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An empirical investigation of the influence of sulfur additives on the catalytic rate of coke deposition and CO formation in the steam cracking of LPG over Incoloy 600 and stainless steel

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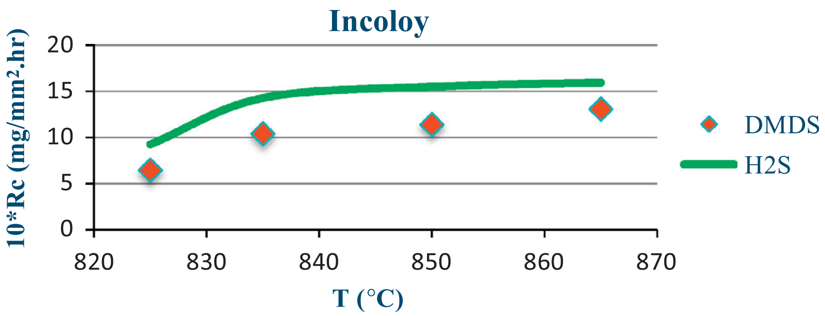
HIGHLIGHTS

- The influence of sulfur additives in the steam cracking of industrial LPG feedstock.
- The impact of H_2S on the rate of CO and coke formation over Incoloy and stainless steel.
- The empirical models of the coke deposition rate and CO formation over Incoloy and stainless steel.

GRAPHICAL ABSTRACT

Influence of H_2S in comparison with DMDS on the rate of catalytic coke deposition on Incoloy.



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ABSTRACT

In the current paper, the influence of sulfur additives in the steam cracking of LPG (liquefied petroleum gas), as an industrial feedstock, has been investigated. The effect of hydrogen sulfide (H_2S) and dimethyl disulfide (DMDS) on the rate of catalytic coke deposition and CO formation have been examined over Incoloy 600, and stainless steel. The impact of sulfur concentration, temperature, and residence time on the rate of catalytic coke formation over each metal, and the CO formation have been investigated using the central composite design (CCD) technique for designing the experiments. Furthermore, the empirical models of the coke deposition rate and CO formation have been proposed for Incoloy and stainless steel individually, based on the statistical analysis of the experimental results. Then, the performance of DMDS was compared with H_2S at some of the selected conditions observed for the H_2S addition.

1. Introduction

Thermal cracking of hydrocarbon feedstocks ranging from ethane to gasoil is the main source of olefin production. One of the main problems of steam cracking is the formation of carboneous material inside the radiant coil and the tubes of TLEs [1,2], that terribly impacts on product yield, energy consumption and run length [3]. Furthermore, carbon monoxide formed during the steam cracking acts as a poison for the catalyst used in the downstream acetylene hydrogenation reactors [4]. In industrial olefin plants, additives are commonly used to control CO production, and inhibit coke formation. Thus, different types of anti-coking chemical additives are employed commercially and/or under study, i.e. sulfur containing compounds, such as dimethyl sulfide (DMS), dimethyl disulfide (DMDS), hydrogen sulfide (H_2S), benzothiophenes, and bibenzyl sulfide; organo-phosphorus chemicals

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[5,6], e.g. Nalco's trademarked COKE-LESS; sulfur-silicon additive liquids [3,7], e.g. CLX family offered by Atofina (now Arkema)/ Technip; and tin-based (tin/silicon mixtures, etc.) [8] additives such as Chevron Phillips CCA500 (coke controlling additive 500) [9]. The most prevalent conventional approach to coke suppression in cracking process is the intentional addition of sulfur compounds, i.e., dimethyl sulfide (DMS) or DMDS to the feedstock [3,4,9]. The influence of the inhibitors on the steam cracking products, and specifically the rate of coke formation and CO production, has been extensively studied by different researchers. In general, the role of mentioned additives on diminishing the CO formation is approved in literature; but the effect of the different inhibitors on the rate of coke formation is complex and debatable. The impact of sulfur compounds on coke reduction is highly dependent on the metal composition [10,11], the application method [12], the concentration [10,12], as well as the chemical nature of the sulfur species [10,11].

The metal surface (i.e. Ti, Cr, Fe and Ni) of the cracker coil catalyzes the growth of a filamentary type of coke which is believed to be produced catalytically by reactions of the metal coil tube surface and carbon formed in the steam cracking [9,13]. The catalytic activity of the tube metals can be classified in the order of Ti < Cr < Fe < Ni [2,9,14], and the sorting of active gas phase species to form filamentous coke deposits is: acetylenes > olefins > paraffins [2]. Directly on top of the filamentous encapsulated coke is the second layer of continuous high-density asymptotic coke which is originated from the heterogeneous non-catalytic mechanism between the coke precursors in the gas phase, such as radicals, unsaturated molecules, and aromatics, with active sites located in the coke matrix [2,9,13,15,16]. Above this is a layer of low-density discontinuous, agglomerated hard coke particles produced by the condensation, polymerization, and/or agglomeration of heavy components in gaseous phase [2,13,16]. However, the difference between the rate of coke formation in the alloys could be reduced by the pre-reduction of them [14]. Sulfur is believed to passivate active nickel sites of the cracking coil material by forming nickel sulfides, which do not catalyze coke gasification, in contrast to nickel metal and nickel oxides. This explains why CO production is high (up to 1% in the cracked gas) if the feedstock is free of sulfur [17].

It was observed that the role of sulfur compounds in hindering the yield of catalytic coke deposits on nickel–iron particles can be classified by the order of DMDS < DMS < H_2S (25–150 ppm range) in the steam cracking of ethane. But, the trends were indistinguishable as the concentration of each additive was progressively raised above 150 ppm; then, it became the same with all three sulfide compounds at additive levels in excess of 500 ppm [10]. On the contrary, Reyniers and Froment [11] and Wang et al. [12] depicted that the continuous injection of sulfur additives, i.e., DMDS [11,12], CS_2, thiophene and benzothiophene [11] cause an increase in coking rate in n-hexane cracking process [11,12], in a mixed reactor of Incoloy 800H and Inconel 600 [11]. Dhuyvetter et al. concluded that there is no direct relation between the amount of CO produced and the quantity of coke formed, and recommended the pre-sulfidation followed by continuous dosing as the optimal procedure to reduce both CO and coke formation in the naphtha steam cracking in a reactor made of Incoloy 800HT [4].

Under the conditions existing in the cracking coil, thermal decomposition of DMDS will occur, which results in the main products of dimethyl sulfide, methanethiol, carbon disulfide, and hydrogen sulfide [4,18]. The most abundant sulfur-containing species is H_2S; consequently, the formed H_2S plays the principal coke inhibiting function [12,18]. It is concluded that the effect of H_2S addition on the rate of coke formation in the pyrolysis of hydrocarbons is ambiguous.On one hand, observations indicate that H_2S retards coke formation via forming a metal sulfide film on the sample wall that hinders the secondary reactions [19]; on the other hand, H_2S species/radicals play the initiating/accelerating role in enhancing the rate of coke deposition [12,20]. Trimm and Turner depicted that the effect of continuous addition of H_2S on coke formation in the steam cracking of propane depends on the material on which the coke is deposited [21]. Recently, Jazayeri and Karimzadeh denoted that the presulfidation of the samples made of Cr, Fe, and stainless steel with H_2S, reduces the rates of coke formation up to 20%, 45%, and 30%, respectively in the steam cracking of ethane. But, they reported a contradictory behaviors for the continuous injection of H_2S depending upon the temperature; so, that the rate of coke formation increased by 20–120% at higher temperatures but decreased by 25–30% at lower temperatures [22].

The present paper focuses on the substitution of DMDS employed in Iran olefin plants with H_2S gas, due to the abundant sources of pollutant H_2S offgas streams in refineries and petrochemical plants of Iran, from the experimental viewpoints. The industrial aspects that shall be considered to evaluate the feasibility of replacement has been presented by Rahimi et al. [23]. Therefore, the appropriate substitution of DMDS with the H_2S offgas not only provides a very low-priced supply for replacement with DMDS in olefin plants, but also restrain emitting the poisonous H_2S offgas to the environment. LPG feedstock is extensively employed in Iran olefin plant; but to the best of our knowledge, the impact of H_2S in the steam cracking of LPG has not been reported in the literature so far; consequently, this industrial feedstock has been considered for studying the sulfur replacement. The influence of H_2S on coke deposition and CO formation is investigated over Incoloy 600 and stainless steel, individually in the steam cracking of LPG in a lab-scale system.

2. Experiments

H_2S gas diluted with nitrogen (the concentration of 0.05 mol% or 500 ppm), and DMDS (dimethyl disulfide) were employed as the inhibitors. LPG (28 wt% mixed-butanes (i-butane, n-butane), 70 wt% propane, 2 wt% ethylene) was introduced as the hydrocarbon feedstock in thermal cracking experiments which was mixed with nitrogen (99.9% purity) as a diluent. The refinery gas analyzer (RGA) analysis indicated that LPG did not contain ppm amount of CO_x or other types of impurities. Coupons made of stainless steel 316 (Cr: 17%, Ni: 12%, Mg: 1%, Fe: balance) and Incoloy 600 (Ni: 73%, Cr: 16%, Mg: 0.5%, Fe: balance) were employed for measuring the rate of coke formation.

The experiments were performed in a laboratory unit consisting of five main sections, i.e. the feeding, the pre-heater, the furnace and reactor, the cooling, and the analysis. The schematic of the experimental setup is shown in Fig. 1. The feedstock and the additive were mixed and introduced to the pre-heater after controlling their flow rates by three MFCs (Brooks). The constant concentration of sulfur compounds was added continuously during each test run.

The required flow of water or the solution of water and the desired amount of DMDS was transferred to the preheater by a peristaltic pump (Heidolph Co.), following to weighing them by a balance. The pre-heater and reactor are located inside the furnace box, the coupon is placed in the specific place at the bottom of the reactor in all the experiments. The schematic figure of the pre-heater and reactor are shown in Fig. 2. Then, nitrogen flow is passed through the set-up to purge it from impurities and test the leakage. After that, the furnace is heated with the rate of 50 °C/min to reach to the adjusted temperature in the presence of nitrogen. Meeting the set-point, the feed is introduced to the pre-heater and simultaneously the nitrogen flow is reduced to