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Sensitivity analysis of a light gas oil deep hydrodesulfurization process via catalytic distillation

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Abstract

In this work, a sensitivity analysis of a light gas oil deep hydrodesulfurization catalytic distillation column is presented. The aim is to evaluate the effects of various parameters and operating conditions on the organic sulfur compound elimination by using a realistic light gas oil fraction. The hydrocarbons are modeled using pseudocompounds, while the organic sulfur compounds are modeled using model compounds, i.e., dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT). These are among the most refractive sulfur compounds present in the oil fractions. A sensitivity analysis is discussed for the reflux ratio, bottom flow rate, condenser temperature, hydrogen and gas oil feed stages, catalyst loading, the reactive, stripping, and rectifying stages, feed disturbances, and multiple feeds. The results give insight into the qualitative effect of some of the operating variables and disturbances on organic sulfur elimination. In addition, they show that special attention must be given to the bottom flow rate and LGO feed rate control.

Keywords: Hydrodesulfurization; Catalytic distillation; Reactive distillation; Gas oil; Diesel

1. Introduction

Environmental regulations to reduce the sulfur concentration in diesel have become stricter in recent years and this tendency will continue. In the US, the sulfur in diesel must be reduced to less than 15 ppm from 2006 to 2010 [1], while in the EU it must be reduced from 50 ppm in 2005 to 10 ppm by 2009. In Mexico, current legislation allows a sulfur concentration in diesel of up to 500 ppm. However, it must be reduced to 15 ppm by 2009, except near the northern border where the reduction must be made by 2007 [2]. On the other hand, heavy oil production with high sulfur content has been increasing during the last decades, while light oil production has been decreasing. In Mexico, it is expected that from the year 2006 to 2016, the crude oil API gravity will decrease from 22° to 17° API, while the sulfur content will increase from 3.8 to 4.42 wt% [3]. In this context, refineries will be forced to upgrade their hydrodesulfurization (HDS) technology in order to process heavy oils and comply with the new regulations. There are a number of ways to address this issue, i.e., reactor design, FCC pretreatment, improved HDS, new catalysts, etc. Among them is catalytic distillation (CD), which is a novel technology that has been proposed to improve the conventional HDS process.

Recently, CD has caught the attention of both industry and academia because of its numerous potential benefits. This process integrates the reaction and separation into a single unit; therefore, it's more efficient than the conventional reactor/separation system. This characteristic simplifies the process and reduces operational and fixed costs. Among the advantages of CD are: the simplification or elimination of the separation section, improved reactant conversion, improved selectivity, reduced catalyst requirements, a longer catalyst life than fixed bed reactors, reduced by-product formation, and heat integration [4–6]. Many traditional processes are currently being researched in an attempt to discover possible improvements through the application of this new technology, with over 70 industrial applications of CD being reported to date [7].

Hidalgo-Vivas and Towler [8] proposed CD for gas oil HDS and presented several column configurations. Using a real gas oil fraction, Vargas-Villamil et al. [9,10] proposed a light gas oil (LGO) HDS process via CD, and then compared the conventional and the catalytic distillation processes, showing

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the economic advantages of the latter. In this process, a CD column substitutes the conventional process reactor section, followed by H_2 purification and recycling. Although the resulting process is less complicated, the conversion is similar to the conventional process at less severe operating conditions. In this process, the hydrogen and gas oil flows are counter-current. So, the H_2 acts both as a reactant and as a stripping agent. As a result, the catalyst life is increased since heavy oil fractions remain in the column bottom and fresh hydrogen washes the reactive section. In addition, less catalyst volume is necessary than in conventional co-current operation [11,12]. The H_2S inhibits HDS reactions; however, in counter-current operation a low H_2S concentration profile is favored. Therefore, its inhibition effect is reduced, improving the sulfur compound conversion [11,12], which is specially important for deep hydrodesulfurization (DHDS) [13]. On the other hand, CD Tech is commercializing an HDS process via CD for gasoline and for jet fuel/kerosene [14,15]. Its efficiency has been demonstrated at the Motiva's Port Arthur Refinery [16]; at the Irving Oil's St. John, New Brunswick Refinery [17]; and at the ChevronTexaco Pembroke Refinery [15]. In these refineries, a 90% desulfurization of FCC naphtha has been achieved, while the catalyst has lasted for over 5 years. By the year 2004, 8 units were in operation and 10 units were in engineering and construction.

In spite of its potential benefits, CD is a complex process. The integration of both reaction and *in-situ* separation leads to complex interactions between several phenomena that are frequently at odds with one another [18,19]. The coupling of chemical kinetics and phase equilibria may lead to multiple steady states or reactive azeotropes [20–22]. Thus, new reactive distillation process is difficult to design and/or analyze because of the intricate interaction between reaction and separation; furthermore, there are a large number of design and operating parameters [23,24]. Nevertheless, the influence of design, operating conditions, and disturbances on the sulfur elimination can be carried out via sensitivity analysis [25–27], which is the focus of this work.

Sensitivity analysis in a process consists of varying input parameters over a reasonable range and estimating the relative changes of the output variables. Such knowledge is important in order to: determine the factors that mostly contribute to output variables, i.e., conversion or product purity; understand the behavior of the process resulting from a small variation in operating variables; and identify optimal regions. Chemical reactors such as CSTR's or fixed bed catalytic reactors have been tackled by sensitivity analysis [25].

In this work, a sensitivity analysis of a light gas oil deep HDS catalytic distillation column is presented. The following parameters are investigated: the reflux ratio (RR), the bottom flow rate (B), the condenser temperature, the hydrogen and gas oil feed stages, the catalyst loading, the reactive, stripping and rectifying stages, feed disturbances, and multiple feeds.

2. The light gas oil fraction

During refinery modeling, the petroleum fractions are frequently represented by pseudocompounds. They represent boiling ranges with a cut temperature that can be defined by the true boiling temperature and ASTM-D86 distillation curves. The boiling point range for the fraction used in this work is 180–370 °C [28]. Three pseudocompounds are defined, representing the light, medium, and heavy fractions (PC_1, PC_2, and PC_3, respectively), and are defined by the molecular weight (MW), normal boiling point (NBP), and specific gravity (SG) (Table 1).

Table 1
Light gas oil fraction pseudocompounds

Compound	MW	NBP (K)	SG
PC_1	166.6	475.1	0.7963
PC_2	227.9	554.6	0.8380
PC_3	296.3	626.1	0.8731

The organic sulfur compound composition and type vary according to the crude's origin. They differ in the structure and location of the sulfur atom in the molecule. This is important because the chemical nature of the organic radicals and the presence of aromatic rings influence the reactivity during the HDS process. The reactivity decreases with the presence of aromatic rings in the following order: thiophenes > benzothiophenes > dibenzothiophenes [29]. Dibenzothiophenes are among the most difficult molecules to remove and their reactivities decrease when they have alkyl substitutes. The reactivity decreases as follows: DBT > 4-MDBT > 4,6-DMDBT [30].

In this work, DBT and 4,6-DMDBT are used as model compounds to represent the organic sulfur compounds. DBT and 4,6-DMDBT are representative molecules of the most refractory compounds and are the most abundant in gas oil [31–33]. Moreover, for DHDS at least one of the alkyl dibenzothiophenes must be considered.

3. The hydrodesulfurization kinetics

Research on HDS kinetics has been growing throughout the last few decades. Several works address the HDS of DBT [34–39]; however, most of these works present first order kinetics and do not account for the influence of H_2S and reaction products. Broderick and Gates [40] developed a Langmuir–Hinshelwood–Hougen–Watson (LHHW) type equation that takes into account the H_2S and reactant inhibitions. Edvinsson and Irandoust [41] developed an LHHW type equation in a monolithic reactor, but they neglected the H_2S inhibition. Vanrysselberghe and Froment [42] developed a rate expression that takes into account H_2S, product, and reactant inhibition. On the other hand, there are several works addressing the HDS of 4,6-DMDBT [38,39,43,44,34,45]; nevertheless, Vanrysselberghe et al. [45] present an LHHW rate expression that includes the influence of H_2S, reaction products, and the influence of DBT. The reaction kinetics of both the DBT and 4,6-DMDBT have two reaction paths, hydrogenolysis (Eqs. (1) and (3)) and hydrogenation (Eqs. (2) and (4)) [42,45]. They are:

$$\mathrm{DBT} + 2\mathrm{H_2} \rightarrow \mathrm{BiPh} + \mathrm{H_2S} \qquad (1)$$

$$\text{DBT} + 5\text{H}_2 \rightarrow \text{CHB} + \text{H}_2\text{S} \quad (2)$$

$$4,6\text{-DMDBT} + 2\text{H}_2 \rightarrow 3,3'\text{-DMBPH} + \text{H}_2\text{S} \quad (3)$$

$$4,6\text{-DMDBT} + 5\text{H}_2 \rightarrow 3\text{-MCHT} + \text{H}_2\text{S} \quad (4)$$

where BiPh is biphenyl, CHB is cyclohexylbenzene, 3,3′-DMBPH is 3,3′-dimethyl biphenyl, and 3-MCHT is 3-methyl-cyclohexyltoluene. In this work, the reaction rates proposed by Vanrysselberghe and Froment [42] are used for the DBT, and the reaction rates proposed by Vanrysselberghe et al. [45] are used for the 4,6-DMDBT.

4. The light gas oil deep hydrodesulfurization distillation column

Fig. 1 shows the CD column studied in this work. It has four rectifying stages, four stripping stages, five reactive stages, a partial reboiler, and a partial condenser. It uses CoMo/Al_2O_3 as a catalyst. The distillate has two streams, a vapor stream which mainly contains H_2, and a liquid stream which mainly contains light gas oil fractions. The vapor stream is recycled. The bottom stream produces hydrodesulfurized diesel. The light gas oil, which contains sulfur compounds, is fed above the reactive stages while the recycled hydrogen is fed below them (Fig. 1). The hydrogen/hydrocarbon feed ratio, which is the relationship between the hydrogen and gas oil flow feeds, is 2413 ft^3 of H_2 at standard conditions per barrel of gas oil. This H_2/HC ratio is important since it is related to the diesel quality specifications. The LGO total sulfur content is equivalent to 7805 ppm (0.78 wt%). The objective is to produce 4600 barrels/day of hydrodesulfurized diesel. The total catalyst mass hold up is equivalent to that used in a conventional HDS process. The operating pressure is 13 bar, the RR is 0.24, the condenser temperature is 385 K, and the bottom flow rate is 50 kmol/h.

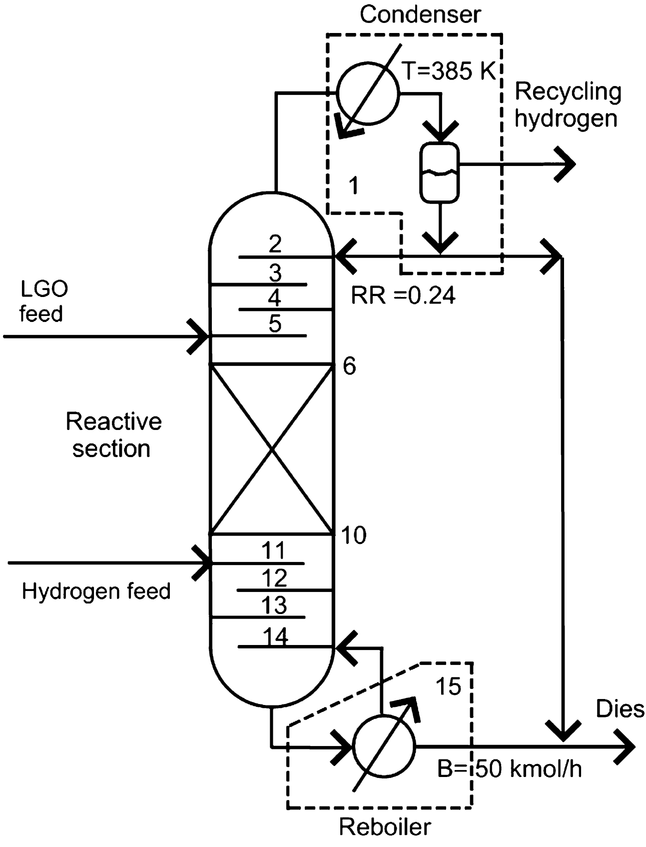

Fig. 1. Case of study: the light gas oil DHDS catalytic distillation column.

The case of study results is summarized in Table 2, where a considerable reduction of DBT (98.5%) and 4,6-DMDBT (99.5%) is shown. The sulfur compounds in the diesel stream represent 98 ppm of total sulfur. Most of the DBT forms BiPh, while most of the 4,6-DMDBT forms 3,3′-DMBPH. It is observed that the temperature in the reactive section is between 633 and 647 K (360–374 °C) (Fig. 2a), which is inside the catalyst temperature operating range, 613–648 K (340–375 °C). A higher temperature is observed in the stripping section mainly because of the presence of heavy gas oil fractions. Fig. 2b shows the pseudocompound profiles. Higher concentrations of heavy and medium fractions (PC_2 and PC_3) remain in the stripping section while the lighter fraction (PC_1) is concentrated in the rectifying section. The sulfur compounds, DBT and 4,6-DMDBT, are eliminated in the reactive stages (Fig. 2c).

5. Sensitivity analysis

Sensitivity analysis is the study of the effects of various parameters and initial value changes on system behavior. It is useful to identify the factors that mainly contribute to output variability. In this work, one parameter continuation technique is used to analyze the CD column represented by a nonlinear algebraic system $F(\mathbf{x}, \lambda) = 0$, where F is the vector of functions that represent the vapor–liquid equilibria, mass, and energy balances; $\mathbf{x}$ is the vector of state variables (stage mol fractions, stage molar flows, and stage temperatures); and λ is the continuation parameter. For each continuation parameter λ, a sequence is generated which leads to a solution set (X_1, λ_1), (X_2, λ_2), …, (X_p, λ_p). The set $\{\lambda, X\}$ represents the system's sensitivity analysis. The analysis was carried out using ASPEN Plus. An equilibrium stage model has been used for all simulations, and reactions are assumed to take place in the liquid phase. The Peng–Robinson [46] equation of state is used to represent the VLE. Both Peng–Robinson and Soave are recommended for systems that contain H_2, H_2S, and hydrocarbons [47,48].

5.1. Reflux ratio

A high RR may increase the conversion because it recycles unreacted reactants and increases the residence time in the reactive stages; however, this is not always true. In addition, a high RR is not economically attractive because it requires large equipment, thus increasing the energy requirements. In Fig. 3a, the RR is varied from 0.1 to 10. It shows that during this interval, the DBT conversion is greater than 94%, while the 4,6-DMDBT decreases monotonically from 98 to 63%. This is the combined result of kinetics and distillation effects. When 4,6-DMDBT is not eliminated in the reactive section it

Table 2
Case study: column streams (kmol/h)

Compound	Hydrogen feed	LGO feed	Recycling hydrogen stream	Diesel stream
H_2	525.688	–	509.646	0.671
H_2S	12.874	–	18.546	0.501
DBT	–	5.074	–	0.073
BiPh	–	–	0.059	4.932
CHB	–	–	–	0.010
4,6-DMDBT	–	1.177	–	0.006
3,3'-DMBPH	–	–	0.008	0.991
3-MCHT	–	–	–	0.172
PC_1	0.049	50.748	2.141	48.656
PC_2	0.041	42.420	0.031	42.431
PC_3	0.018	18.251	–	18.269

accumulates in the column bottom since it is the heaviest sulfur compound. Fig. 2b shows that the total sulfur concentration in diesel reaches a minimum at RR = 0.51 (58 ppm). Nevertheless, at this point, the reactive section temperature profile is above the catalyst operating temperature (Table 3). It would damage the catalyst. The maximum conversion that satisfied the catalyst operating temperature is reached when RR = 0.25. Therefore, a low RR is recommended to avoid a high temperature profile in the reactive section, poor 4,6-DMDBT conversion, and catalyst damage.

5.2. *Bottom flow rate*

At constant heat duty, a bottom flow rate variation affects the vaporization rate, which modifies the column flow rate profile. Fig. 3c shows that the DBT conversion is above 90% when *B* is varied from 20 to 110 kmol/h. However, the 4,6-DMDBT conversion decreases considerably when the flow rate is higher than 62.4 kmol/h. This is mainly the effect of a decrease in the reactive section temperature profile and residence time which mainly reduces the 4,6-DMDBT reaction rates. Fig. 3d shows that a total sulfur concentration lower than 59 ppm can only be achieved when the flow rate is between 57.4 and 62.1 kmol/h. At this bottom flow rate the temperature operating condition holds (Table 4). Fig. 3d also shows that this system is very sensitive to disturbances in the bottom flow rate since a small increase in the bottom flow rate increases the sulfur concentration dramatically. Therefore, a tighter controller must be designed for the bottom flow rate.

5.3. *Condenser temperature*

When the condenser temperature is varied from 350 to 450 K, no significant variation in the temperature profile is

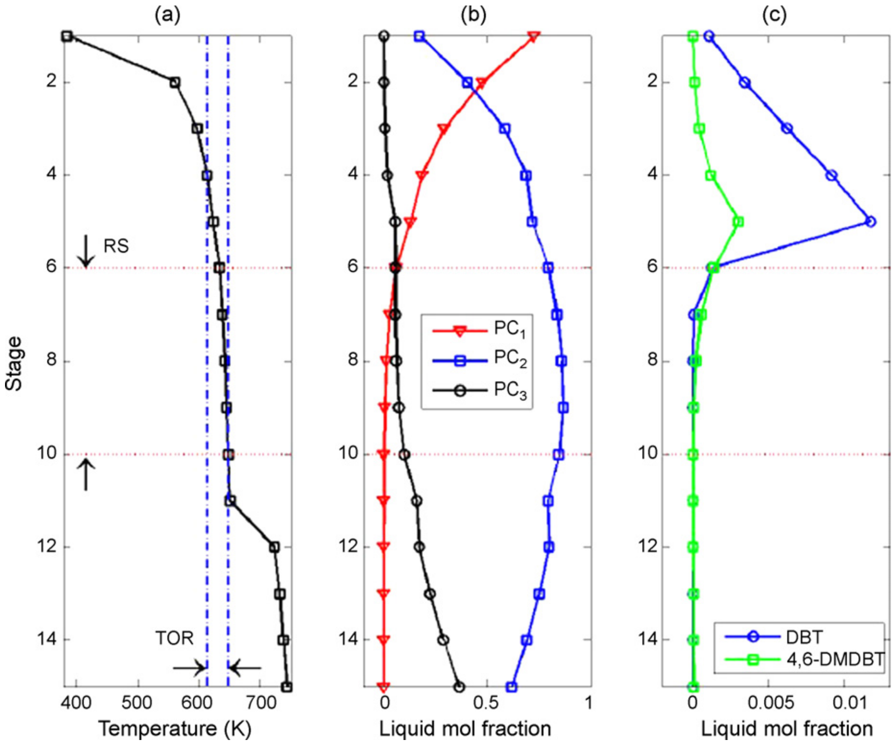

Fig. 2. Case of study: temperature and concentration profiles.

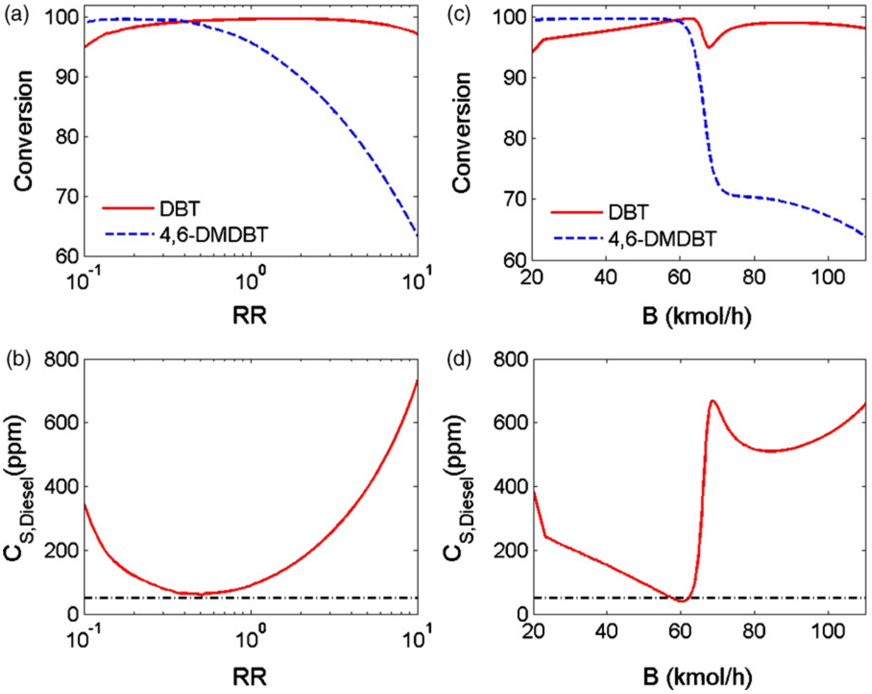

Fig. 3. The effect of the reflux ratio and bottom flow rate on the sulfur conversion.

Table 3
Effect of RR on diesel total sulfur and temperature in reactive section

RR	*S* (ppm)	*T* (K)
0.25	98	634–648
0.51	58	662–676

observed. DBT and 4,6-DMDBT conversions are not greatly affected since the RR is low. However, the lower the condenser temperature is, the larger the condenser.

5.4. Hydrogen and gas oil feed stages

Fig. 4 shows that sulfur concentrations lower than 50 ppm cannot be achieved varying the H_2 feed stage while keeping the LGO feed stage constant (stage 5). The temperature profile remains in the operating range ($613 < T < 648$ K) at all times. However, when the H_2 is fed into the reboiler its heat duty and temperature are reduced (Table 5). Thus, some H_2 may be fed into the reboiler since high temperatures favor coke formation. On the other hand, Fig. 4c and d show that sulfur concentrations lower than 50 ppm can be achieved varying the LGO feed stage while keeping the H_2 feed stage constant (stage 11). Maximum conversion is achieved between the 6th and 7th stage, 99.8% for the DBT and 99.6% for the 4,6-DMDBT. Thus, more than one feed may be used.

Table 4
Effect of *B* on diesel total sulfur and temperature in reactive section

B (kmol/h)	*S* (ppm)	*T* (K)
57.4	50	627–646
60.4	39	618–641
62.1	50	610–637

5.5. Catalyst loading

The catalyst hold up is related to the residence time and affects the sulfur conversion. The catalyst loading in each stage was varied from 5000 to 20,000 kg (Fig. 5a and b). High DBT conversions (above 98%) are observed for the entire range. However, for 4,6-DMDBT high conversion requires a minimum of 6500 kg of catalyst. On the other hand, the total sulfur in the diesel stream is below 100 ppm using 12,000 kg of catalyst loading per stage (98.53% of conversion for DBT and 99.6% for 4,6-DMDBT). Temperature profiles are poorly influenced by catalyst loading. In this case, more catalyst loading does not improve sulfur elimination; therefore, a combination of operating and design variables should be used to do so.

5.6. Stripping, rectifying, and reactive stages

Reactive stages were varied from 1 to 15 (Fig. 5c and d), while stripping and rectifying stages were fixed at five (case study). High conversions are obtained for DBT when more than two stages are used, and high conversions are observed

Table 5
Effect of the H_2 feed stage on the reboiler

Feed stage	T_B (K)	Q_r (MM kcal/h)
6	743	5.428
15	662	4.584

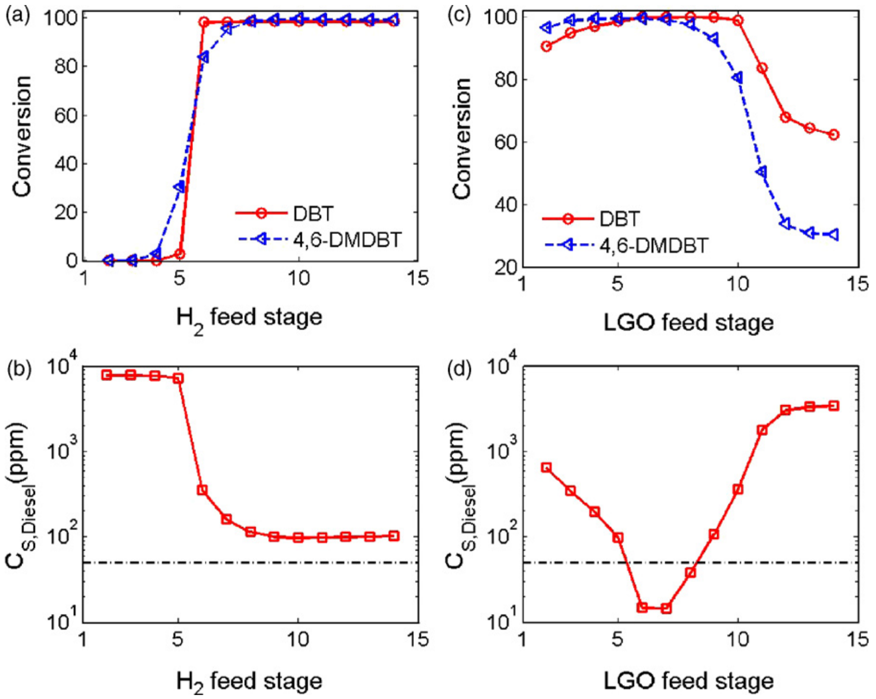

Fig. 4. The effect of the H_2 and LGO feed stages on the sulfur conversion.

for 4,6-DMDBT when more than four stages are used. Above six reactive stages, the conversion for both compounds does not show an appreciable change.

In the HDS of LGO via CD the rectifying section should: (a) recycle unreactant light sulfur compounds, and (b) remove H_2S from the reactive section. Fig. 6a shows that high conversions are obtained using more than five rectifying stages, mainly because DBT and 4,6-DMDBT are recycled and eliminated in the reactive section. Fig. 6b shows that adding rectifying stages is favorable for the deep HDS of LGO.

In the HDS of LGO via CD the stripping section should: (a) concentrate heavy fractions of LGO, and (b) remove light compounds from the diesel product. Adding stripping stages may be not favorable because heavy sulfur compounds will also tend to concentrate themselves in the bottom stream (Fig. 6c and d).

5.7. Feed flows

Fig. 7 shows the effect of the H_2 and LGO feed flows on the sulfur conversion. The H_2/hydrocarbon ratio cannot be varied

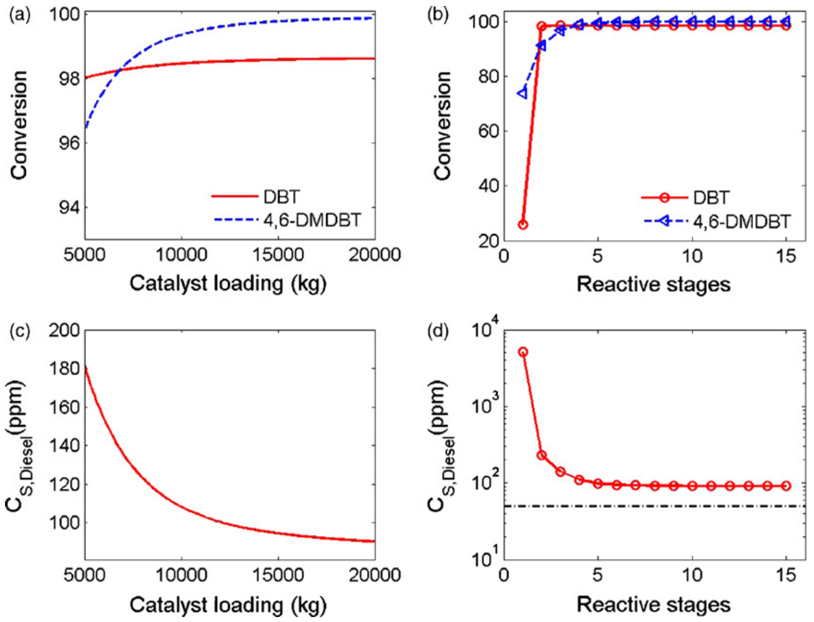

Fig. 5. The effect of catalyst loading per stage and number of catalytic stages on sulfur conversion.

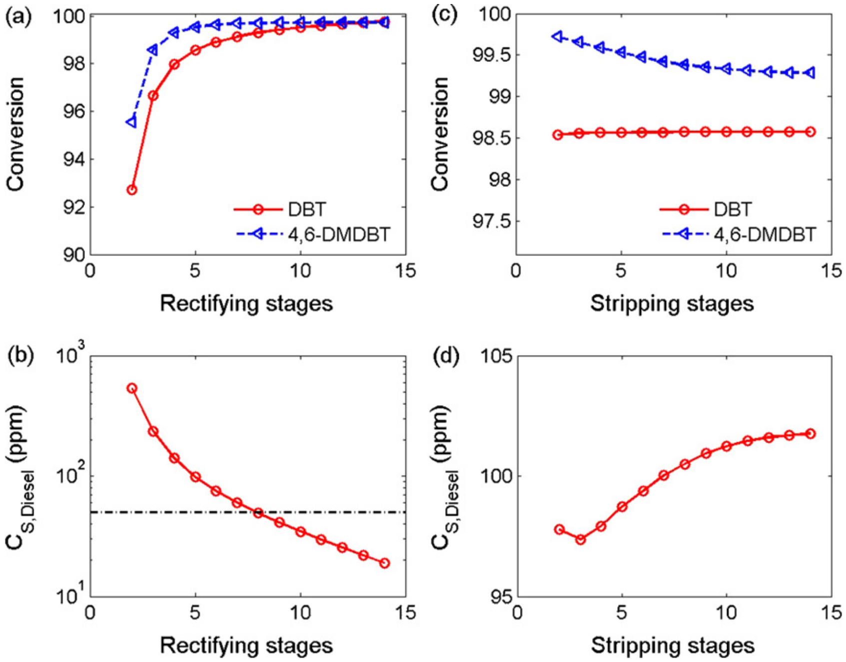

Fig. 6. The effect of the number of stripping and rectifying stages on sulfur conversion.

since it is a quality specification of the diesel; however, their individual flow rates may be disturbed during operation. Fig. 7 shows that sulfur conversion is more sensitive to disturbances on the LGO feed rate. Therefore, the control of the LGO feed rate must be tighter. Fig. 8 shows the effect of the LGO feed temperature and concentration of sulfur in the LGO feed. Relatively small variations in both LGO feed temperature and sulfur concentration result in small variations on the sulfur conversion. Disturbances in the hydrogen feed temperature do not have a significant effect on the sulfur conversion.

5.8. *Multiple feeds*

Multiple feeds may enhance the catalytic distillation performance and reduce the annualized cost [23]. Fig. 9 shows

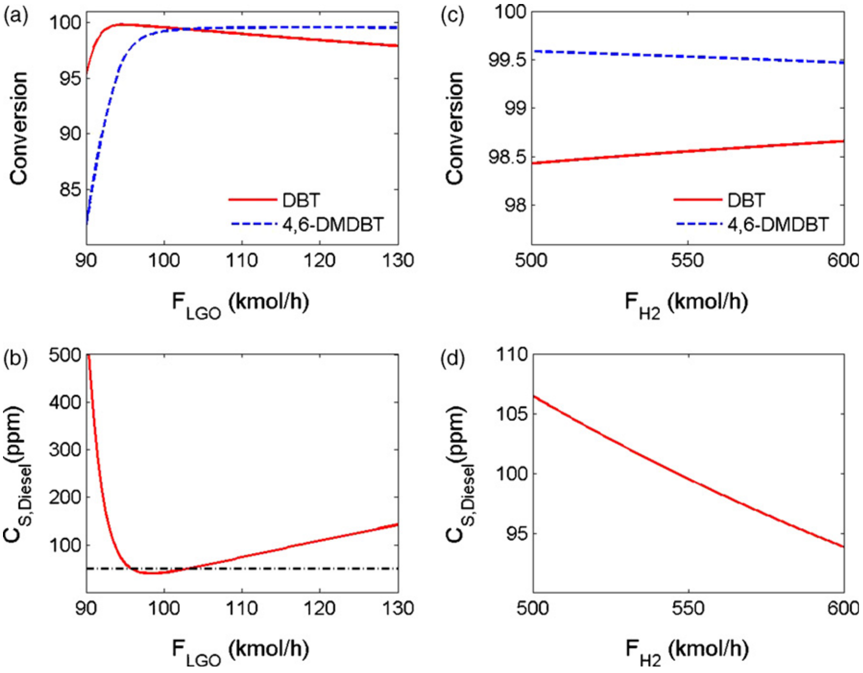

Fig. 7. The effect of the H_2 and LGO feed flows on sulfur conversion.

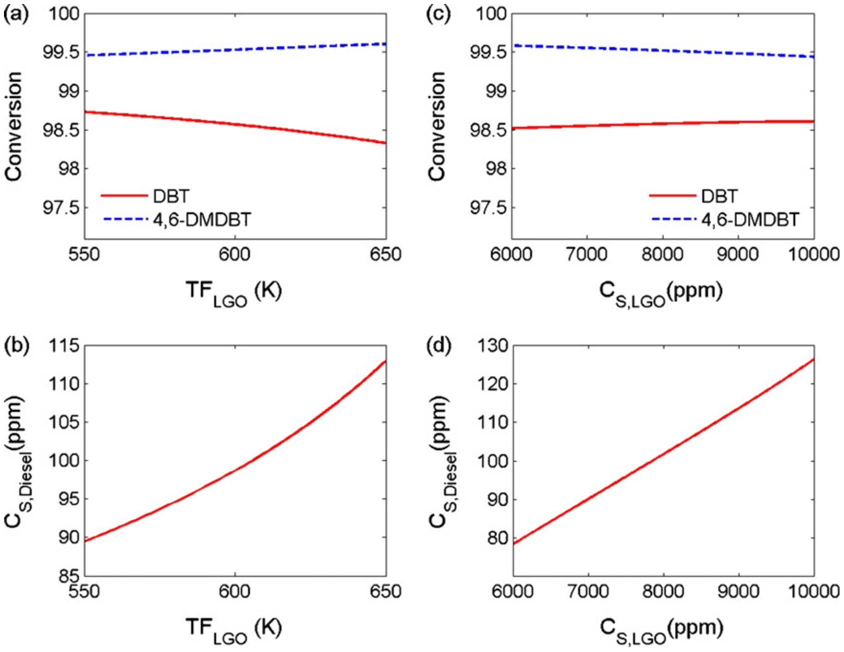

Fig. 8. The effect of the LGO feed temperature and feed sulfur concentration on sulfur conversion.

the effect of H_2 and LGO multiple feeds on sulfur conversion. The feed molar flows are kept constant and divided by the number of feeds (Fig. 10). The numbers of H_2 feeds are varied in Fig. 9a and b as follows: two feeds (stages 10 and 11); three feeds (stages 9, 10, and 11); four feeds (stages 8, 9, 10 and 11), and so on. LGO is fed in stage 5. Similarly, the number of LGO feeds is varied in Fig. 9c and d as follows: two feeds (stages 5 and 6); three feeds (stages 5, 6, and 7), and so on. H_2 is fed in stage 11. Results show that sulfur conversion is not sensitive to the number of H_2 feeds, while it is very sensitive to the number of LGO feeds. Fig. 9c and d shows that the number of LGO feeds have contrary effects on DBT and 4,6-DMDBT conversions. As the number of feeds increases, the unreacted DBT decreases in the rectifying section; while at the same time, the 4,6-DMDBT concentration increases in the stripping section. This can be explained in terms of their different reactivities and the feed position in the reactive section. Maximum conversion is achieved with four LGO feeds.

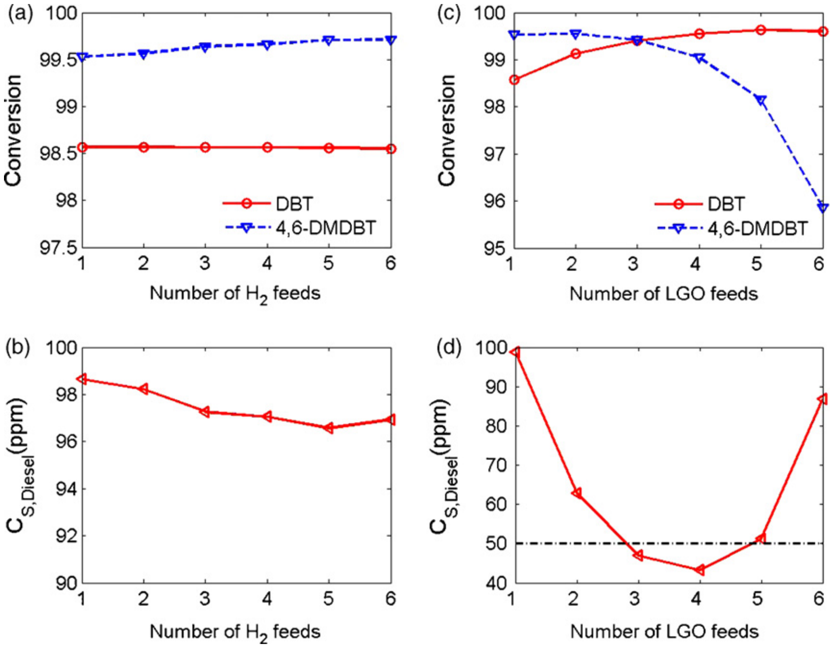

Fig. 9. The effect of LGO and H_2 multiple feeds on sulfur conversion.

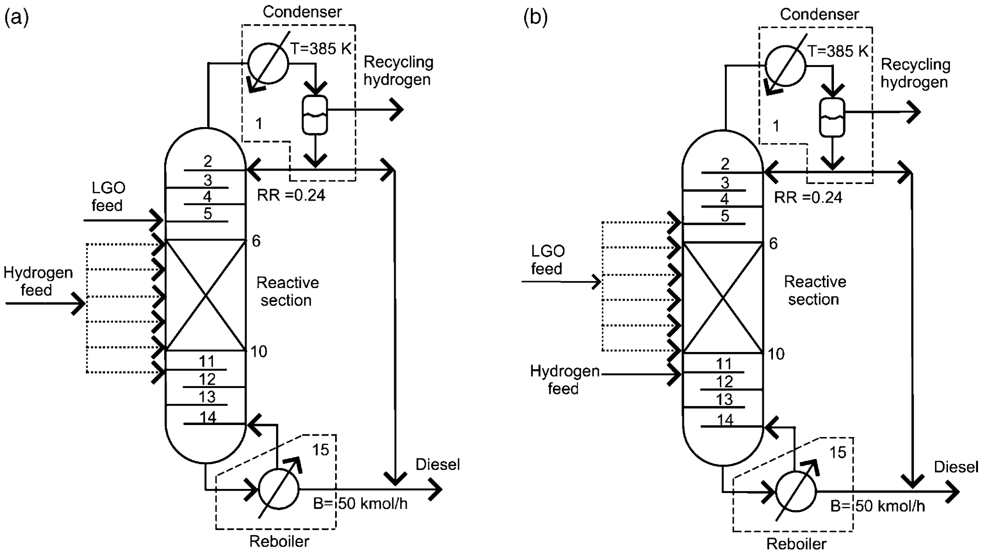

Fig. 10. DHDS distillation column with multiple feeds (a) multiple H_2 feeds and (b) multiple LGO feeds.

6. Conclusions

In this work, a sensitivity analysis of a light gas oil deep HDS catalytic distillation column is presented.

Results show that the RR has a limited effect on the sulfur conversion and that it must be small. As a consequence, the condenser temperature does not considerably affect the column temperature profile and sulfur conversion. The maximum sulfur conversion occurs when the RR is between 0.3 and 0.8. The sulfur conversion is very sensitive to the bottom flow rate, achieving its minimum at 60 kmol/h. The catalyst loading and the number of reactive stages have a major effect on sulfur conversion when the load is lower than 12,000 kg of catalyst and the reactive stages are less than five. When various H_2 and LGO feed streams are considered, interesting results are obtained. The number of H_2 feeds has no significant effect on the sulfur conversion, though it is very sensitive to the number of LGO feeds. The higher sulfur conversion is achieved for four LGO feeds having opposite effects for the DBT and the 4,6-DMDBT conversions. Feeding the hydrogen in the last stage favors sulfur elimination and maintains the reactive section temperature profile into the operating range. Special attention must be given to the bottom flow rate and LGO feed rate control since they have a significant effect on the sulfur conversion.

The results provide insight about the qualitative effect of some operating variables on the sulfur elimination. Future work will focus on optimization, multiple steady states, and dynamic aspects.

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