and cyclic propylene steaming laboratories units points out that the CD procedure achieves more realistic deactivation of FCC catalysts. Also, Lin et al (2006) refers that CD procedure provides a close simulation of the FCC operation and is one of the best deactivation approaches to address additive deactivation. Psarras et al (2008) also investigates advanced laboratory deactivation techniques of FCC catalysts via FTIR acidity studies using CPERI's cyclic deactivation and cyclic propylene steaming laboratory units where new deactivation protocols tested, (2step CD, advance CPS). In this study a promising pathway to the optimization of laboratory deactivation methods is presented. Tailoring and consequent optimization of lab deactivation protocols can be achieved by two combined strategies: i) proper selection

of the required parameters in order to perform a simulating hydrothermal deactivation and manage to produce the equilibrium sample's properties and ii) by accurate selection of the needed redox cycles in order to prevent the exaggeration of the metal effects and to retain the acidity at the required values. The pilot CD unit, presented, during the design, construction and operation use this knowledge to be a flexible deactivation unit.

2.1 Cyclic deactivation unit description

A simple diagram of the pilot cyclic deactivation unit is showed in figure 1. The main parts of the unit are:

1. The feed system consists of a heated and weighted feed vessel. The enclosed VGO with the contaminant metals are heated and circulated by a pump to be homogenous and with a second pump delivered into the reactor during the cracking step. The volume of the vessel is 30 lt.

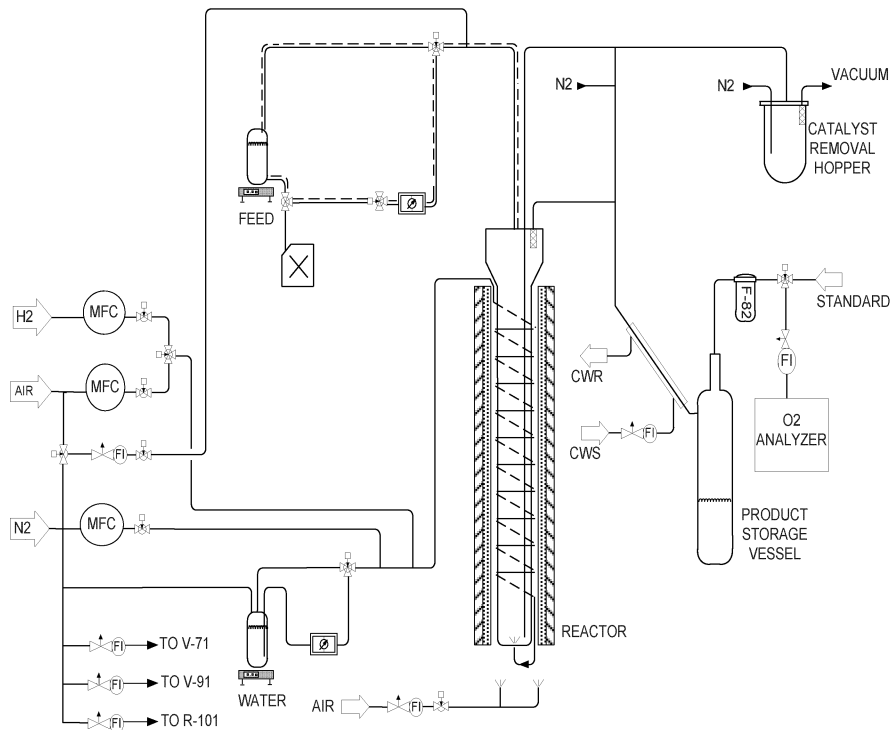


Figure 1: A simple diagram of the pilot cyclic deactivation unit

2. The metal reactor is placed in an oven with three heating zones. The catalyst is fluidized and heated. The catalyst weight is 5 kg. The oven's power is 16.5 KW and each heated zone is controlled using the internal catalyst temperature, using thermocouples placed in the middle and along the catalyst inventory.

With this technique the catalyst has homogenous and stable temperature in each step of the deactivation procedure.

3. The products apparatus where a double pipe heat exchanger condenses the products of the cracking reaction and collects the liquids into a weighted vessel, the volume of the vessel is 35 lt.
4. The steam system is consists of a weight vessel with distilled water and a pump that delivers the water to an external to reactor spiral tube around the reactor vessel where is vaporized and is inserted to the fluidized catalyst during the steaming deactivation step.
5. The gasses feed system.
6. The systems for removal and adding catalyst during the deactivation procedure.
7. The DCS for the control of the unit and the procedure bellow there is presented in more detailed below.

The cyclic deactivation unit operates automatically and is equipped with several safety switches, which assure the operation to stop in case high pressure, overheating and running out of control occurs.

2.2 Cyclic deactivation unit - DCS

The complexity of the experimental protocol requires high accuracy in the execution of the control tasks and actions. The automated operation of the process unit was implemented using a novel control scheme, based on a distributed control system (DCS, DeltaV by Emerson). The objective of the control scheme was to satisfy the requirement for the unit to operate unattended for long periods of time. Also special consideration was given at the design phase in order to provide personnel and equipment safety. The architecture of the implemented distributed system utilizes the technological advancements in process monitoring, control and industrial automation. The capability of intelligence extraction that resides on the DCS network, in combination with optimizing features of the modern process control, makes both operational functions and parametric protocol development more flexible and reliable. An operator interface was developed after analyzing and subsequently synthesizing requirements of the unit protocol, by specifying reasonable, simple and fully functional program modules.

3. Cyclic deactivation procedure testing

The tested CD-run consists of seven cycles, while each cycle includes:

1. The cracking step, where the VGO feed with the contaminant metals is delivered to the catalyst and during the cracking reaction which performs the metals poisoning of the catalyst. The cracking step is flexible with a catalyst-oil ratio ranging between 5 to 10 and cracking temperature used is between 920°F to 1050°F.
2. The stripping step, where the products of the cracking reaction are removed.
3. The regeneration step, where air is delivered to the catalyst to remove the coke and to regenerate the catalytic sites. The range of the regeneration temperature is between 1150°F and 1350°F.

4. The steaming deactivation step, where steam runs through the catalyst reduces the catalytic activity. The normal steaming temperature is 1450°F.
5. The cooling step, where the temperature of the catalyst is reduced from the steaming temperature to the cracking temperature.

After this step the procedure returns to step 1 and is carried out for 6 cycles.

A typical run is showed in figure 2.

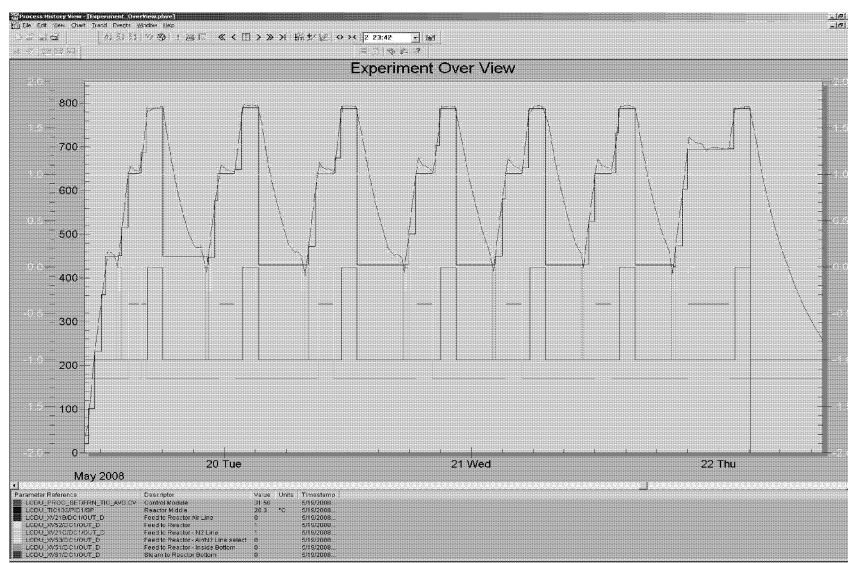


Figure 2: Preliminary Cyclic Deactivation run

The retention properties of the deactivated catalyst that are achieved with the procedure followed in Pilot CD unit can be compared with the retention properties of the deactivated catalyst that Psarras et al (2008) refers using CPERI's bench scale cyclic deactivation unit with the classical procedure (a) and the 2step CD (b) procedure and with the e-cat properties. The properties compared are the total surface area (TSA), the zeolite surface area (ZSA), and the matrix surface area (MSA) between the fresh catalyst and the deactivated catalyst. Table 1 shows this comparison between the CD units and the procedures followed.

Table 1: Comparison between the CD units and the procedures followed.

	a. Classical CD	b. 2Step CD	Pilot CD	e-cat
% Retention of TSA	62.61%	72.16%	56.54%	49.14%
% Retention of ZSA	61.87%	69.66%	56.28%	49.24%
% Retention of MSA	65.00%	80.18%	57.52%	48.85%

As showed at the above table 1 the pilot CD unit mimics more the retention of the e-cat properties.

4. Conclusions

The present work investigates the challenges that arise from the automated operation of a deactivation process unit using a novel control scheme, based on a distributed control system (DCS). The design and development a control scheme, which is based on a state of the art control system was presented where the complexity of the experimental protocol requires high accuracy in the execution of the control tasks and actions. Experiments showed that the unit runs effectively showing stability under a wide range of experimental conditions. The control scheme showed exceptional response subjected to constrains posed by the evaluation protocol. The obtained results revealed the ability of the system to accurately operate according to the predefined procedure. As shown by the comparisons presented by the reference units that operate currently in CPERI's laboratory, the unit is providing with deactivated catalyst according to specified requirements by the deactivation protocol.

5. Acknowledgments

The authors would like to acknowledge the following support personnel Nikos Georgiou, Aris Moudiotis and Niki Drakaki, for their important contribution on the construction, commissioning and troubleshooting phases of this work.

References

- Bendiksen M., Tangstad E., Myrstad T., 1995, A comparison of laboratory deactivation methods for FCC catalysts, *Applied Catalysis A: General* 129, 21-31.
- Cerqueira H.S., Caeiro G., Costa L., Ramoa Ribeiro F., 2008, Deactivation of FCC catalysts, *Journal of Molecular Catalysis A: Chemical* 292, 1-13.
- Lin L., Darrell R., Jorge A.G., 2007, Laboratory deactivation testing fort he stability of FCC CO combustion promoters, *Applied Catalysis B: Environmental* 72, 212-217.
- Psarras A.C., Iliopoulou E.F., Kostaras K., Lappas A.A., Pouwels C., 2008, Investigation of advanced laboratory deactivation techniques of FCC catalysts via FTIR acidity studies, *Microporous and Mesoporous Materials*, article in press.
- Psarras A.C., Iliopoulou E.F., Nalbandian L., Lappas A.A., Pouwels C., 2007, Study of the accessibility effect on the irreversible deactivation of FCC catalysts from contaminant feed metals, *Catalysis Today*, 127, 44-53.
- Rawlence D.J., Gosling K., 1991, Irreversible deactivation of FCC catalysts, *Catalyst Today*, 11, 47-59.