EFFECT OF THE HEATING METHOD ON THE PERFORMANCE OF HYDRODESULPHURIZATION REACTIVE COLUMN

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Abstract

In the new hydrodesulphurization (HDS) process by integrating the reaction and separation units in a single reactive column, the fixed cost and operating costs can be reduced, as well more flexible operating conditions will be achievable. For investigating both the design and operating aspects of reactive columns, computer simulation is needed. This study was performed using the innovative RIPI (Research Institute of Petroleum Industry) method in different conditions such as various operating temperatures and pressures for gas oil feed. In this paper, the effect of changing the feed temperature on the simulation results will be investigated. Moreover, since the heating of a pilot scale column using an external jacket is possible, the simulation results of an lateral heated reactive column is presented.

Keywords: Hydrodesulphurization, reactive column simulation, operating parameters

1. Introduction

Sulfur compounds in crude oil and cracking products, in the presence of the catalyst, react with hydrogen and convert to hydrogen sulfide and sulfur-free hydrocarbon. One of the most common processes which are used for desulfurization of oil cuts such as gasoil, kerosene, etc. is hydrodesulphurization (HDS) process. HDS reaction can be generally shown as the following reaction [1, 2]:

$$R - SH + H_2 \rightarrow R - H + H_2 S \tag{1}$$

In the conventional HDS units, after reaction between sulfur compounds and hydrogen in a trickle-bed reactor, produced gas should be passed through the separators and a stripper column, to separate $H_2 S$ and remained H_2 gases from the sweetened liquid oil. Using a reactive column is more efficient than the conventional separation/reaction schemes because it integrates the reaction and the separation in a single operating equipment. The HDS via reactive column may improve the efficiency of the conventional HDS unit because it uses the reactants, the energy, and the services efficiently. This reduces the fixed cost and operational costs [3]. Furthermore, the disadvantageous of using the co-current gas-liquid down flow trickle-bed reactors for hydroprocessing of heavy oils is that reactions such as hydrodesulphurization and hydrogenation are inhibited by hydrogen sulphide formed [4].

The removal of sulfur from heavy oil generally follows second-order kinetics in sulphur concentration, which is a reflection of the presence of a variety of sulphur containing compounds with different reactivities. The second- order kinetics imply that a relatively large proportion of sulphur is removed in an early stage of the process (due to conversion of the bulk of reactive molecules) while removal of the remaining sulphur takes place much more slowly in later stages. This means that the bulk of the $H_2 S$ is generated in a small inlet part of the bed and that this $H_2 S$ exerts its inhibiting influence in the remaining part

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of the bed. It can be seen that in co-current operation the larger part of the bed operates under a H$_2$S-rich regime. The situation is clearly more favorable in the counter-current mode of operation since in this case the major part of the bed operates in the H2S lean regime. The counter-current reactor shown in Figure 1 is essentially a reactive column wherein the H2S is stripped from the liquid-phase and carried to the top. Other examples of application of reactive distillation can be found in esterification processes [3], separation of isomers [5], and in the manufactures of "antiknock" enhancers such as methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) [6].

There are a wide range of sulfur compounds in an oil cut which the type of them depend on the boiling range of the cut. Whatever the oil cut be heavier, its sulfur compounds will be heavier and removed more difficult. In this work, the dibenzothiophene (DBT) is used to represent the sulfur compounds since it is one of the less reactive sulfur organic compounds present in gas oil. In addition, its concentration is significant. For kinetic modeling of a chemical reaction, several models such as power law, Langmuir-Hinshelwood and Riedel can be used. In this study, the first two models were applied in the simulations. The related equations of these models are presented in the next section [7].

Modeling of reactive separation processes requires simultaneous prediction of reaction and separation. The RIPI innovative method was presented to solve the equilibrium-based equations of distillation column models. Using a tray by tray algorithm and the shooting method, RIPI method has a high flexibility for implementing the heating and cooling in the column stages and using the kinetic equations in the form of Langmuir-Hinshelwood equation or power law kinetic equation [8]. For investigating the effect of gas oil feed temperature on the performance of the HDS reactive column, the feed inserted to the column with various temperatures. Furthermore, since the current work was performed for designing a pilot scale HDS reactive column, using the external jackets was evaluated by means of stage by stage heating the column is simulations. The simulation results approved the capability of the RIPI method in predicting the HDS reactive columns.
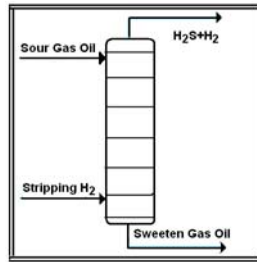

Fig. 1- The schematic shape of HDS reactive stripper column

2. Mathematical modeling and kinetic characteristics

The basic equations usually used in steady state distillation column modeling (MESH equations), are as below [9]:

Mass balance,

$$M_{i,j} = L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j} - (L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j} + V_{H_j}\sum_{n=1}^{NR} v_{i,n}r_{j,n} = 0 \qquad (2)$$

Equilibrium,

$$E_{i,j} = y_{i,j} - k_{i,j}x_{i,j} = 0 \qquad (3)$$

Summation,

$$(Sy)_i = \sum_{i=1}^{C} y_{i,j} - 1.0 = 0 \qquad (4)$$

$$(Sx)_i = \sum_{i=1}^{C} x_{i,j} - 1.0 = 0 \qquad (5)$$

Energy balance,

$$H_j = L_{j-1}h_{L_{j-1}} + V_{j+1}h_{V_{j+1}} + F_j h_{F_j} - (L_j + V_j)h_{L_j} - (V_j + W_j)h_{v_j} - Q_j + Q_r = 0 \qquad (6)$$

The new algorithm developed at RIPI is shown in Figure 2. In contrast with the conventional methods such as simultaneous correction or homotopy continuation, RIPI method after assuming a series of initial assumptions such as liquid and vapor flows, and temperature and concentration profiles along the column solves stage by stage the MESH equations (i.e. performing the flash calculations). Then the initial values can be modified by replacing the new obtained values. This modification can be carried out by different ways. For instance,

after performing the flash calculation for stage j, the obtained specs for stream L_j which leaves stage j as liquid product, is used as the specs of liquid feed for stage j+1 (i.e. L_{j+1}). This will be continued until the flash calculations for all stages are finished. At the end of each computational step, the error of computations can be estimated by the following equation:

$$\varepsilon = \sum_{j=2}^{NS}\left(\left(T_j^{VP} - T_{j-1}^{VF} \right)^2 + \left(F_j^{VP} - F_{j-1}^{VF} \right)^2 + \sum_{i=1}^{NC}\left(y_{i,j}^{VP} - y_{i,j-1}^{VF} \right)^2 \right)^{0.5}$$ (7)

VP and VF in eq.7 refer to specs of vapor product and vapor feed, respectively. Since the vapor product of each stage is equal to the vapor feed of its upper stage (the properties of this stream are assumed or calculated at previous step), the convergence is achieved when all of their specs were the same.

Moreover, F_0, $z_{i,0}$ and $h_{F,0}$ in the mentioned equations, are the flow rate, concentration and enthalpy of the liquid feed stream entered to tray 1, respectively. In addition, F_N, $z_{N,0}$ and $h_{N,0}$ are the flow rate, concentration and enthalpy of the Vapor feed stream entered from the bottom of the column. Since the reactive column in the present work is assumed to be a reactive absorber, the flow rates of other feed streams were set equal to zero.

The reaction of dibenzothiophene (DBT) and hydrogen (H_2) can be simply shown as below:

$$DBT + 2H_2 \rightarrow BiPh + H_2S$$ (8)

where BiPh is biphenyl. Ganji et al. [10] proposed the following power low kinetic model for this reaction:

$$\frac{1}{n-1}\left[\frac{1}{C_p^{n-1}} - \frac{1}{C_f^{n-1}} \right] = \frac{k}{LHSV}$$ (9)

where C_p and C_f are reactant concentration in product and feed streams based on weight percent, respectively. n is the reaction order, and LHSV is the heterogeneous catalytic reactions parameter (h^{-1}) which is equal to the ratio of catalyst volume to feed volumetric flow rate. Also, k is the reaction constant which is defined as below:

$$k = k_0 \exp\left(-\frac{E}{RT} \right)$$ (10)

where k_0 is Arhenious constant, E is reaction activation energy (kJ/kmol), R is gas constant (kJ/mol.K) and T is the temperature (k). According to the experiments accomplished by Ganji et al. [10] the HDS reaction order (n) for gas oil feed is equal to 1.5 and k_0 and E are $2.7*10^9$ and 92660 kJ/kmol, respectively. Also, with respect to feed flow rate in the simulations (i.e. 1 lit/h) and selecting a catalyst volume of 1 lit., LHSV become equal to 1 h^{-1} which is an appropriate value in practice. Therefore, if 20 equilibrium reactive stages be considered, catalyst volume for each stage will be equal to 1/20 lit.
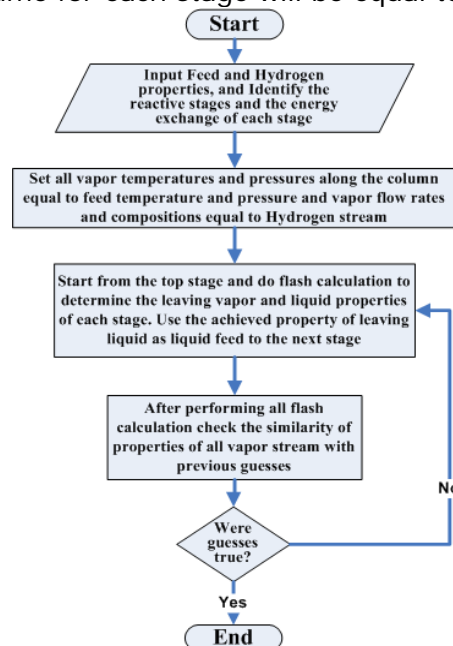

Fig. 2- The innovative RIPI method algorithm [8]

3. Simulation of HDS reactive column without heating

In this section, a reactive column with 20 theoretical stages is simulated. The characteristics of the gas oil feed entered from the top of the column and the hydrogen stream entered from the bottom of the column are presented in Table 1 and Table 2, respectively.

Table 1 The characteristics of the gas oil feed entered to the HDS reactive column

Property	Value
Std volume flow	1 lt/hr
Temperature	370°C
Pressure	70 bar
Mass flow of DBT	0.0691

Table 2 The characteristics of the hydrogen gas entered to the HDS reactive column

Property	Value
Mass Flow	0.0222 kg/hr
Temperature	370°C
Pressure	70 bar

Figure 3 shows the temperature profile along the reactive column. As indicated in this figure, the temperature of stages 1 to 16 was almost constant and equal to 370°C. Since the solving of hydrogen in the gas oil is endothermic, the temperature decreased after stage 8.

Figure 4 and Figure 5 present the changes in mass flow rates of liquid and gas, respectively. According to Figure 4, there is a decreasing path for mass flow rates of liquid which can be related to converting the liquid phase dibenzothiophene (DBT) to gas state H_2S. Figure 5 shows the same trend for mass flow rates of gas along the column. As described before, since the most of DBT react with H_2 in the earlier stages of the column (i.e. at the top of the column), the flow rate of the gas stream in the upper stages of the column was more than the lower stages.
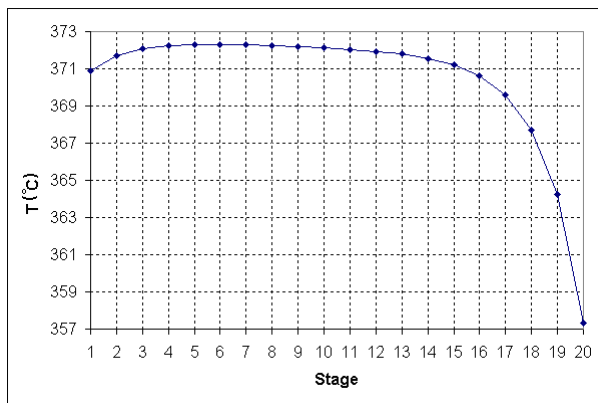
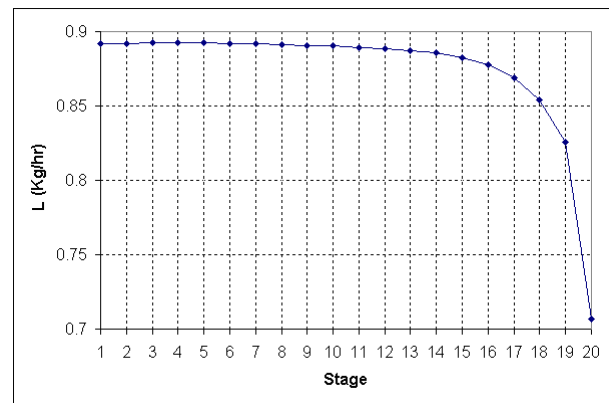Figure 3 The temperature profile along the HDS reactive column

Figure 4 The changes in mass flow rates of liquid stream along the HDS reactive column

Furthermore, figure 6 shows the sulfur content of liquid stream along the column. As shown in this figure, the sulfur content has reached to its proper range, i.e. under 50 ppm, next to stage 10. Although, according to this figure the existence of just ten stages seems to be enough to obtain the acceptable range of the sulfur content, but since the entered hydrogen decreases the column temperature, the other stages may be necessary to remain the stages temperature near to appropriate reaction temperature. However, one of the outcomes of this study can be determining the required equilibrium and reactive stages.
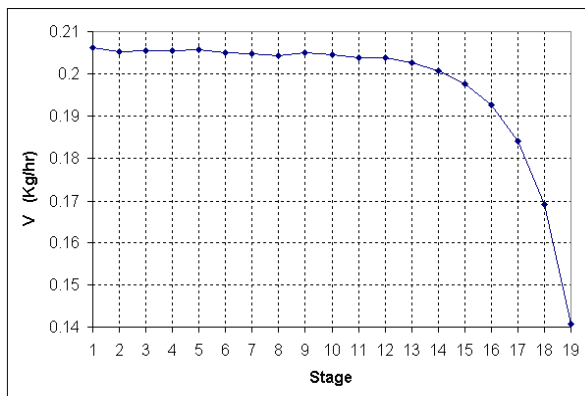
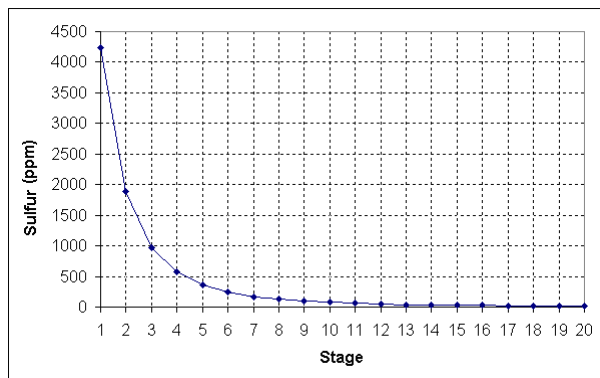Figure 5 The changes in mass flow rates of gas stream along the HDS reactive column

Figure 6 The sulfur content of liquid stream along the HDS reactive column

4. Simulation of HDS reactive column with heating

In this section, a column with 20 reactive stages was simulated, which in terms of heating aspects is divided in to two sections. At the first section, included 5 top stages, the amount of heating energy given to the each stage was equal to 35 W. The next section included the remained stages receive no heating energy. This energy can be provided using an external electrical heating jacket. The characteristics of inputted gas oil and hydrogen to the column is similar to Table 1 and Table 2, unless the temperature of the H2 and gas oil streams is supposed to be 25°C. Figure 7 shows the temperature profile along the reactive column with lateral heating. As indicated in this figure, the temperature along the upper stages which are exposing the heating jacket is gradually increasing until reach to the proper temperature, i.e. about 370°C. The temperature lost occurred at the last stages is because of endothermic mixing of gas oil and H_2, as discussed before.

Figure 8 and figure 9 present the changes in mass flow rates of liquid and gas of heated reactive column, respectively. As indicated in Figure 7, the temperature rises to over 350°C after stage 5. The reason of increasing pass of liquid mass flow rate in Figure 8, can be related to the vaporization of lighter components in the heated gas oil after this stages. These components are condensed and turn back to the liquid phase, in confront with cold liquid entering to the top of the column. Therefore, a mass accumulation may be occurred in middle stages of the column which can be observed in Figure 8. The same explanation can be expressed for mass flow rate of gas stream along the reactive column with lateral heating, in figure 6. Moreover, figure 10 shows the sulfur content of liquid stream along the heated column. As shown in this figure, the sulfur content has reached to its proper range, next to stage 15.
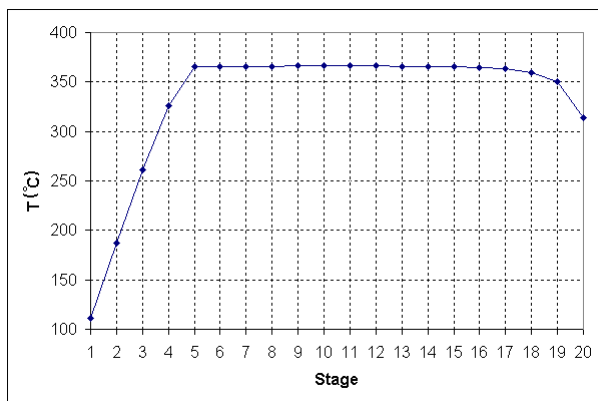

Figure 7 The temperature profile along the HDS reactive column with lateral heating
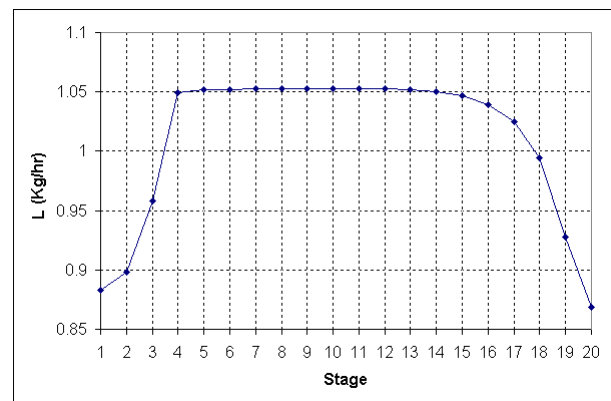

Figure 8 The changes in mass flow rates of liquid stream along the HDS reactive column with lateral heating
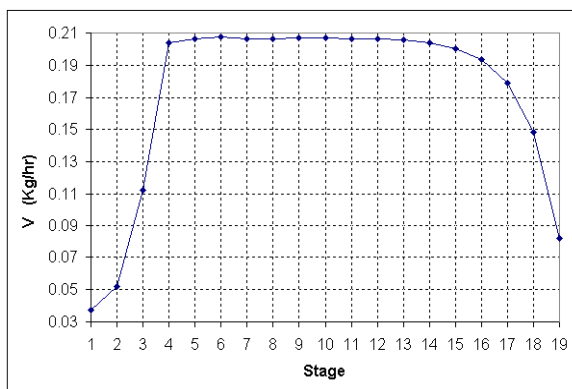

Figure 9 The changes in mass flow rates of gas stream along the HDS reactive column with lateral heating
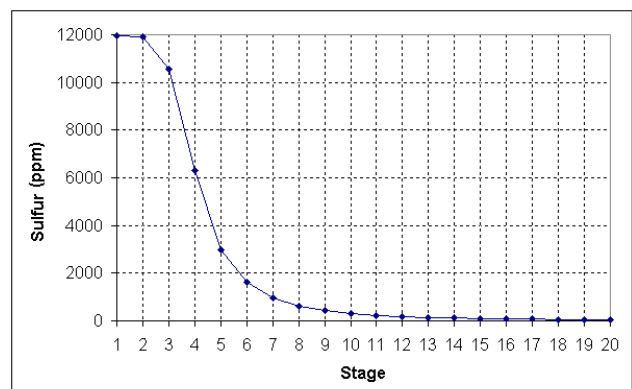

Figure 10 The sulfur content of liquid stream along the HDS reactive column with lateral heating

A compression between the achieved results if these two simulated cases, i.e. entering the feed in high temperature and cold gas oil together with lateral heating, it seems that the first case may be more proper than the other one, because more stages are operating in the appropriate temperature. On the other hand, in the second case, some stages are

required to reach the temperature of the gas oil up to the reaction temperature. Therefore, the hydrodesulphurization reaction will be started later in comparison with the first case. Moreover, entering the feed in high temperature without lateral heating is more similar to actual case.

5. Conclusions

In new hydrodesulphurization (HDS) process, by replacing a reactive column instead of separators and stripper, fixed and working capital can be reduced, and also it is possible to work in modified operating conditions such as lower temperature and/or lower pressure. In this work, using a new method developed at Research Institute of Petroleum Industry (RIPI), a computer simulation was performed to evaluate the design and operation aspects of a HDS reactive column for gasoil feedstock. This method was able to evaluate the effect of temperature changes on the reactive column behaviors. Moreover, the simulation results of the stage by stage heating of a hydrodesulphurization reactive column were presented, which can be applied for designing a pilot scale HDS unit. The achieved results showed that the entrance of gas oil feed in its actual temperature seems to be more appropriate rather than using cold feed by lateral heating.

Nomenclature

C: Concentration
E: Activation energy
F: Feed flow rate
H: Enthalpy
h: Specific enthalpy
k: Reaction rate constant
k_o: Arrhenius constant
L: Liquid flow rate
M: Mass
NC: Number of components
NR: Number of reactions
NS: Number of stages
P: Pressure
Q: Heat flow rate
R: Gas constant
r: Reaction rate
S: Summation

W: Vapor side stream flow rate
x: Liquid component fraction
y: Vapor component fraction
z: Feed component fraction
Superscripts
n: Reaction order
F: Vapor feed
VP: Vapor product
Subscripts
r: Reaction
i: Component Index
j: Stage Index
p: Product
f: Feed
n: Reaction order
Greek
v: Stoichiometric coefficient

List of Abbreviations

BiPh: BiPhenyl
DBT: Dibenzothiophene
LHSV: Liquid Hourly Space Velocity

T: Temperature
U: Liquid side stream flow rate
V: Vapor flow rate
VH: The volumetric liquid holdup

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