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Study of the catalyst deactivation in an industrial gasoil HDS reactor using a mini-scale laboratory reactor

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ABSTRACT

The activity of a hydrodesulphurization catalyst loaded in an industrial hydrotreater is studied at start up and end of run. Catalyst initial and final activity was determined by performing HDS experiments at industrial conditions in a laboratory mini-scale hydrotreater. The results show that the deactivation of the catalyst samples collected from three different places of the industrial reactor do not vary significantly, the maximum difference among the catalyst samples, being less than ±4%. The experimentally determined deactivation level of the catalyst samples is compared with the deactivation estimated for the same industrial reactor and the same load using a hybrid neural network model trained with operational data of the industrial and the results are in close agreement. Catalyst deactivation appears to be faster for hydrogen consumption reactions than for hydrodesulphurization reactions indicating a decreasing hydrogen consumption trend with time in operation for specific sulphur content in the product.

1. Introduction

The demand for cleaner fuels has actuated most of the countries to set down very strict specifications for the automotive diesel. The commission of the European Communities has already instituted that all petrol and diesel sold in its area must contain less than 50 ppm sulphur after January 1st, 2005 and has proposed 10 ppm after January 1st, 2011 [1]. For the achievement of these specifications the refineries must perform the HDS process at stricter reaction conditions. As a result, the deactivation rate of the HDS catalysts increases and the study of the evolution of its activity becomes more imperative, so that the operation conditions of the industrial HDS reactors to be optimized and the used catalysts time on stream to increase.

The deactivation rate of HDS catalysts depends on the feed quality (content of aromatics, organometallic compounds, asphaltenes) [2,3], and it passes through three different phases. A rapid loss of activity due to coke formation on the catalyst surface, a slower phase where metals cover the catalyst surface and the final phase where rapid loss of activity occurs due to metals and coke plugging the catalyst pores [4,5].

As, it was presented by Thakur and Thomas [6] the coke fouling starts with high rates from the first day of HDS catalyst's operation, causing a rapid loss of the catalyst activity. This period could be considered as the stabilization time of the catalyst. The coke fouling shortly reaches a maximum value, thus the deactivation of the catalyst follows a fairly shorter rate, mainly due to metal deposition. The actual deactivation rates cannot be predicted as they depend on catalyst surface characteristics, pre-sulphidation procedure and feed quality which vary significantly within the operation period of the catalyst and from unit to unit.

The axial deactivation profile of a catalyst in an industrial reactor depends on the configuration of the reactor and the feeds used. For a gas liquid downflow reactor with one catalyst bed without intermediate quenches and cooling the deactivation close to the reactor exit is higher due to higher operation temperatures [7]. In contrast, for reactors with intermediate cooling between the catalyst beds the catalyst activity at the end of run is more uniform. This happens because quenches help in keeping reduced reaction temperatures close to reactor exit resulting in more uniform catalyst deactivation.

For the study of deactivated HDS catalysts many works have appeared and the mechanisms of the catalyst's deactivation have been described by many authors [2,6,8]. Different types of reactors have been used to perform HDS experiments simulating the operation of industrial HDS reactors, e.g., autoclave reactors [2,8,9] or large scale bench and pilot fixed bed reactors [4,7,10]. However, the study of HDS reactions as well as the deactivation rates of HDS catalysts appears to be more efficient in small scale laboratory fixed bed rectos [11–13]. The main problem with small laboratory units is that the velocities of gases and liquids need to be much lower than those of industrial units in order to operate at the same LHSVs and gas/oil ratios as those in industrial units. As a result, fluid dynamics problems as well as wall effects and incomplete catalyst particle irrigation may appear and investigators are called

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Nomenclature

a	catalyst activity, dimensionless
A_R	reactor across area (m^2)
CH	specific H_2 consumption Nm^3 H_2 m_{Oil}^{-3}
CHT	maximum specific H_2 consumption (Nm^3 H_2 m_{Oil}^{-3})
C_S	organic sulphur concentration (ppm)
d_{bed}	density of catalytic bed ($kg\,(m^3)^{-1}$)
E	activation energy ($J\,mol^{-1}$)
f	objective function
HDS	hydrodesulphurization
i	experiment number
$(G/L)_{out}$	gas to liquid ratio at the outlet of the reactor (Nm^3 H_2 m_{Oil}^{-3})
k_{CH}	reaction constant of hydrogen consumption reactions ($(m_{Oil}^3)^2$ kg_{cat}^{-1} s^{-1} bar H_2^{-1} Nm^3 H_2^{-1})
K_{H_2S}	inhibition factor (Pa H_2S^{-1})
k_{HDS}	HDS reactions rate constant (kg_{Oil} ppm_S^{1-n} kg_{cat}^{-1} s^{-1} Pa H_2^{-1})
LHSV	liquid hourly space velocity (h^{-1})
MB_{H_2S}	molecular weight of hydrogen sulphide ($kg\,mol^{-1}$)
M_{Oil}	oil mass flow rate (kg_{Oil} s^{-1})
n	reaction order
N_{H_2}	hydrogen molar flow rate ($mol\,s^{-1}$)
N_{H_2S}	hydrogen sulfide molar flow rate ($mol\,s^{-1}$)
P	partial pressure (Pa)
R	ideal gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$)
r	reaction rate (ppm_S kg_{Oil} s^{-1} kg_{cat}^{-1} for HDS and Nm^3 H_2 s^{-1} $kg_{cat}^{-1}$for CH)
T	absolute reactor temperature (K)
z	reactor length (m)

Subscripts

bed	reactor catalytic bed
HDS	hydrodesulphurization reactions
CH	hydrogen consumption reactions
in	reactor inlet
out	reactor outlet
mod	predicted values from the model
exp	experimental values
S	sulphur

Superscript

DEACT	deactivated catalyst
FRESH	fresh catalyst

to either estimate their impact on reactor behavior or find ways to eliminate them [14]. In order to overcome these problems the use of diluted beds operated in downflow mode has become an effective concept of operation of laboratory fixed bed reactors [11–13,15]. Problems like wall effects, low catalyst utilization, incomplete wetting and axial back mixing have been minimized by putting small diameter inert fines to fill the voids between the catalyst extrudates [15]. The improved performance of the diluted beds operating in downflow mode is attributed to restricted liquid axial dispersion and the much higher liquid hold-up [15] that mainly leads to improved wetting and utilization of the catalyst particles.

In a previous work [16] a hybrid model was presented, which can be used to estimate the degree of catalyst deactivation during operation using only operational data of the unit. Although the predictions of this model for various feeds and operating conditions were very satisfactory there was no experimental verification of the catalyst activity level using samples from the reactor.

In this work the deactivation of a catalyst from an industrial reactor is studied using samples collected from the three catalyst beds at the end of run. A mini-scale laboratory reactor was employed for the study of deactivation. The deactivation level determined from the experiments is compared with the predictions of a hybrid model built to follow up the catalyst activity during operation.

2. Experiments

The HDS experiments were carried out in a mini-scale laboratory unit operated at constant pressure and temperature. In Fig. 1 a simple flow sheet of the unit is presented. The main parts of this unit are a stainless steel reactor of 8×10^{-3} m internal diameter, a high pressure gas–liquid separator, a piston pump to feed the liquid phase in the reactor and a hydrogen cylinder. The unit is fully automated and it is able to work for a long period, up to one year, continually.

In this work three deactivated catalysts samples were collected from an industrial reactor after its uploading that occurred approximately 22 months after its loading. This industrial reactor consists of a single vessel with three beds in series. The first sample was collected almost from the middle of the first bed of the reactor, the second one from the middle of the second bed and the third one from the middle of the third bed. These samples were used to estimate the deactivation of the industrial HDS catalyst and to compare the results with the deactivation estimated with a hybrid model.

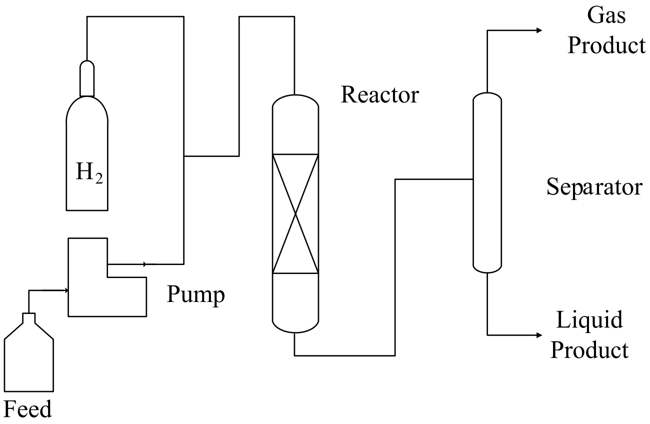

Fig. 1. Flow sheet of the mini-scale laboratory HDS unit.

Four catalyst beds were loaded and tested to study the activity of the fresh catalyst as well as the activity of the three deactivated catalyst samples. The first catalyst bed (B1) was loaded with 5.5×10^{-3} kg fresh commercial catalyst CoMo, was diluted with 7×10^{-3} kg of inert SiC particles of mean diameter 0.08×10^{-3} m, and it was sulphided with DMDS according to the instructions of the catalyst provider. The other three catalyst beds, each loaded with 5.5×10^{-3} kg CoMo deactivated catalyst sample, were diluted with 7×10^{-3} kg inert SiC particles without being sulphided. The catalyst bed B2 was loaded with catalyst from the first bed of the industrial reactor, the catalyst bed B3 with catalyst from the second bed of the industrial reactor and the catalyst bed B4 with catalyst from the third bed of the industrial reactor.