Chemical Engineering Science 191 (2018) 183–190

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Quantitative relationship between olefin saturation and octane loss during HDS process: An insight from molecular structure to experimental activity

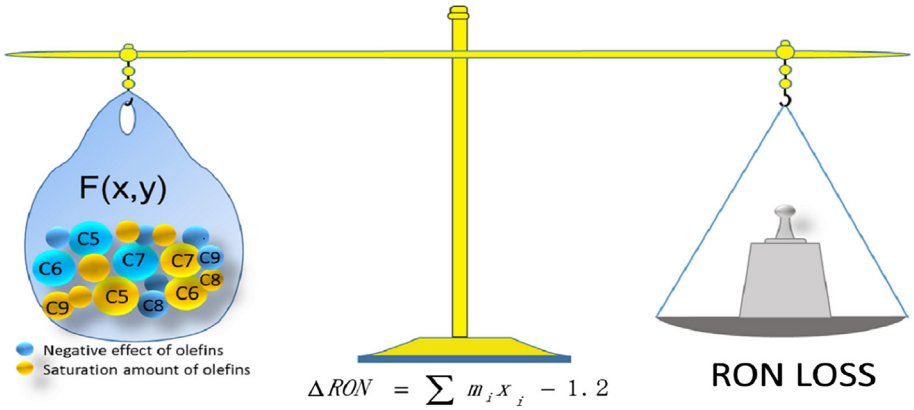
Lixia Dong [a], Kaiwei Luo [a], Liang Zhao [a,*], Yuhao Zhang [a], Jinsen Gao [a], Tianzhen Hao [b], Chunming Xu [a]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), Beijing 102249, People's Republic of China
[b] Hebei Jingzhi Technology Co., LTD, Heibei 061000, People's Republic of China

HIGHLIGHTS

- A formula of the loss of octane number has developed to be used in FCC gasoline hydrogenation.
- The negative effect of C5-C7 olefins on octane number of gasoline is larger than that of C8-C10 olefins.
- C5 ~ C7 olefin hydrogenation is the dominating source of loss of octane number.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 February 2018
Received in revised form 14 May 2018
Accepted 23 June 2018
Available online 25 June 2018

Keywords:
Hydrodesulfurization
Olefin hydrogenation
Research octane number
Gasoline
Loss of octane number

ABSTRACT

Given the demand for clean gasoline with ultralow sulfur and olefin contents, reduced olefin content, which inevitably results in a large octane number loss, is urgently needed. The key to finding a solution for octane number loss is to identify the relationship between olefin hydrogenation and the loss of octane number of gasoline. The negative effect of certain olefins on octane number was first investigated by setting different olefins saturated in the same amount. C5–C7 olefins exhibit the most adverse effect on octane number than others. In addition, the saturation amounts of various olefins were also studied by fluid catalytic cracking (FCC) gasoline hydrogenation experiment. Given the negative effect and saturation amount, the sequence of octane number loss based on olefin hydrogenation is C5 ≈ C6 > C7 > C8 > C9 > C10, wherein C5–C7 olefins, which present high saturation amounts in the hydrogenation experiment, are the main contributing factors of octane number loss in gasoline hydrogenation. Based on the above studies, the formula of the loss of octane number was developed, which can estimate the loss of octane number of gasoline with the error range of less than 0.5 units Research Octane Number.

1. Introduction

Owing to increasing environmental concern, the demand for clean gasoline with ultralow sulfur (<10 mg/L) and low olefin contents (<18 v.%) have become increasingly significant.

* Corresponding author.
E-mail address: liangzhao@cup.edu.cn (L. Zhao).

https://doi.org/10.1016/j.ces.2018.06.060
0009-2509/

Hydrodesulfurization (HDS), such as Prime-G+ (Babich and Moulijn, 2003), SCANfining (Ghosh et al., 2006), and CDHydro/CDHDS (Gardner, 2001), is the most widely used technology in industries because of its capability to remove sulfur at low cost and high efficiency (Brunet et al., 2005). However, parts of olefins, which are the main octane number (ON) contributors in gasoline, are inevitably saturated during HDS, leading to octane number loss (ΔON). Furthermore, additional olefins must be eliminated from gasoline because of the strict requirements for olefin contents, possibly resulting in large ON loss if the olefin fractions are improperly treated. Thus, the kinds of olefin that must be retained to maintain high ON of gasoline and the olefins that can be eliminated without considerable adverse effects on gasoline properties were questioned. The quantitative relationship between olefin saturation and octane loss during HDS has garnered increasing attention.

First, the loss value of octane number caused by the hydrogenation of various types of olefins varies (Hancsók et al., 2011). For example, the loss of octane number is 26.0 if *n*-pentene is hydrogenated to *n*-pentane, 62.9 if *n*-hexene is hydrogenated to *n*-hexane, and 23.7 when methyl-pentene is hydrogenated to methyl-pentane. Based on the loss of octane number of pure compounds, each olefin contributes differently to the octane number of gasoline; both structure and carbon number of olefins markedly affects ΔON loss (Golombok and de Bruijn, 2001). However, further studies on real gasoline or mixture of hydrocarbons are rarely reported.

In addition, the hydrogenation activity of olefins is closely related to the final loss of octane number. This activity determines how much olefin can be hydrogenated and which kind of olefin react easily. Therefore, the reactivity of olefins with different carbon numbers and structures must be studied. Current studies mostly focus on the hydrogenation of olefins with low carbon number (Badawi et al., 2010; Magyar et al., 2007; Magyar et al., 2008; Morales-Valencia et al., 2015). Choi et al. (2004) examined the hydrogenation of 2,3-dimethyl-2-butene and 1-hexene in the presence 3-methylthiophene over sulfided $CoMo/Al_2O_3$ and proposed that olefin hydrogenation is a highly structure-sensitive reaction. They believed that olefin hydrogenation activity is mainly influenced by the number of functional groups around the CdbndC double bond (Toba et al., 2007), which decreases with increasing number of alkyl groups around the CdbndC double bonds on the $CoMoS/Al_2O_3$ catalyst (Badawi et al., 2010; Brémaud et al., 2005). Morales-Valencia et al. (2015) studied the reactivity of different types of olefins in model FCC naphtha over $CoMoS/Al_2O_3$; in addition to the effect of methyl groups bonded to olefin carbons, steric hindrance is affected by skeleton structure, and cyclic olefin exerts the strongest inhibition effect on the hydrogenation (HYDO) reaction. Magyar et al. found that the rate of olefin hydrogenation decreases with the carbon number of olefins (Magyar et al., 2008). Thus, the reactivity of olefins is significantly affected by the structure and low carbon number; high carbon numbers, such as C7 and C8, are not well investigated.

Given the distribution and reactivity of olefins in FCC gasoline, the hydrogenation amount of olefins in real HDS reactions varies. By combining the substantial differences in ΔON and hydrogenation amount, ΔON caused by different olefin hydrogenation in HDS process is distinctly amplified. Present studies on the negative effect of olefins on the ON of gasoline only focus on the reactivity of different olefins and disregard hydrogenation amount and different ΔON of various olefins.

Therefore, the negative effect of different types and carbon number (from C5 to C10) of olefins on ON and different hydrogenation amounts caused by the reactivity and distribution of olefins were studied to show the quantitative relationship between olefin saturation and octane loss during HDS. To conveniently predict the loss of octane number in the HDS process, we established the formula of the quantitative relationship between ΔON and saturation amount of olefins in this study.

2. Methods and experiments

2.1. Feedstock and catalyst

Three kinds of full-fraction FCC gasoline A (from Jinan Refinery), B (from Cangzhou Refinery), and C (from Golmud Refinery) were selected as feedstock. The negative effect of olefin hydrogenation was investigated based on the kinds of gasoline. The compositions were analyzed by gas chromatography (GC) as listed in Table 1. Research ON (RON) listed in Table 1 were obtained according to gasoline composition.

For comparison with existing research, the catalysts selected in the study were commercial $CoMoS/Al_2O_3$ containing 2 wt% CoO and 8 wt% MoO_3 on an Al_2O_3 support.

2.2. HDS performance

HDS performance was investigated in a fixed-bed microreactor (Fig. 1). The catalyst was first pre-sulfided at 503 K for 2 h and then stored for 4 h at 593 K with a mixture of 3 wt% CS_2 in H_2 under a pressure of 2.5 MPa. Thereafter, the catalyst was cooled to reaction temperature under N_2 flow. When the desired reaction conditions were achieved, the gasoline feedstock was pumped into the reactor

Table 1
Composition of FCC gasoline feedstocks.

Hydrocarbon (wt.%)	A	B	C
Paraffins (P)	4.40	6.49	6.09
iso-Paraffins (I)	31.36	21.54	26.77
Olefins (O)	31.01	22.18	47.32
Naphthenes (N)	10.27	9.16	5.04
Aromatics (A)	22.96	40.63	14.78
GC-RON[a]	89.6	90.7	93.5

GC-RON[a]: research octane number calculated by the software of Sinopec Research Institute of Petroleum Processing.

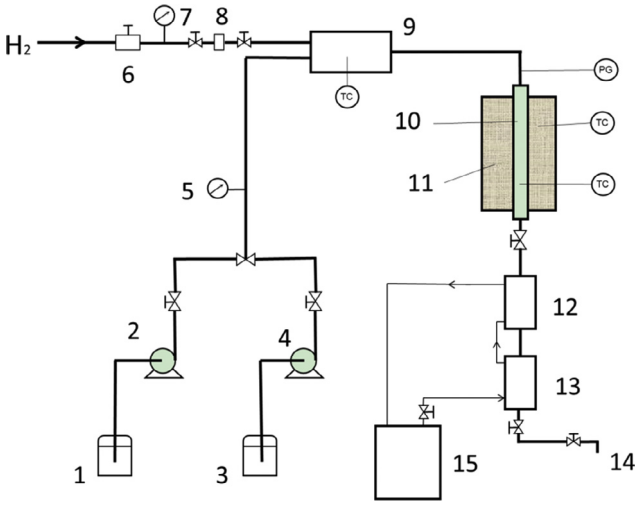


Fig. 1. Schematic of fixed-bed micro-reactor. 1. 3 wt% CS_2; 2. Pump; 3. FCC gasoline; 4. Pump; 5. Pressure meter; 6. Pressure reducer; 7. Pressure meter; 8. Mass flow meter; 9. Preheating furnace; 10. Reactor; 11. Heating furnace; 12. Helically coiled; 13. Liquid storage tank; 14. Product port; 15. Outer loop condenser; (TC, thermocouple; PG, pressure gauge).