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A novel configuration for Pd/Ag/α-Al_2O_3 catalyst regeneration in the acetylene hydrogenation reactor of a multi feed cracker

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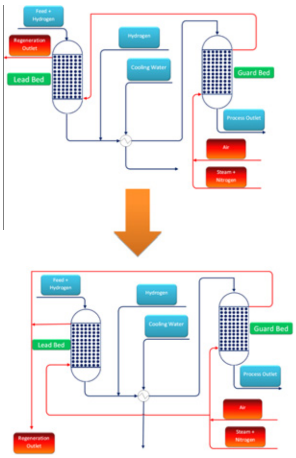
HIGHLIGHTS

- Some problems were observed on acetylene hydrogenation plant for regeneration protocol.
- Catalysts could not appropriately regenerate and so their life cycle decreased significantly.
- New configuration is suggested for solving this issue.

GRAPHICAL ABSTRACT



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ABSTRACT

Acetylene is one of the byproducts of olefin plants with the potential to poison the catalysts in polymerization plants, which can be avoided by reducing the acetylene concentration to less than 1 ppm. Catalytic hydrogenation in tail-end systems is the method most commonly used in the industry to eliminate the acetylene. The Pd/Ag/α-Al_2O_3 catalysts used in this process undergo moderate deactivation due to coke and green oil formation, necessitating their regeneration after certain runtimes. The domestic petrochemical plant which has been investigated in this research is an olefin plant. Close monitoring of the two regeneration cycles in this plant, have revealed complications that caused a dramatic reduction in catalyst lifetime and also disrupted the temperature profile in the reactor overtime. In the present study, a new configuration of regeneration process is suggested based on inspecting the conventional protocol and a comparative analysis to other plants. The results emphasize the need to reconfigure the reactors and pipelines in order to achieve complete regeneration throughout the reactors.

1. Introduction

1.1. Ethylene and acetylene

Ethylene is a flammable, non-polar molecule which is one of the most important productions of petrochemical industry. It has wide

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Nomenclature

ΔH	enthalpy change of formation (kcal mol^{-1})	cp_c	heat capacity of catalyst (J Kg^{-1} K^{-1})
m_s	steam flow rate (Kg h^{-1})	ΔT_c	temperature change of catalyst (°C h^{-1})
cp_s	heat capacity of steam (J g^{-1} K^{-1})	V_c	reactor volume (m^3)
ΔT_s	temperature change of steam (°C)	F_{air}	air flow rate
m_c	total mass of catalyst (ton)	F_{steam}	steam flow rate

applications in the production of different chemicals such as polyethylene and vinyl acetate. A vast majority of ethylene is produced by pyrolysis of hydrocarbons, which involve the thermal cracking of paraffin feedstocks such as ethane, propane and naphtha.

Acetylene is among the main undesirable byproducts of this system, with yields ranging from 0.5 to 2.5 tons per 100 tons of ethylene, depending on the feedstock and cracking conditions. Nearly 0.26% by weight of the product will be acetylene if ethane is used. However, for other liquid feeds, this quantity can become as large as 0.95% by weight. Such a high concentration of acetylene not only contaminates the catalysts in polymerization plants, but might also form metal acetylides which are explosive. As a result, the concentration of acetylene should be decreased dramatically to meet the 1 ppm threshold for polyethylene processes [1]. Table 1 demonstrates typical specifications of exported ethylene to polymerization plants.

Acetylene can be omitted from ethylene through two different methods: by hydrogenation and by removal from the main stream. The latter is typically unfavorable due to high cost and potential operational hazards, so hydrogenation has become the most common method for acetylene separation, in which acetylene is selectively hydrogenated in an adiabatic fixed-bed catalytic reactor [2]. If an acetylene hydrogenation reactor works deficiently, it can lead to up to five million dollars per year in losses [3–5]. There are two distinct methods to produce ethylene from acetylene in petrochemical industries: tail-end and front-end systems [6]. Most of studies are related to the tail-end systems in which pure reactants and arbitrary operating conditions (even far from industrial plants) are implemented [7,8].

1.2. Acetylene hydrogenation catalyst

Use of catalytic hydrogenations dates back to 1948, Anderson et al. introduced nickel sulfide catalyst based on alumina or silica [9]. In the 1980's cadmium, calcium, barium, strontium or magnesium on Cr_2O_3 were used in some cases while Muller et al. proposed to utilize nickel or zinc metals to gain more selectivity [10]. In 1995 Godinez et al. found that the best metal to use as a catalyst for this process was palladium on the base of alumina and after that the researchers tried to improve its selectivity and resistance [11].

Proper structure (suitable support) is detrimental to catalyst stability depend on high temperatures [12]. Although Pd/TiO_2 catalysts showed sintering at 500 °C under the influence of hydrogen, Pd/Al_2O_3 catalysts were found to be more resistant under the same conditions [13]. These catalysts usually consist of low palladium (0.015–0.05 wt.%) and are promoted by another metallic constituent such as Ag [14].

1.3. Catalyst deactivation

Catalyst performance decays naturally over the course of industrial chemical and petrochemical process due to coke deposition [15]. One of the main reasons for catalyst deactivation is Oligomer that consists of unsaturated aliphatic hydrocarbons. Yajun et al. found the structure of green oil (Oligomer) to be complex, but proposed the general formula: $C_nH_{(1.8-1.9)n}$ ($14 < n < 17$) [16]. Sarkany et al. suggested that green oil can be presented as $(C_2H_3)_n$, with n varying between 4 and 22 [17–19]. Green oil precipitation produces a sticky layer that covers catalyst surfaces. Deposits accounting to is 10% or more of the catalyst weight, lead to deactivation [20].

Initially, small acetylene molecules can diffuse through the layer and reach the active sites. However, as this layer grows the distance between the active surfaces and acetylene molecules increase and as a result fewer molecules can access the appropriate sites to react with hydrogen. Therefore, catalyst activity decline noticeably and ethylene selectivity is lost. To recover the activity loss, the temperature of beds should rise steadily to gain suitable and commercial conversion rates [20]. Although no correlation was found between the amount of carbon and catalyst activity, Kelmm et al. discovered that coke formation on the active sites and coke formation on the support have to be considered separately [21].

1.4. Catalyst regeneration

The major mechanisms of catalysts deactivation are: poisoning, thermal degradation, mechanical failure, chemical degradation,

Table 1
Ethylene product specification for export to polymer plant.

Component	Specification	Test method	Testing apparatus
Ethylene	99.95 vol%	By calculation	100-(sum of the impurities)
Methane and ethane	500 ppm vol max	ASTM D6159	GC FID
Hydrogen	5 ppm vol max	ASTM D2504	GC FID
Total C3 and higher	10 ppm vol max	ASTM D6159	GC FID
Acetylene	1 ppm vol max	ASTM D6159	GC FID
Carbon monoxide	0.03 ppm vol max	ASTM D2504	GC methanizer FID
Carbon dioxide	0.1 ppm vol max	ASTM D2504	GC methanizer FID
Oxygen	0.1 ppm vol max	ASTM D2504 or field testing	GC TCD or portable oxygen analyzer
Total combined sulfur	1 ppm vol max	ASTM D6667	Ultra violent fluorescence analyzer
Water	0.1 ppm vol max	ASTM D5454 field testing	Portable water dew point meter
Methanol	0.5 ppm vol max	ASTM D4864	GC FID
Total combined nitrogen	0.2 ppm vol max	ASTM D4629	Pyro-oxidation-chemiluminescence analyzer
Oxygenated compounds	0.5 ppm vol max	ASTM D4864	GC FID
COS	0.02 ppm vol max	ASTM D6228	GC FID
Mercaptans	0.3 ppm vol max	ASTM D6228	GC FID