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Process heat integration of a heavy crude hydrotreatment plant

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Abstract

The present paper focuses on the study of process alternatives for heat integration of a heavy crude oil hydrotreatment plant. Experimental information obtained from a pilot scale, kinetics and reactor modeling tools, and a commercial process simulator were employed to develop mass and energy balances. Four study cases, which employ a combination of quenching and heat exchangers, were identified and evaluated. The results indicated that the case with two quenches with hydrogen and three heat exchangers is the best process heat integration (PHI) option from an energetic point of view.

Keywords: Hydrotreatment; Heavy crude oil; Heat integration; Quench

1. Introduction

Due to the increasing production of heavy crudes and the worldwide demand for cleaner fuels, new alternatives must be found for satisfying these requirements. On the other hand, the production of light crudes is decreasing, and hence, refineries will have to process higher amounts of heavy crudes in the future. The great challenge for the refineries is to transform heavy crudes and residua into valuable products and to maximize the production of light fractions for the elaboration of fuels that satisfy the environmental regulations [1].

Among several options for upgrading of heavy oils and residua, hydroprocessing continues to be one of the most utilized approaches due to its flexibility for handling different petroleum fractions, ranging from light naphtha to heavy residue. During hydroprocessing, various reactions such as hydrodemetallization (HDM), hydrodesulfurization (HDS), hydrodeasphaltenization (HDAs), and hydrodenitrogenation (HDN) occur, substantially reducing the content of those impurities and thereby providing additional amounts of better quality feedstock for downstream refinery processes. Hydrocracking (HYC) is another important reaction which is also present during hydroprocessing, and its extent depends on the severity of the reaction [2].

The difficulty of heavy oils hydroprocessing due to the complex nature of the heteroatom bearing molecules is well known. Such heteroatoms escape from the reactor as gaseous products, while metals are irreversibly deposited on the catalyst causing permanent deactivation [3]. Various technologies are available for converting heavy oils into lighter products, which are strongly influenced by the nature of the catalysts used, the quality of the feed, the design of the reactors, the method of feed introduction, the arrangement of the catalyst beds, the reactors' mode of operation, and, of course, the desired quality of the hydrotreated (HDT) product.

The common approach during heavy oils hydroprocessing is to operate the reaction system at severe conditions to achieve a certain level of conversion that guarantees the production of light fractions. The operation of hydrotreatment processes at moderate reaction conditions is not common commercially, mainly because of the necessity to produce sufficient amounts of high quality distillates.

In the Mexico's case, the increasing production of heavy crude oils, e.g., Maya, has forced the Mexican Oil Company (PEMEX) to reconfigure its refineries in order to be able to process such a heavy oil. In addition, the Mexican Institute of

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Petroleum (IMP) has been developing a hydrotreatment process for converting heavy crude oils into lighter ones, whose main characteristic is operation at moderate reaction severity [4].

The IMP hydrotreatment process employs a system of two reactors in series with selective catalysts: the first one for hydrodemetallization and asphaltene hydrocracking, and the second one for hydrodesulfurization and hydrodenitrogenation. Reactor configuration and operating conditions can be adapted depending on the feed quality and desired removal of impurities.

Since the reactions occurring during hydrotreatment are mostly exothermic, controlling the reaction temperature becomes very important in order to prevent carbon deposition on the catalyst and to keep the product's quality at desired levels. For the process configuration with two fixed-bed reactors in series, the common method of controlling the reaction temperature is by introducing part of the hydrogen recycle stream between the reactor beds, the so-called "quench" [1]. The problem with quenching with hydrogen is its availability in refineries. Hydrogen is also needed to keep the hydrogen-to-oil (H_2/oil) ratio along the reactors, which is a design condition that influences product quality. At high H_2/oil ratios, the product's quality is improved, but the size of the equipment after the reaction section increases considerably, which increases the investment costs. Quenching with hydrogen takes place in some part of the reactor length and has two main functions: (1) control of reaction temperature and (2) improvement of flow distribution in the reactor bed. The quench zone is commonly a mixing chamber where the bed effluent is mixed with the hydrogen recycle stream.

Energetically speaking, all processes have certain potential to be improved and the IMP hydrotreatment process is no exception [5]. Since high temperatures are employed in hydrotreatment operations, hot effluents can be used to heat other cold process streams. Pinch analysis is the most utilized tool for the design of heat exchanger networks with an optimization methodology to minimize the amount of heating and cooling utilities and heat transfer area.

The aim of the present paper is to describe and analyze the different alternatives for a heavy oil hydrotreatment plant's process heat integration (PHI), and to select the best option based on energy consumption and total heat transfer area requirements.

2. Summary of experiments

Hydrotreating experiments were conducted in a high pressure pilot plant described elsewhere [3], which operates isothermally. A heavy oil that has the following properties: 21.3° API, 3.57 wt% sulfur, 3200 ppm nitrogen, 11.3 wt% asphaltenes, and 352 wppm Ni + V was employed as feed. Two γ-Al_2O_3 supported catalysts having the following properties were loaded to the HDT reactors:

- *Catalysts in first reactor*: 175 m^2/g specific surface area, 0.56 cm^3/g pore volume, 127 Å mean pore diameter, 10.7 wt% Mo, and 2.9 wt% Ni.
- *Catalysts in second reactor*: 248 m^2/g specific surface area, 0.51 cm^3/g pore volume, 91 Å mean pore diameter, 12.9 wt% Mo, and 2.5 wt% Co.

Table 1
Properties of the heavy crude oil and hydrotreated crude oil

	Heavy crude oil	Hydrotreated crude oil
Specific gravity 20/4 °C	0.923	0.887
API gravity	21.3	27.5
HDS (%)	69.8	
HDN (%)	52.0	
HDAs (%)	67.6	
HDM (%)	56.8	

More details about catalyst loading and sulfiding, operating conditions, reactor characteristics, and sample characterization were reported in previous papers [2,3,6].

In our research laboratory, we have been conducting different tests for hydrotreatment of heavy oils either in one reaction stage [3] or two reaction stages [2]. Catalyst deactivation has been studied with time-on-stream at constant [7] and variable [8] operating conditions, different catalysts have been developed for HDM and HDS applications [9–12], and asphaltenes from heavy oils and hydrotreated products have been precipitated and extensively characterized [13–15]. All these experimental studies have been used to develop kinetic models [16–18] which have been integrated into a hydrotreatment reactor model [19,20]. These modeling tools have allowed us to predict the expected behavior of commercial reactors operated in adiabatic mode, such as temperature and concentration profiles along the reactor, flow rate and location of quenches, reactor delta-T, number and length of catalyst beds, etc.

3. Results and discussion

3.1. Hydrotreatment experiments

Table 1 shows some experimental results of average levels of impurity removals in the two-stage hydrotreatment process. Considerable reductions of sulfur, nitrogen, and metals are achieved. API gravity is also substantially increased, which

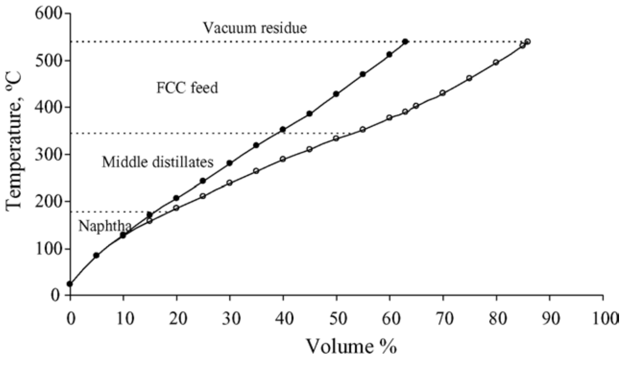

Fig. 1. TBP distillation curves of heavy crude oil (●) and hydrotreated crude oil (○).

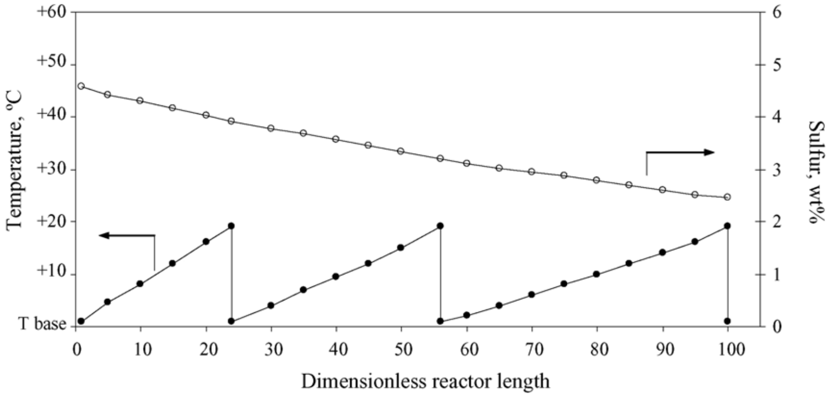

Fig. 2. Profiles of temperature (●) and sulfur content (○) in product as function of reactor length.

implies that lighter fractions are produced. This can be clearly seen in Fig. 1, in which TBP distillation curves of heavy crude oil and hydrotreated crude oil are plotted. From this figure, it is observed that middle distillates yields (jet fuel, kerosene, and light straight-run gas oil) and catalytic cracking (FCC) feed (heavy straight-run gas oil and vacuum gas oils) are increased approximately 11.2 vol% and 8.9 vol%, respectively; naphtha yield remains almost unchanged, and vacuum residue yield reduces drastically, approximately 22.9 vol%.

3.2. Results of reactor modeling

Fig. 2 presents an example of temperature and sulfur content profiles in the product as a function of reactor length for the first hydrotreatment reactor. In this case, three catalytic beds are employed and the catalyst distribution in each bed was 24%, 32%, and 44% from the top to the bottom of the reactor.

3.3. Hydrogen balance

To calculate the number of quenches in each reactor, it is necessary to make a hydrogen balance, which must take into account hydrogen consumption, hydrogen for quench, purges, and hydrogen in other streams. Once hydrogen balance has been determined, hydrogen-to-oil ratio can be estimated according to the following equation:

$$\text{Total}\ \frac{H_2}{\text{oil}}\ \text{ratio} = \sum_{i=1}^{N}\left[\frac{H_2}{\text{oil}}\right]_i X_i \qquad (1)$$

where N is the number of catalytic beds in the reactor and X_i is the amount of catalyst in each bed with respect to the total amount of catalyst in the reactor.

With this procedure, seven hydrogen balances were determined by changing the number of hydrogen quenches

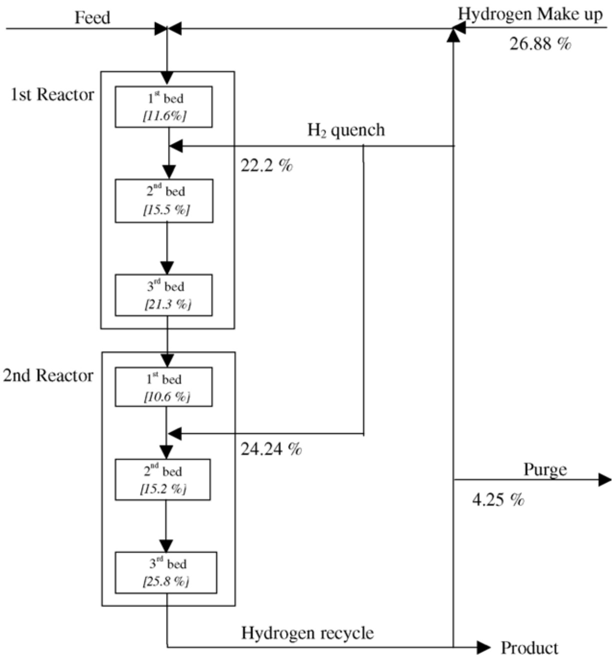

Fig. 3. Hydrogen balance of Case 4.

Table 2
H_2/oil ratio of the developed balances

Case	Number and position of hydrogen quenches		H_2/oil ratio (ft^3 std/bbl)			Absolute error (%)
	First reactor	Second reactor	First reactor	Second reactor	Average	
1	2	2	2688	4277	3483	25.9
2	2	0	4835	5072	4954	5.3
3	0	2	3499	4288	3894	17.2
4	1 (1st bed)	1 (1st bed)	4314	4838	4576	2.7
5	1 (2nd bed)	1 (2nd bed)	3978	4504	4241	9.8
6	1 (1st bed)	1 (2nd bed)	4318	4505	4411	6.2
7	1 (2nd bed)	1 (1st bed)	3961	4835	4398	6.5
Exp.	Without quench	Without quench	4665	4743	4704	–

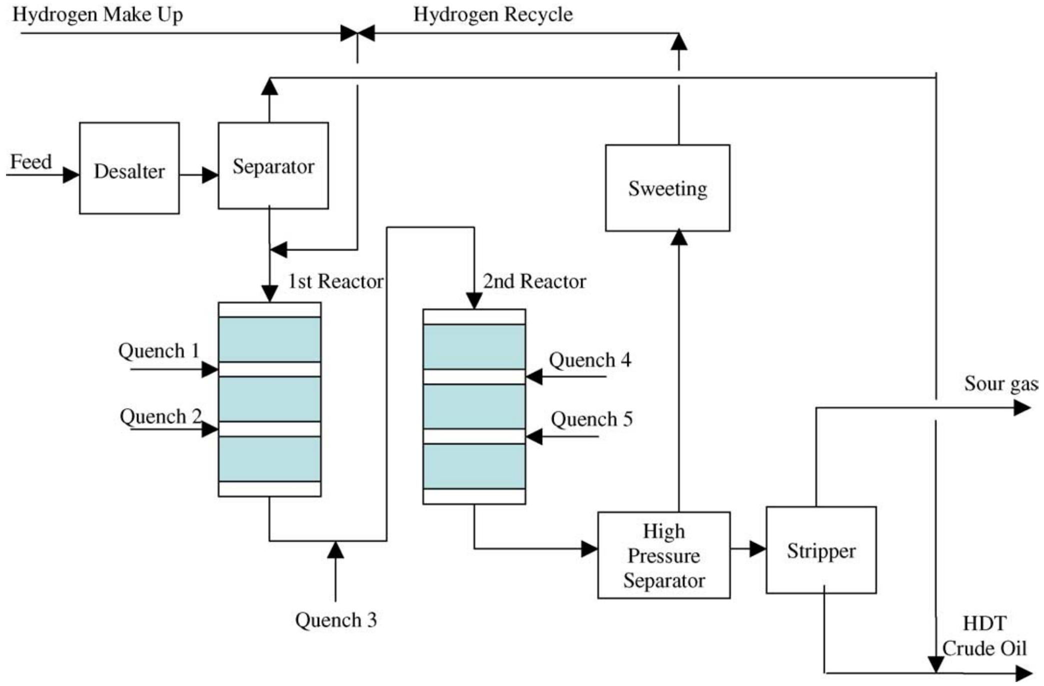

Fig. 4. Process scheme of the two-stage hydrotreatment process [4].

and their position along the reactors. The results are summarized in Table 2. The experimental values of H_2/oil ratio are also reported in the same table. Case 4 better represents the H_2/oil ratio reported at the isothermal pilot plant with an absolute error of $<3\%$. The errors for the other cases were $>5\%$. Fig. 3 shows an example of the results obtained for the case 4 hydrogen balance, which was performed with a Hysys process simulator. The values of hydrogen flow rate are presented as percentages with respect to the hydrogen recycle flow rate. Hydrogen consumption is also indicated in each catalytic bed (in parentheses) as a percentage with respect to the total hydrogen consumption.

3.4. Process heat integration

The number and location of required quenches in each of the two reactors were determined with the previous results. Now, process heat integration can be performed. A simplified process scheme of the two-stage hydrotreatment process is shown in Fig. 4. PHI is divided into two parts: PHI with heat exchangers and PHI with heat exchangers and hydrogen quenches. For each option, two cases were identified:

(a) PHI with heat exchangers: cases A and B.
(b) PHI with heat exchangers and hydrogen quench: cases C and D.

The description of each case is as follows:

- *Case A*: Two heat exchangers to preheat the hydrogen and three heat exchangers to preheat the feed, the desalted crude, and the heavy fraction of the crude.
- *Case B*: Identical to case A except that the bottoms stream of the stripping column is employed to preheat the feed.
- *Case C*: One hydrogen quench in the first reactor; one hydrogen quench in the second reactor; and three heat exchangers to preheat the feed, the desalted crude, and the heavy fraction of the crude.
- *Case D*: Identical to case C except that the bottoms stream of the stripping column is employed to preheat the feed.

The methodology for performing hydrotreatment process heat integration is based on the widely used Pinch analysis, which was taken from the literature [5,21]. With this approach, the following issues can be determined:

- energetic flow diagram,
- hot and cold process streams,
- composite curve,
- grand composite curve,
- utilities,

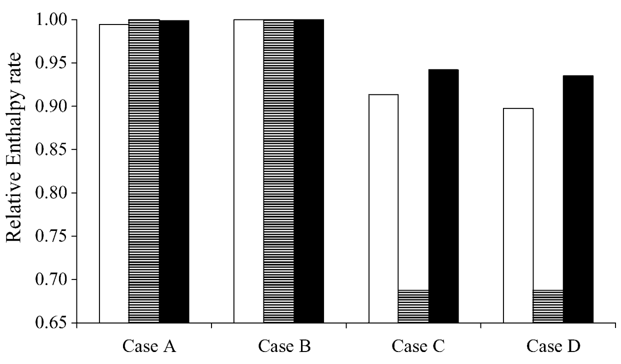

Fig. 5. Total cold (□) and hot (▤) utility requirements and heat recovery (■).

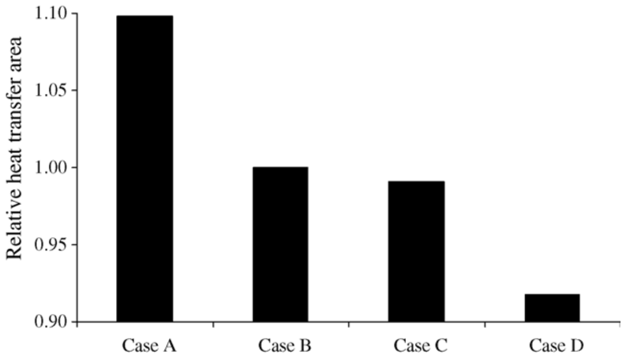

Fig. 6. Total heat transfer area.

- grid diagram for heat exchanger network, and
- heat transfer area.

Fig. 5 shows a comparison of heating and cooling utility requirements and recovered heat for the four cases. The results are presented as relative values with respect to case B, which presented the highest requirements. Cases C and D, which combine hydrogen quench and heat exchangers, have lesser utility requirements compared with cases with only PHI (Cases A and B). Total heat transfer (Fig. 6) exhibited the same behavior. Among all cases, case D showed the lowest utility requirements and heat transfer area, since this case takes advantage of the maximum available temperature among process streams.

4. Conclusions

Process heat integration is an important aspect to be considered when designing hydrotreatment plants for heavy oils upgrading. Quenching with hydrogen is a good, common option, but it is not the optimum approach from an energetic point of view. A combination of hydrogen quench and heat exchangers was the best alternative for heat integration in a heavy crude oil hydrotreatment plant, reducing utility requirements and total heat transfer area.

References

[1] E. Furimsky, Appl. Catal. A 171 (1998) 177–206.
[2] J. Ancheyta, G. Betancourt, G. Marroquín, G. Centeno, L.C. Castañeda, F. Alonso, J.A. Muñoz, M.T. Gómez, P. Rayo, Appl. Catal. A 233 (2002) 159–170.
[3] J. Ancheyta, G. Betancourt, G. Marroquín, A. Pérez, S.K. Maity, M.T. Cortes, R. del Río, Energy Fuels 15 (2001) 120–127.
[4] J. Ancheyta, G. Betancourt, G. Marroquín, G. Centeno, F. Alonso, J.A. Muñoz, Process for the catalytic hydrotreatment of heavy hydrocarbons of petroleum, U.S. Patent pending.
[5] L. Biegler, I. Grossmann, A. Westerberg, Systematic Methods of Chemical Process Design, Prentice Hall, New Jersey, 1997.
[6] G. Marroquín, J. Ancheyta, J.A.I. Díaz, Catal. Today 98 (2004) 75–81.
[7] J. Ancheyta, G. Betancourt, G. Centeno, G. Marroquín, F. Alonso, E. Garciafigueroa, Energy Fuels 16 (2002) 1438–1443.
[8] J. Ancheyta, G. Betancourt, G. Centeno, G. Marroquín, Energy Fuels 17 (2003) 462–467.
[9] S.K. Maity, J. Ancheyta, L. Soberanis, F. Alonso, M.E. Llanos, Appl. Catal. A 244 (2003) 141–153.
[10] S.K. Maity, J. Ancheyta, L. Soberanis, F. Alonso, Appl. Catal. A 250 (2003) 231–238.
[11] S.K. Maity, J. Ancheyta, L. Soberanis, F. Alonso, Appl. Catal. A 253 (2003) 125–134.
[12] S.K. Maity, J. Ancheyta, F. Alonso, M.S. Rana, Catal. Today 98 (2004) 193–199.
[13] J. Ancheyta, G. Centeno, F. Trejo, G. Marroquín, Energy Fuels 17 (2003) 1233–1238.
[14] J. Ancheyta, G. Centeno, F. Trejo, Pet. Sci. Technol. 22 (2004) 219–225.
[15] F. Trejo, G. Centeno, J. Ancheyta, G. Marroquín, Fuel 83 (2004) 2169–2175.
[16] M.A. Rodríguez, J. Ancheyta, Kinetics and reactor modeling of the hydrodesulfurization of heavy crude oils, in: CAMURE-5 and ISMR-4 Symposium, Portorose, Slovenia, June 2005.
[17] S. Sánchez, M.A. Rodríguez, J. Ancheyta, Kinetic model for moderate hydrocracking of heavy oils, Ind. Eng. Chem. Res., in press.
[18] F. Trejo, J. Ancheyta, Kinetics of asphaltenes conversion during hydrotreating of Maya crude, Cat. Today 109 (2005) 99–103.
[19] M.A. Rodríguez, J. Ancheyta, Energy Fuels 18 (2004) 789–794.
[20] F.S. Mederos, M.A. Rodríguez, E. Arce, J. Ancheyta, Dynamic modeling and simulation of HDS, HDN and HDA reactions in hydrotreating process, Energy Fuels, submitted for publication.
[21] Linnhoff March, Introduction to pinch technology, 1998 (http://www.linnhoffmarch.com).