Chemical Engineering Journal 106 (2005) 119–131

Chemical Engineering Journal
www.elsevier.com/locate/cej

Conceptual design of a reactive distillation process for ultra-low sulfur diesel production

Tomás Viveros-García, J. Alberto Ochoa-Tapia, Ricardo Lobo-Oehmichen, J. Antonio de los Reyes-Heredia, Eduardo S. Pérez-Cisneros*

Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa,
San Rafael Atlixco 186, C.P. 09340, México, D.F., Mexico

Received 12 July 2004; received in revised form 15 November 2004; accepted 17 November 2004

Abstract

Based on a thermodynamic analysis in terms of reaction-separation feasibility, a conceptual design of a reactive distillation column for ultra-low sulfur diesel production has been developed. The thermodynamic analysis considers the computation of reactive and non-reactive residue curve maps for a mixture that models the sulfured diesel fuel. The visualization of the reactive residue curves is posed in terms of elements. From the reactive residue curve maps, it is found that there is a high temperature region where the vaporization of hydrogen sulfide favors the elimination of the heavier organo-sulfur compounds. Considering the differences in volatility and reactivity of the organo-sulfur compounds and the phase behavior through the residue curve maps, a conceptual reactive distillation column design was developed. The reactive distillation column considers two reactive zones: In reactive zone I, located above the hydrocarbon feed stream, thiophene and benzothiophene are preferentially eliminated. In reactive zone II, located below the feed stream, dibenzothiophene and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) are mostly consumed. To validate the conceptual design, rigorous steady state simulations were performed. The design goal was stated to produce 4000 bbl/day of ultra-low sulfur diesel with a 99% conversion of 4,6-DMDBT. It is shown that reactive distillation may be considered a viable technological alternative for deep HDS of diesel.

Keywords: Ultra-low sulfur diesel; Reactive distillation; Reactive residue curves

1. Introduction

The worldwide regulations of diesel fuel are increasing the pressure on the oil industry. The European Union agreed that the maximum permissible sulfur content of diesel would be 350 wppm from the year 2000, and 50 wppm from the year 2005. This mandatory reduction is promoting changes in the oil refineries in terms of modifying the catalyst used and/or in the technology involved in the hydrodesulfurization (HDS) process. That is, higher activity of the commercial catalyst, and structural changes in the reactor configuration to increase the sulfur-compounds conversion, are needed. Specifically, the diesel produced in Mexican refineries contains around 500 wppm of sulfur and it is thought that the reduction to 50 wppm will require a very important economical investment [15]. Therefore, the study and analysis of the different technological alternatives are considered to be of high priority.

In conventional HDS process [12] several types of commercial catalytic reactors (fixed-bed, moving-bed, LC-fining, etc.) are used and they operate under similar principles. However, the fixed-bed reactor is preferred to process light feeds, while the moving-bed reactor is selected for heavy feeds hydroprocessing. The catalysts are chosen depending on the feed properties and usually include supported molybdate and tungstate catalysts promoted by either Ni or Co. γ-Alumina, zeolites, silica and silica aluminates are the typical supports.

---

* Corresponding author. Tel.: +52 55 58 04 46 44;
fax: +52 55 58 04 49 00.
E-mail address: espc@xanum.uam.mx (E.S. Pérez-Cisneros).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.11.008

Nomenclature

A	element A: organic part of the organo sulfur compound
AB	molecule AB: dibenzothiophene
AC	molecule AC: biphenyl
B	element B: sulfur atom
BD	butadiene
BPH	biphenyl
BT	benzothiophene
C	element C: hydrogen molecule
CB	molecule CB: hydrogen sulfide
D	element D: *n*-hexadecane
DBT	dibenzothiophene
3-3′ DMBPH	3-3′ dimethyl-biphenyl
4,6-DMDBT	4,6-dimethyl-dibenzothiophene
Et	ethylbenzene
H	molar liquid hold-up (mol)
HDS	hydrodesulfurization
Th	thiophene
W_j	element fraction for element j
x_i	liquid mole fraction of specie i
$\overline{V}$	molar vapor flow rate (mol/h)

Knudsen et al. [18] have pointed out that there are two types of alternatives to achieve deep HDS of diesel: (1) increasing catalyst activity, and (2) improving the performance of the reaction unit. In order to develop new catalysts for deep HDS, strong efforts are being devoted to establish relationships between the catalyst structure and the reactivity towards different molecules [36]. Recently, Argonne scientists [4] identified several new diesel fuel desulfurization catalysts with improved HDS activity and selectivity, among a fair amount of publications devoted to this topic in both open and patent literature. These researchers synthesized and tested the new catalysts at 673.2 K and 27.21 atm, and they believe that it may be possible to achieve optimal HDS processing at lower temperatures and/or pressures—even for heavy crude oils. The influence of the amount of catalyst, hydrogen partial pressure, gas/oil recycle ratio, and vapor/liquid distribution, have thoroughly been discussed by Knudsen et al. [18] and Song and Ma [33]. From these works, it is apparent that by increasing the hydrogen partial pressure and reducing the hydrogen sulfide concentration in the reaction unit would lead to increase the sulfur elimination.

Van Hasselt et al. [38] pointed out that a counter-current operation of a trickle-bed reactor leads to a higher reduction of sulfur content than the conventional co-current operation. They showed that flooding limitations (i.e., commercial flow rates) could be overcome by using finned monolith catalyst packing. However, the difficulty of counter-current designs in the case of distillate hydrotreating is vapor–liquid contacting and the prevention of hot spots within the reactor [33].

Reactive distillation has become a highly promising hybrid process for many reactive systems. The application of this combined reaction-separation process was considered useful only for reactive systems limited by chemical equilibrium and it has been applied successfully to the methyl acetate and methyl-*tert*-butyl ether (MTBE) production [2,32]. The increasing interest in reactive distillation has been accompanied by the development of various simulation algorithms related to process operation and control [1,21]. The design of reactive distillation columns (RDC) has also received some attention. Most of the existing work related to RDC design is based on the transformed composition variables proposed by Doherty's group [5,9,37,6]. An alternative to this approach is the element composition concept proposed by Pérez-Cisneros et al. [27]. The main advantage of this element composition representation is that it reduces the composition space domain and simplifies the phase equilibrium with chemical reaction (equilibrium or kinetically controlled) calculations [31]. Also, the graphical visualization of the reactive phase behavior through reactive phase diagrams and/or reactive residue curve maps, constructed in terms of these element composition variables, is simplified. Specifically, the reactive residue curve maps are highly useful tools to visualize and elucidate conceptual designs of reactive distillation processes [35]. Through reactive residue curve maps it is possible: (i) to visualize the influence of the chemical reaction on the phase behavior; (ii) to observe how far from chemical equilibrium is the reacting mixture thermal condition and (iii) to identify the presence of reactive and non-reactive azeotropes [37].

Up to now, only few papers have addressed the application of reactive distillation to the deep hydrodesulfurization of diesel. Taylor and Krishna [34] discussed the possibility to apply reactive distillation concepts to hydrodesulfurization of heavy oils. Recently, Krishna [19] showed how this technology could be used. Hidalgo-Vivas and Towler [16] presented several alternative reactive distillation flowsheets to reduce the sulfur content below 500 wppm without a significant increase in process hydrogen consumption and with energy integration. However, they did not show how to apply this technology. Similarly, CdTech Company [8] claims to have the complete development of the reactive distillation technology for ultra-low sulfur diesel production, but that information is not open to the public.

An analysis of the operating conditions to obtain ultra-low sulfur diesel in a conventional HDS process [18,38] suggests that reactive distillation could be an interesting technological alternative for deep HDS of diesel. In a reactive distillation process, the countercurrent operation is the natural operation mode and the internal flows requirement can be obtained through the catalyst packing arrangement, regulating the reflux and/or the boiling ratio, and properly placing the sulfured hydrocarbon feed. A comparison between deep