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Modelling coke formation and deactivation in a FCCU

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Abstract

In this paper we describe a new model of catalyst deactivation due to riser reactions in a FCCU. For this purpose, we analyse different coke types and model the formation of each type based on oil feed properties rather than considering all cokes as being equal like other authors do. Thereafter, we examine different deactivation kinetic equations and propose an alternative that describes catalyst deactivation against coke as opposed to against time as in conventional approaches. Although it is easier to model deactivation against time, our model is more flexible and intuitive since it can simulate special situations, such when the catalyst is partially regenerated.

Keywords: Coke; Catalyst deactivation; Deactivation by coke; Riser; FCCU

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1. Introduction

In the following we present our model for catalyst deactivation in a FCC unit riser. This model adds to earlier work (Garcia-Dopico and Garcia [1,2]). Catalyst deactivation should be examined in detail to correctly model a FCC reactor, as catalyst activity has a big impact on cracking reactions and, therefore, on product distribution.

The main obstacle for building a good FCC unit model is that the kinetics of both the deactivation and cracking reactions taking place in the riser are unknown, whereas the fluid dynamics is well established. Deactivation is especially complicated, which means that most models take the approach of assuming that catalyst deactivation takes place against time rather than against coking, as it is really the case. In this paper, on the other hand, we will look at coke formation in detail and establish a catalyst deactivation model against coking on this basis.

There are several causes of catalyst deactivation (Mihalcea et al. [3]). Catalyst deactivation can take place because of:

- Poisoning due to chemisorption of some impurity.
- Erosion and breakage.
- Hydrothermal ageing, that is, loss of surface area because of exposure to high temperatures and steam.
- Coke deposition.

The first three are irreversible and do not modify catalyst activity from the riser entrance to exit very much (although they can have a big impact on the catalyst properties in the unit). The fourth is reversible and it is the main cause of rapid deactivation. As coke deposition inside the porous structure of the catalyst is what conditions catalyst activity, we focus on this question. Specifically, we will look first at coke and its different types, then at the model that we propose for coke formation and, finally, at the model developed for catalyst deactivation.

2. Coke and coke types

The term coke, as established in the literature, includes all the carbonated materials that are left in the catalyst after reaction. It is not a single species, but a material that includes species with a high condensation rate and pseudographitic structure. Its general composition is $(CH_n)_x$, which, with a value of $n = 2$, is initially hydrogen rich, but then evolves in time as a result of degradation reactions, “n” falling through dehydrogenation and “x” rising through condensation.

The value of “n” depends on several factors, including the oil feed, although the structure of the coke becomes more

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uniform after stripping. Other authors have given the following values for "n":

- $0.5 < n < 2$ according to Lasa and Grace [4].
- $0.4 < n < 2$ according to Mihalcea et al. [3].
- $0.4 < n < 1$ according to Azkoiti [5].
- $0.4 < n < 1.2$ according to Turlier et al. [6].

The mechanisms of coke formation are complex and are not absolutely clear, as it involves many processes that depend on countless parameters, the main ones being:

- Oil feed composition, especially the relative quantities and structure of alkanes, alkenes, naphthenes, aromatics, heterocycles, etc., as well as the presence of impurities (metals, especially Ni).
- Catalyst properties, related to the number, type and accessibility of the catalyst active centres, which depend in turn on other more elementary variables, such as composition, preparation, as well as internal structure and pore size.
- Operating conditions, of which time on stream, gas–oil feed flow, pressure and riser temperature are noteworthy.

One way of classifying coke is to grade it by source, according to which coke can be divided into four categories:

- Catalytic coke: coke that is produced when a hydrocarbon is cracked on an acid catalyst, i.e. is a by-product of the sought-after reaction. The size of the deposit depends on conversion and catalyst contact time with the reacting mix.
- Contaminant coke: coke that is produced as a result of the presence of dehydrogenating pollutants like Ni, Cu, V or Fe.
- Additive coke: coke produced by those feedstock fractions that are not volatile under riser working conditions and which, therefore, are deposited on the catalyst, that is, condense. Additive coke is related primarily to Conradson Carbon, but also to nitrogenated molecules.
- Cat-to-oil coke: the fraction of the oil feed that is trapped or occluded in the catalyst, but could potentially be extracted by means of a stripping process. It is not really coke, as it has a high hydrogen content. Nevertheless, it has to be taken into account because it will burn in the regenerator if it is not extracted in the stripper. It is very much related to riser pressure, as more hydrocarbons will be trapped at higher pressures.

3. Modelling coke formation

Now that we have analysed the different coke types present in the riser, we move on to model them. Because of its special properties, coke cannot be dealt with like the other products (it is not even a product). In the literature several authors give special-purpose equations for coke. Some of these are:

- Pope and Ng [7] calculate catalyst coke content as a function of contact time and activity:

  $$m_s = A_v t_c \tag{1}$$

  Obviously, this expression is of no use for us to calculate coke content, as we do not know what catalyst activity is as yet, and this equation is only practical if activity is calculated from contact time.
- Hovd and Skogestad [8] use the Kurihara equation, according to which the increase of coke in the catalyst is a function of contact time, of the concentration of coke from the regenerator and of temperature:

  $$C_{\mathrm{cat}} = k_c \sqrt{\frac{t_c}{C_{\mathrm{rc}}^n} \exp\left(\frac{-E_{\mathrm{cf}}}{RT_1}\right)} \tag{2}$$

  It is a well-known and valid equation, the only snag being that it makes no distinction between different coke types, which then complicates the calculation both of deactivation, as they do not all participate equally, and of the balance of material in the stripper, because they cannot remove all the coke adsorbed on the catalyst.
- McFarlane et al. [9] rate coke yield as a function of flows, residence type and oil feed properties (Ψ_f):

  $$F_{\mathrm{coke}} = \frac{1.3557 \cdot (F_3 + F_4) F_B \tau_r^{-1.9843}}{100\mathrm{WHSV}} \tag{3}$$

  $$F_B = \frac{\Psi_f F_3 + 3F_4 + 2F_1 - 0.8F_2}{F_3 + F_4} \tag{4}$$

  To get the coke content in the catalyst, it would be necessary to divide by the cat/oil (catalyst to oil feed ratio). In any case, these expressions do not have a physical meaning, and are more akin to an empirical than a theoretical model.
- Sadeghbeigi [10] expresses coke yield as a function of cat/oil, temperature, residence time and oil feed properties (Zi):

  $$\mathrm{Coke} = g(Z_1, \ldots, Z_n)(\mathrm{C/O})^n (\mathrm{WHSV})^{n-1}\, e^{\Delta E_c / RT_{\mathrm{rx}}} \tag{5}$$

  To calculate the concentration, again it would be necessary to divide by cat/oil. It is a valid expression that has the same hitch as the above-mentioned Hovd and Skogestad [8] equation.

Apart from the above-mentioned problems of not all the cokes playing the same role in deactivation and only one being able to be retrieved in the stripper, if no distinction is made between different coke types, such disparate findings can be reached as:

- Turlier et al. [6] claim that coke yield is not influenced by temperature, although coke content rises at high temperatures.
- Arandes et al. [11], on the other hand, say that coke yield drops at low temperatures.