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Crude-specific optimal operation of hydrodesulfurization

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Crude oil has different characteristics according to its origin, and this difference causes suboptimal operation if not considered. Similar to other refinery operations, hydrodesulfurization suffers from lacking this knowledge. Information on the true boiling point curve of the feed, next to its sulfur concentration, can be used to optimize the operating temperature. In this work, an optimization problem is demonstrated for two manipulated temperatures of the system and solved by using a gradient-based and a gradient-free algorithm. While the gradient based solution has a single objective of minimum sulfur content, the gradient-free solution has three objectives: minimum sulfur, inlet temperature, and secondary hydrogen flow rate. A continuous lumping model is used to predict the temperature and sulfur responses of a real hydrodesulfurization plant. An adaptive approach is preferred for the model to cope with the catalyst deactivation interference on the product sulfur content constraint. The effect of changing feed on optimality is demonstrated by using eight types of feeds with varying true boiling point and sulfur content. In addition to that, the impact of catalyst age is shown on similar feed processed on different dates.

1. Introduction

Hydrodesulfurization units help treat either the feed or the product of other refinery operations, assuring low sulfur fuel production. With the improved environmental protection laws, the operational restrictions of hydrotreaters have increased, and the need to meet the market demand has been prioritized over the optimal operation. The lack of online feed characterization is another barrier in front of the optimization studies. The sulfur content, the true boiling point curve, and the sulfur distribution on this curve affect the required temperatures.

Studies on the optimization of operating conditions can be found in the literature. Abbasi and Fatemi (2009) used an isothermal dynamic model for prediction and optimized it with a genetic algorithm. They assumed constant feed characteristics and optimized superficial mass velocities, temperature, and pressure, using sulfur content in the objective function. Miranda-Galindo et al. (2014) used a similar approach, but they formulized the problem as multiobjective optimization. They showed how a wide range of optimization variables, including temperatures, pressures, flow rates, and amount of catalyst, affect the sulfur content of the product, total annual cost, and CO_2 emissions of the process. Silva and Secchi (2018) optimized the blending of different streams entering a diesel hydrotreatment unit to reach the desired sulfur content while keeping operational costs low. The assumption of static feed is a good approach for design optimization or refineries that process a single crude. However, a change in the feed shifts the optimal operating conditions that can be calculated using the true boiling point curve and the sulfur content.

Hydrodesulfurization in fixed bed reactors suffers from catalyst aging due to coke and metal deposition in the catalyst's porous structure (Maity et al., 2013). Therefore, the temperature of the system has to increase to reach the same level of sulfur removal. An optimization schedule cannot succeed without a model, considering catalyst aging as the model's prediction capability decreases over time with the severity of aging.

In this work, an optimization schedule is suggested for a hydrodesulfurization reactor, considering its changing feed characteristics and aging catalyst. The details of the optimization and the model used for prediction are given in the next section. The results of the two optimization algorithms and their difference with respect to the feed characteristics and the catalyst age are presented in the results and discussions section. Finally, the conclusions of this study and possible future directions can be found in the last section.

2. Methods

Continuous lumping models are often used for petrochemical applications to represent a hydrocarbon mixture using the assumption of a continuous attribute (e.g., true boiling point, carbon number). The model used in this work is based on a continuum of reactivity of the feed contents.
The mass and energy balances are given in Eq(1) and Eq(2). The correlation of true boiling point and reactivity is derived by Sau et al. (1997) and given in Eq(3). Eq(4) shows the normalization of the true boiling point, and Eq(5) is the sulfur distribution. First-order kinetics are selected for all the reactions. Further details of the model can be found in Elizalde and Ancheyta's work (Elizalde & Ancheyta, 2012).

$$\frac{dc(k,z)}{dz} = -\frac{1}{\vartheta} k e^{-Ea/R(1/T-1/T_0)} c(k,z) \tag{1}$$

$$\frac{dT}{dz} = \frac{1}{\vartheta \cdot c_p} \int_0^{k_{max}} k e^{-Ea/R(1/T-1/T_0)} c(k,z) D(k) (-\Delta H(k)) dk \tag{2}$$

$$k = k_{min} - k_{max} ln(e^{-1} - 1) \theta^{1/\beta} \tag{3}$$

$$\theta = \frac{TBP - min(TBP)}{max(TBP) - min(TBP)} \tag{4}$$

$$D(k) = \frac{di}{d\theta}\frac{d\theta}{dk} = N\frac{d\theta}{dk} \tag{5}$$

$$\frac{1}{N}\int_0^{k_{max}} D(k) dk = 1 \tag{6}$$

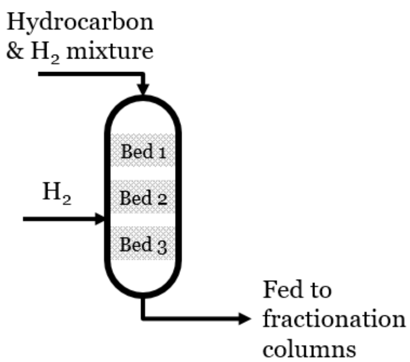

Figure 1: Hydrodesulfurization reactor with three catalyst beds.

Figure 1 shows the industrial hydrodesulfurization reactor with three catalyst beds. Between the second and the third beds, there is a secondary hydrogen inlet used for temperature control. Therefore, inlet temperatures of the first bed and the third bed were selected as optimization variables. The mass flow rate, true boiling point curve, and the feed's sulfur content were the optimization inputs. Two methods were tested to solve the problem, a gradient-based and a genetic algorithm. While minimization of product sulfur concentration was the only aim of the first one, three optimization objectives are selected for the latter, the sulfur content of the product, minimum feed temperature for catalyst protection and energy-saving, and minimum secondary hydrogen flow rate for resource-saving. For both solutions, MATLAB solvers were used, namely *fmincon* using interior-point algorithm and *gamultiobj*. Eight different feeds were selected from industrial data with different properties and processed on different dates, and both optimization methods were tested on each feed. Catalyst aging was considered by updating the parameters of Eq(3), k_{min}, k_{max}, and β; as they define the reaction rate. These parameters were updated within a ± 20 % range of their last value when the bed exit temperature prediction had an error over 2 K.

3. Results and Discussions

In this section, the optimal temperature results obtained by two different solution methods based on real data are given and discussed according to the properties that shift the optimal operating points.

3.1 Gradient-based solution for product sulfur minimization

Feed flow rate, true boiling point, and sulfur content data were used to demonstrate the changing temperature requirements of varying feed conditions to reach minimum sulfur content in the product. True boiling point curves of the selected feeds are given in Figure 2; the relative process date and sulfur content are shown in Table 1 next to the resulting temperature outputs of the optimization, aiming minimum sulfur content in the product.
When the suggested temperatures by the optimizer are compared for feeds different in boiling range and equal in sulfur content, similar values are found if the measurements are within a limited period, enough to ignore the effect of aging catalyst. *Feed 1* and *Feed 2* were processed nine days apart. Although the model parameters of the first bed are updated in between, the optimization results are almost equal (Table 1). These temperatures are a result of considering only the product sulfur content in the objective function.

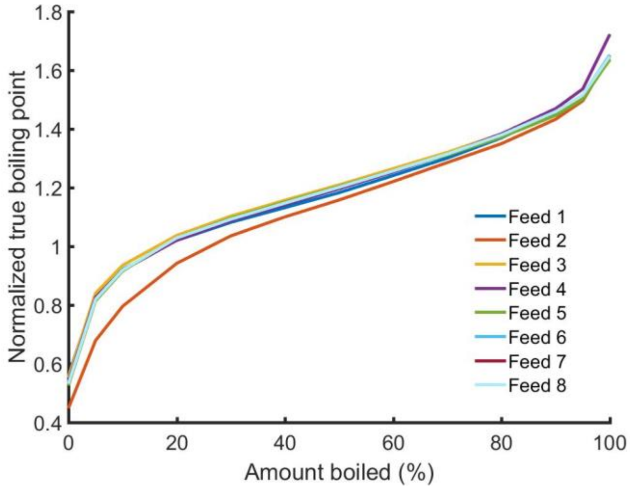

Figure 2: True boiling point curves of selected feeds.

Table 1: Dates and sulfur properties of selected feeds and optimized temperature results.

Feed	Day	Sulfur content (ppm)	Optimal reactor inlet temperature (K)	Optimal third-bed inlet temperature (K)
Feed 1	54	0.82	641.3	647.4
Feed 2	62	0.82	642.0	648.0
Feed 3	0	1.16	645.8	646.4
Feed 4	48	1.16	645.9	649.5
Feed 5	33	1.50	638.9	648.0
Feed 6	78	1.50	644.0	649.4
Feed 7	57	0.88	642.4	648.0
Feed 8	58	1.03	647.4	648.1

When there is a long time between similar feeds, the effect of catalyst aging is observed. Given the characteristics of *Feed 3* and *Feed 4* in Figure 2 and Table 1, a higher temperature is suggested for *Feed 4*, which is processed 49 days after *Feed 3*, although they have equal amounts of sulfur. Similarly, *Feed 5* and *Feed 6* have equal amounts of sulfur, but they were processed 46 days apart. This long period explains the higher temperature results of the optimizer in both beds.

A sudden increase in the sulfur content of the feed directly affects the optimal temperatures. *Feed 7* and *Feed 8* were processed on consecutive dates, and they have a considerable difference in sulfur concentration. When this information is not used for the controller set points, the product has an unstable quality and needs blending or further processing. In the real case, these two feeds were processed at the same temperature, and their products were affected by this. While product 7 had a slightly lower sulfur content than the market demand, product 8 was over the limit.

3.2 Multiobjective optimization

Minimal sulfur is not the only objective for the industrial hydrodesulfurization application. Avoiding high temperatures if the feed is low in sulfur protects the catalyst from fast aging and saves the energy required for heating. There are two controlled temperature values within this reactor: the reactor inlet temperature and the third-bed inlet temperature. The reactor inlet temperature is adjusted with the help of a furnace, and the liquid temperature increases in the catalyst beds as it reacts due to exothermic reactions. The temperature of the third bed is adjusted with the secondary hydrogen flow rate. The closer the third-bed inlet temperature is to the second-bed outlet temperature, the less hydrogen is required. It should be considered that excess hydrogen is already supplied with the feed; therefore, decreasing the flow rate should not limit the reactions. However, the effect of changing hydrogen partial pressure is not taken into account.

The results of multiobjective optimization for *Feed 1* and *Feed 2* are given in Figure 3. When the temperatures are taken into consideration, the difference between the two feeds affects the solutions. If the catalyst aging of 9 days is ignored, lower temperatures for *Feed 2* can be explained because it is lighter than *Feed 1* (Figure 2).

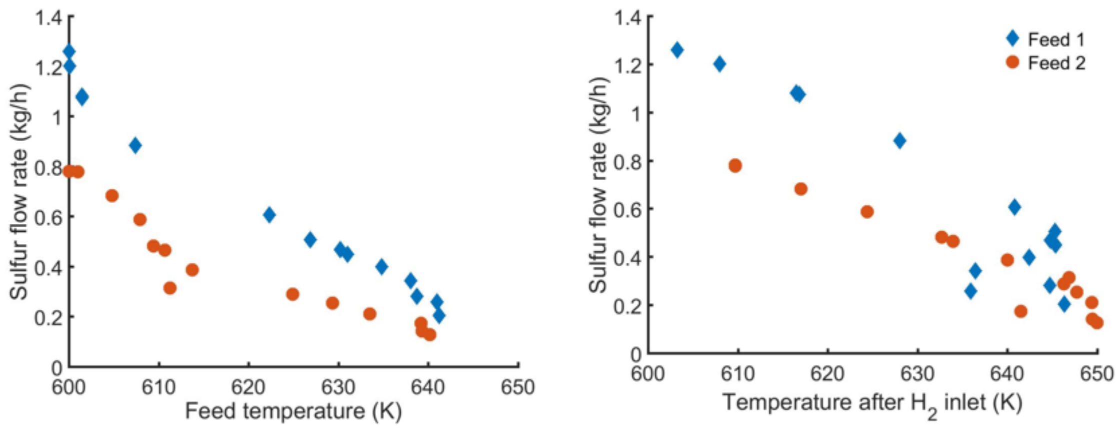

Figure 3: Results of multiobjective optimization for feed 1 and 2.

In Figure 4, the higher temperatures suggested for *Feed 4* are the effect of catalyst aging because *Feed 3* and *Feed 4* have equal amounts of sulfur and similar true boiling point curves. A similar trend is observed for *Feed 5* and *Feed 6*. *Feed 6* that was later processed has higher temperature results of optimization (Figure 5).

To see the effect of a sudden sulfur increase, *Feed 7* and *Feed 8* are also evaluated, and the results are given in Figure 6. A significant difference is detected in the results, especially at the inlet temperature.

For all cases, inlet temperature results create a smoother Pareto front than the third bed's inlet temperature results, although there is no weighting factor assigned to any of the objectives. Most of the sulfur reacts in the first bed; therefore, the third bed might be used only to fine-tune the sulfur removal, and this can explain the irregular Pareto front of its inlet temperature.

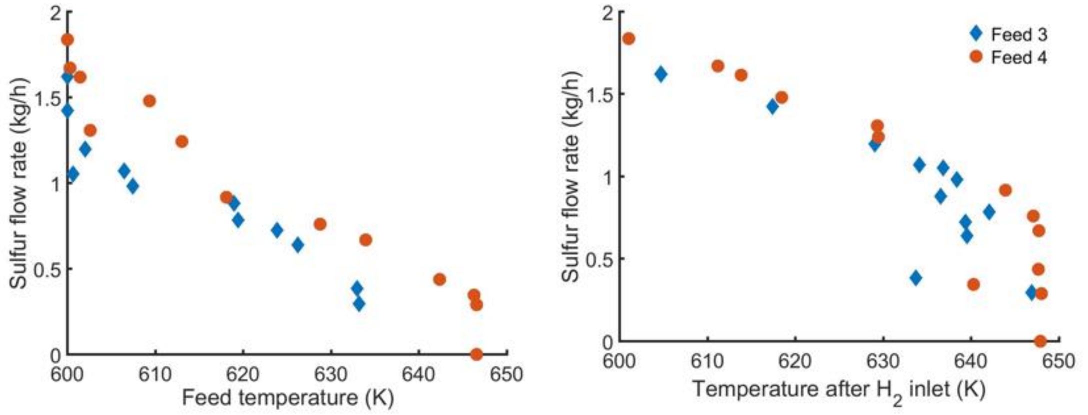

Figure 4: Results of multiobjective optimization for feed 3 and 4.

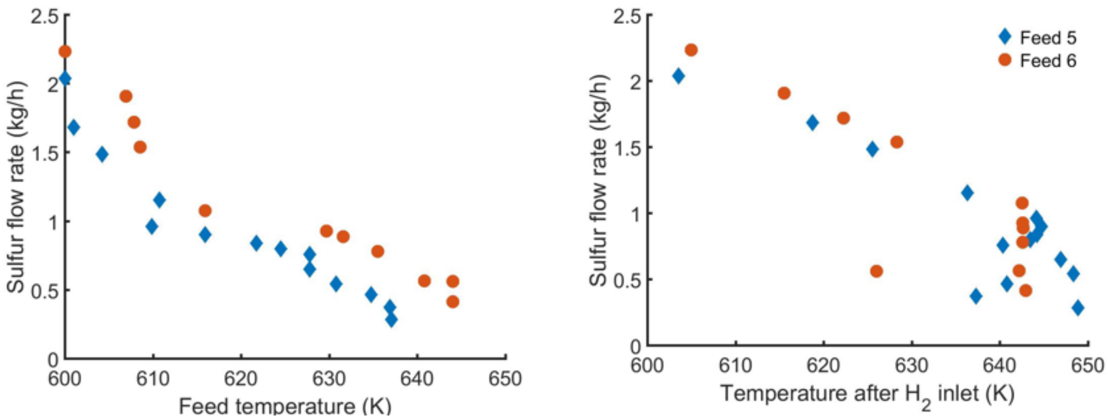

Figure 5: Results of multiobjective optimization for feed 5 and 6.

As can be seen from both sets of results with two different algorithms and objectives, feed characteristics have an essential effect on the optimality of the operation. When the short term changes are not taken into consideration, production cost increases. If the temperature setpoints are greater than necessary, this increases the energy cost and faster aging of the catalyst. For the opposite case, lower temperature setpoints for high sulfur feeds do not reach the required sulfur removal; therefore, either further processing or blending costs should be included.

The gradient-based solution takes around a minute to evaluate by using a detailed physics-based model. Using the same model, multiobjective optimization using a genetic algorithm takes approximately six hours; therefore, it is impossible to utilize it for real-time control. However, drastic changes in the feed properties are observed not more often than twice a week. A six-hour multiobjective optimization can support the operational decisions as the change is mostly planned. Laboratory analysis to characterize the planned feed can supply the necessary information of true boiling point curve and sulfur content. Using the Pareto analysis on contradicting objectives (low temperature and high sulfur removal), an operating temperature range can be decided to maintain the quality of the market while saving energy.

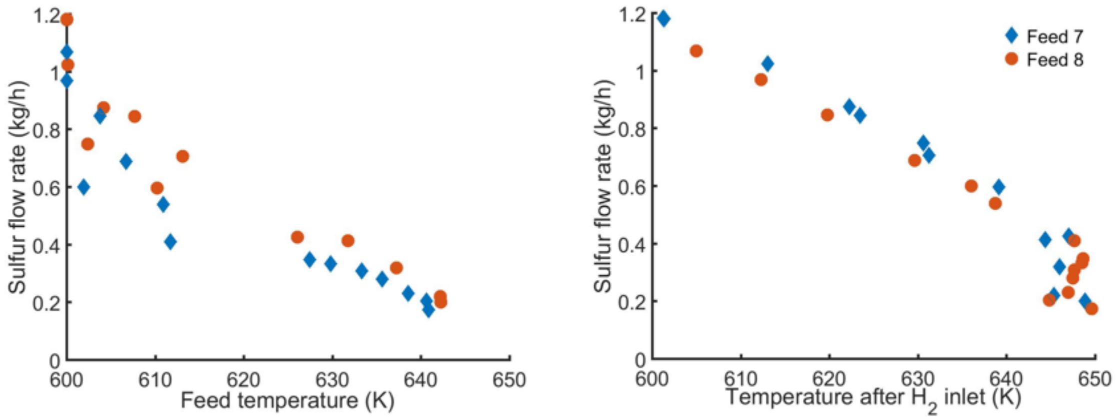

Figure 6: Results of multiobjective optimization for feed 7 and 8.

4. Conclusions

The effect of changing feed characteristics and aging catalyst on the optimal operation of a hydrodesulfurization plant was investigated by using two different algorithms and objectives. Both methods showed a considerable difference in operating temperatures when the information of the feed characteristics was supplied. The multiobjective optimization results should be considered for short-term planning while setting up economic objectives. A supervisory control system can be built using these results; however, a faster model is needed to shorten the evaluation time. In future work, combining results of an online analyzer can be considered instead of laboratory results. This can help stabilize the product quality and include minimum energy demand into refinery objectives if integrated with a faster model.

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