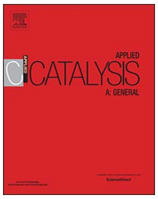
Applied Catalysis A, General xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata



Accelerated deactivation studies of hydrotreating catalysts in pilot unit

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ARTICLE INFO

Keywords:
Hydrotreating
Accelerated deactivation
Normalized reaction temperature

ABSTRACT

In the present paper, a methodology of accelerated deactivation was employed to study the activity loss by coke deposition in short time duration experiments. The loss of activity as function of time is an inherent problem in hydrotreating (HDT) processes. Deactivation at normal operation conditions occurs slowly because of coke formation, commercial catalysts take on average 2–3 years to be replaced. Thus, the accelerated deactivation appears as an instrument capable of providing relevant information on the deactivation phenomenon in reduced time tests. A pilot plant with diesel as feedstock was used under similar conditions to those of industrial units with commercial HDT catalysts. Reaction kinetics was applied to evaluate the deactivation by coke deposition instead of the traditional characterization of residual catalysts. Normalized reaction temperature was related to the initial and residual activities for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) reactions. The reaction temperature of 420 °C in the accelerated deactivation step provided a satisfactory level of deactivation. The catalyst bed configuration proved to be a key factor in order to preserve the residual activity. HDN and HDA activities were more affected than HDS activity by coke deposition in the experimental runs. HDA reaction could reach the thermodynamic equilibrium state when using less severe operating conditions. Finally, the employed methodology led to a proper representation of the industrial HDT deactivation phenomenon.

1. Introduction

One of the major challenges that the oil industry faces is the adequacy of refining facilities to more strict environmental legislation. As a result, the restructuring of old industrial units and the design of new ones will be essential to improve fuel specification [1]. Approximately 50% of the estimated oil world reserves are oil sands, heavy crude oil and bitumen reserves and oil production is estimated to increase from 13 to 18 MMbd (millions of barrels per day) between 2015 and 2035 [2]. Besides, heavy crude oil tends to have higher concentrations of impurities, such as sulfur compounds as well as low yields in light and middle distillates. Then, to achieve high quality and rentable products, catalytic beds with better performance and more severe operating conditions will be indispensable to the refining process.

In this scenario, catalytic hydroprocessing or hydrotreating (HDT) became a fundamental process of the petroleum refining industry from technical, economic and environmental point of view. It has been used for over 60 years to obtain fuels with improved quality from any petroleum fraction. However, as any catalytic process, there is an activity loss due to the deactivation process. Commercial HDT catalysts are continuously deactivated under operation conditions at industrial reactors. Typically, for a middle distillate HDT unit, cycle lengths range from 1 to 6 years. Conversely, the catalyst deactivation for heavy oils hydroprocessing is faster due coke and metal deposition. Besides, studies related to effects of asphaltenes content (coke precursors), feedstock properties, operating conditions, catalysts composition and kinetic modeling are also available in the literature with respect to deactivation process [3–8]. It is noted that these studies have in common the catalytic characterization approach to support the results.

Catalytic activity for industrial operations is maintained through constant increase of the reaction temperature, keeping the desired product specifications as a continuous monitoring of deactivation. Nevertheless, the increase of the reaction temperature has limits due to metallurgical constraints, and also to the process's thermodynamic equilibrium [9]. The deactivation phenomenon may occur by various mechanisms, which are often classified into three large groups: poisoning, thermal degradation (sintering) or deposition (fouling) by coke and/or metals [10]. Among them, deposition is the primary responsible

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http://dx.doi.org/10.1016/j.apcata.2017.06.040
Received 30 April 2017; Received in revised form 23 June 2017; Accepted 30 June 2017

Please cite this article as: Novaes, L.d.R., Applied Catalysis A, General (2017), http://dx.doi.org/10.1016/j.apcata.2017.06.040

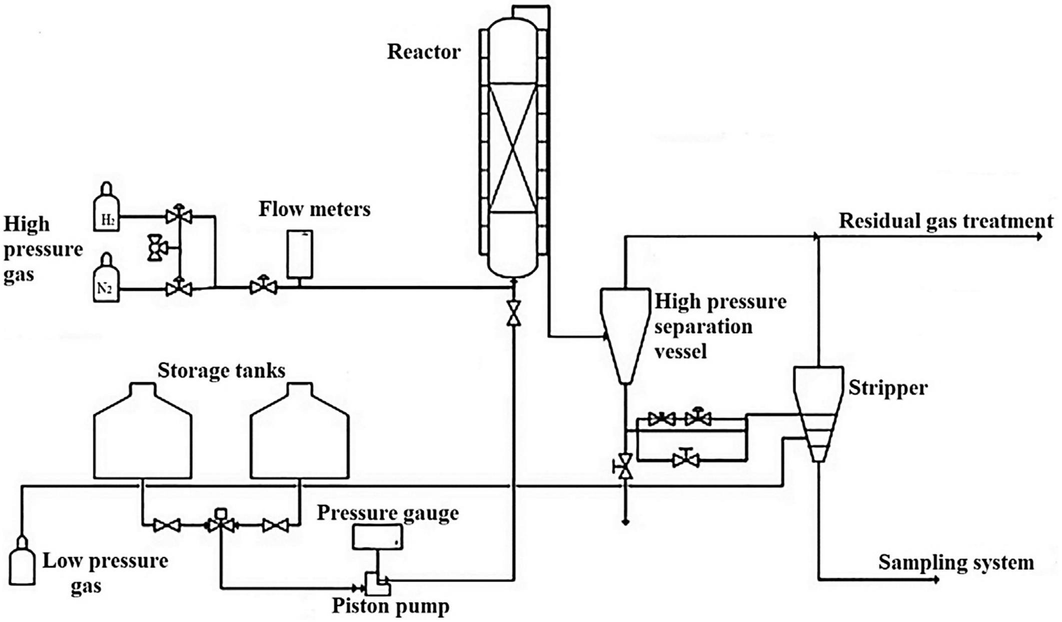

Fig. 1. General scheme of the pilot plant unit.

for the activity loss in the HDT process and can occur directly on the active sites, blocking the catalyst pores or even hindering reactant adsorption/product desorption [10,11]. Coke deposition is part of any HDT process, but the impact of metals, mostly vanadium and nickel, depends on the amount of these compounds in the feed [12].

Because of its industrial importance, the design and development of HDT catalysts with superior cycle length, high performance and more resistant to deactivation have demanded special attention. Indeed, many authors have evaluated the effects of coke or metal deposition by using the characterization of coked catalysts [13–15]. However, this approach has not proved fast enough [16,17]. Thus, the accelerated deactivation appears as an alternative to provide relevant information about the activity loss of the catalyst in short duration experiments. Tanaka et al. [18] carried out tests at high severity conditions to evaluate the effects of coke deposition in the HDT process. They showed that heavier feeds generated greater amount of carbonaceous compounds on the catalytic surface and that this material would be the main reason for the activity loss. The authors emphasized, however, that the high amounts of deposited coke might have been overestimated, thus not representing a real industrial HDT process.

Maity et al. [19] investigated the percentage of deposited metals required to obtain a significant decrease in catalytic activity. In their study, the accelerated deactivations tests were used to evaluate the residual activities in hydrodesulfurization (HDS) and hydrodemetallization (HDM) reactions. Activity studies identified that the deactivation of HDS activity was faster than that of HDM. Probably, the coverage of active sites by vanadium atom hindered the interaction of sulfur compounds with the active phase. Besides, a comparison between regular and vanadium impregnation deactivation was performed. The authors concluded that coke formation at the initial stage caused catalyst deactivation whereas, at later stages, metal sulfide deposition impact was higher.

Ahmed et al. [20] studied the effects of activity loss on vacuum residues through accelerated deactivation conditions. High reaction temperature was employed in the accelerated catalyst aging, which resulted in large amounts of deposited carbonaceous with high aromaticity. This was attributed to the decrease of hydrogenation activity of the catalyst due to coke and metal deposition.

More recently, Pacheco et al. [21] applied an accelerated deactivation methodology to study catalyst deactivation by coke deposition on commercial HDT catalysts. In their study, it is noteworthy: i) the use of reaction kinetics in the activity loss evaluations, ii) the search for experimental conditions to achieve representative catalyst samples to compare with industrial ones. The proposed methodology was effective to deactivate the catalyst and lead to a proper representation of industrial hydrotreating unit at the end of a catalyst life cycle. Venkatesh et al. [22] also evaluated the performance of commercial HDT catalysts to predict a unit cycle length by using accelerated deactivation tests. They observed that, depending on the catalyst deactivation stage, the product quality suffers changes because of high coking and polyaromatic compounds.

Reports on accelerated deactivation of HDT catalysts in the literature are still scarce. Besides, most studies do not evaluate the influence of the operating conditions employed in the experiments. Hence, the results related to the deposited coke often are very different from those observed in industrial units. To overcome this problem, it is essential to know the key-variables that accelerate deactivation and produce a representative coked industrial catalyst sample. Thus, in this study, an accelerated deactivation methodology was employed in the HDT pilot unit under operating conditions similar to those in the industry to obtain relevant information of the loss of activity by coke deposition. In addition to normal hydrotreating operation, using commercial catalysts, another less severe condition was employed to better investigate catalyst deactivation. A kinetic approach of HDT reactions was used to evaluate the deactivation by coke deposition. To increase coke formation, the operational variables modified were temperature and H_2/oil ratio. The normalized reaction temperature was used as analysis tool to evaluate the residual activity after the accelerated deactivation step. Besides, the effect of different compositions of catalytic beds and different temperatures in the deactivation step was evaluated on the residual activities. Kinetic parameters were estimated for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) reactions.

2. Experimental

2.1. Pilot plant

The experiments described in this paper were carried out in a fixed bed pilot plant illustrated in Fig. 1. The unit consists of three sections: feed section, reactor section and product separation section.

The feed supply module consists of a pressurized liquid feed storage