Computers and Chemical Engineering 89 (2016) 158–165

Contents lists available at ScienceDirect

Computers and Chemical Engineering

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

Optimization of crude oil hydrotreating process as a function of operating conditions: Application of response surface methodology

Ahmed A. Bhran[a,*], Abeer M. Shoaib[a], Blessing Umana[b]

[a] Department of Petroleum Refining and Petrochemical Engineering, Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt
[b] Centre for Process Integration, School of Chemical Engineering and Analytical Science, The University of Manchester, UK

ARTICLE INFO

Article history:
Received 12 August 2015
Received in revised form 22 February 2016
Accepted 23 March 2016
Available online 29 March 2016

Keywords:
Crude oil hydrotreating
Hydrodenitrogenation
Hydrodesulfurization
Hydrodemetalization
Response surface methodology

ABSTRACT

In recent years, research has been directed towards upgrading of heavy crude oil as unconventional oil recovery rises. Catalytic hydrotreating of crude oil is an important upgrading option that is rarely discussed in literature. The main aim of crude oil hydrotreating is to reduce adverse environmental effects caused by the concentration of contaminants, increase productivity and improve the quality of middle distillate cuts. In this work, Response surface methodology (RSM) has been adopted to study the influence of various process parameters, such as hydrogen partial pressure, temperature and liquid hourly space velocity on the hydrotreating performance. The significance of these parameters is identified by using the analysis of variance (ANOVA) method. The resulting correlations are capable of predicting sulfur, vanadium, nitrogen and nickel conversions that are in excellent agreement with experimental data. The operating parameters are optimized with LINGO optimization software to achieve maximum conversions of contaminants during hydrotreating processes.

1. Introduction

Crude oil upgrading is one of the most challenging tasks in the petroleum refining industry. This can be attributed to the presence of many compounds and complex structures, in addition to multiple phases in crude oils. The quality of heavy crude oil could be upgraded through a number of technologies. The most common traditional technologies include decreasing the carbon content, increasing the hydrogen content or a combination of both two routes (Luis et al., 2014). The carbon rejection process, could be achieved through visbreaking, coking or solvent deasphalting. The hydrogen addition processes, could be achieved through hydrotreating, hydrovisbreaking, hydrocracking or donor-solvent processes. Hydrogen addition technologies are classified depending on the type of reactor used, e.g., fixed-bed, moving-bed, ebullated-bed and slurry-bed processes. Moreover, a new group of technologies has emerged as a promising solution to the problem of upgrading heavy and extra-heavy crudes, such as ultrasound and extraction. These technologies are focused on upgrading the properties of those crudes, i.e., increase of API gravity, reduction of viscosity and impurities content such as sulfur, nitrogen and metals, either for transportation purposes or as feed to refineries. Such technologies have been reported in many references (Guitian et al., 1988; Silva et al., 1989; Dickenson et al., 1996; Mark and Patrick, 2005).

Crude oil hydrotreating is one of the powerful techniques in upgrading heavy oils. Crude oil hydrotreating is a catalytic process that uses hydrogen at high reaction temperatures and pressures with a high activity catalyst to remove contaminants such as sulfur (S), nitrogen (N), metal (M) and saturate aromatic and olefinic compounds. The process of removal of S, N and M are referred to as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetalization (HDM) respectively. The HDM primarily refers to the hydrodevanadization (HDV) and hydrodenickelation (HDNi) of the raw crude oil. Whole crude oil hydrotreating ensures significant improvement in middle distillate yields and fuel quality (Jarullah et al., 2011a,b). Crude oil hydrotreating in the presence of asphaltenes containing large components of sulfur and metals poses a threat to the sustainability of hydrotreatment units (Jarullah et al., 2011b). The presence of such contaminants in crude oil may have adverse effects on the poisoning of catalysts in conversion processes and deterioration of the final products specifications. Nitrogen compounds reduce catalyst activity and produces toxic effects on the storage stability and color of crude oil products. The impact of nitrogen and sulfur compounds on naphtha, kerosene and

* Corresponding author at: Department of Petroleum Refining and Petrochemical Engineering, Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt.
E-mail addresses: abhrane2015@yahoo.com, abhrane@yahoo.com (A.A. Bhran).

http://dx.doi.org/10.1016/j.compchemeng.2016.03.026
0098-1354/

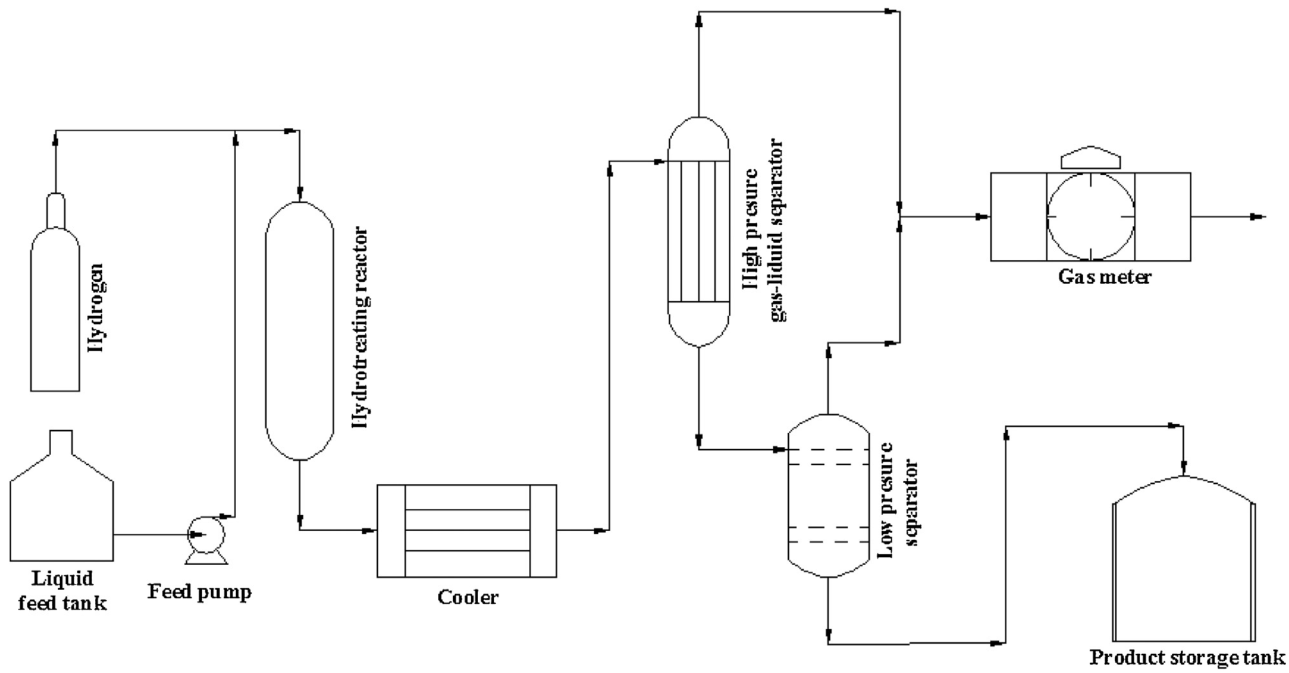

Fig. 1. General scheme of the hydrotreating pilot-plant unit.

diesel fuels during operation proved that these compounds showed unwanted influence on the stability of fuels, in addition to its environmental pollution effects (Andari et al., 1996; Kaernbach et al., 1990; Speight, 2000). Furthermore, there are massive impacts of metallic compounds in crude oil during its hydrotreating (HDT) or the hydrotreating of its fractions. These compounds have a very negative impact on the HDT efficiency, plug the pores of catalysts used, cause rapid deactivation for the HDT catalyst, where they tend to deposit on the catalyst active sites and consequently reduce the HDT activity by decreasing catalyst surface area (Abbas, 1999; Bartholdy and Cooper, 1993; Pereira et al., 1990). These metals include vanadium and nickel, in addition to iron and copper which affects the activity of cracking catalysts, and cause an increase in the level of coal deposited. Furthermore, the ash obtained from the combustion of fuels containing sodium and particularly vanadium reacts with refractory furnace linings to lower their fusion points and hence cause their destruction (Ali and Abdul-Karim, 1986; Gary and Handwerk, 1994; Speight, 2000). The hydroprocessing of heavy crude oils is difficult because of the complex nature of the heteroatom bearing molecules which escape out from the systems as gaseous products and the more refractory compounds remain in the liquid products. During this process, metals get irreversibly deposited on the catalysts causing a serious problem of permanent catalyst deactivation (Ancheyta et al., 2002; Jarullah et al., 2011a).

Several research works have estimated the kinetic parameters obtained from modeling HDN, HDV and HDNi reactions based on experimental data (GPROMS, 2005; Jarullah, 2011). In another research work, the modeling, parameter estimation and simulation of HDS and HDA of crude oil in trickle bed reactors was investigated (Jarullah, 2011; Jarullah et al., 2011c,d, 2012). Mapiour et al. (2010a,b) developed models for hydrotreating activities as functions of operating variables, specifically H_2 purity, pressure, and gas/oil ratio based on heavy gas oil (HGO) feed from Athabasca bitumen.

However, previous works have not considered the modeling of hydrotreating processes of the full crude oil as a function of operating conditions. In this present work, we model the conversions of various hydrotreating processes including HDS, HDN, HDNi, and HDV of crude oil as a function of operating conditions. The principal operating variables commonly monitored in crude oil hydrotreating processes are temperature, hydrogen partial pressure (H_2 PP), and liquid hourly space velocity (LHSV) (Bej et al., 2001; Christian et al., 2003; Gary et al., 2007; Speight, 1981). A trickle-bed reactor (TBR) is used with temperature varying from 335 to 400 °C, H_2 PP from 4 to 10 MPa, and LHSV from 0.5 to 1.5 h^{-1}, while maintaining constant hydrogen to oil ratio (H_2/oil) at 250 L/L (Jarullah et al., 2011b,c, 2012). RSM (Design Experts version 7.1.6, stat ease, USA) is used to correlate the conversions of HDS, HDN, HDNi, and HDV with temperature, H_2PP, and LHSV. Design of experiments is a very useful tool as it provides statistical models, which helps in understanding the interactions among variables to be optimized (Alam et al., 2007). Response surface methodology (RSM) is one of the experimental design methods which estimates the interaction and quadratic effects of independent variables on the responses (Elfghi and Amin, 2013). Additionally, it reveals the best value of the

Table 1
Iraqi crude oil (feed stock) properties (Abbas, 1999).

Specific gravity at 15.6 °C (dimensionless)	0.8558
API (dimensionless)	33.84
Viscosity at 37.8 °C (cSt)	5.7
Pour point (°C)	−36
Sulfur content (wt%)	2.0
CCR (wt%)	5.1
Vanadium content (ppm)	26.5
Nickel content (ppm)	17
Nitrogen content (ppm)	0.1
Asphaltenes content (wt%)	1.2
Ash content (ppm)	80

Table 2
Commercial catalyst (Co–Mo/g-Al_2O_3) specifications (Bhaskar et al., 2002).

Ni O (wt%)	3
Mo O_3(wt%)	15
Na_2 O (wt%)	0.07
Si O_2 (wt%)	1.1
SO_2 (wt%)	2.0
Fe (wt%)	0.04
Al_2 O_3	Balance