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Techno-Economic Evaluation of Quality Improvement of Heavy Gas Oil with Different Processes

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This paper summarizes the results of an engineering study to evaluate the techno-economic feasibility of different types of hydrotreating processes for producing high quality gas oil blending components from heavy gas oil fraction. Hydrotreatment of feed in one-stage on NiMo/alumina and in two-stage on NiMo/alumina followed by on PtPd/zeolite catalysts were investigated. In one stage hydroprocessing sulphur and polyaromatic contents of the products met the requirements of the standard only if strict process parameters were applied which resulted in operation problems and product loss, moreover the advantageous process parameters of hydrodesulphurization and hydrodearomatization did not coincide. In two-stage hydrotreating results showed that the advantageous process parameters for reduction of sulphur and aromatics coincided. Advantageous process parameters to produce gas oil of quality meeting the requirement of the standard were determined. Based on the experimental results model for both alternatives was prepared, and heat and material balances were determined. Heat exchanger network analysis and sizing of main equipments were accomplished. Operating and investment costs were estimated for both processes, which showed that all the cost elements were higher for the two-stage process. But it provides the following advantages in comparison to one-stage process: higher yield of gas oil, better product quality allowing the application of low value hydrocarbon streams in higher quantity at the blending, the lower density of products would be the source of extra profit due to diesel fuels are sold on volume basis at the petrol stations.

1. Introduction

The quantity requirements for good quality diesel fuels having low sulphur and aromatic content increased all over the World in recent years (Stanislaus et al., 2010). The most significant change was become in the maximum allowable sulphur content of diesel fuels (Varga et al., 2003) and more recently (Varga et al., 2014). At the same time, the quality of the available crude oil stocks continuously declined giving tough challenges for refineries to produce high quality diesel fuels in increasing quantity, which can be overcome by change in the refinery configuration (Arora and Mukherjee, 2011) as well as improving the efficiency of the hydrotreating processes (Peng et al., 2012). The economic and political events occurred recently highlight the attention of the refining industry to diversify the crude oil sources and to increase the flexibility of the whole petroleum processing train (Varga and Danics, 2013). Several papers were published to model the reactor of hydrotreating process. De la Paz-Zavala and co-workers (De la Paz-Zavala et al., 2013) prepared a HDS reactor model using data to be obtained in pilot scale experiments, then it was extended to industrial scale. de Oliveira and co-workers (de Oliveira et al., 2012) worked out a hydrotreating reactor model applying the detailed feed composition and modelling the processes being taken place in a hydrotreating reactor using the kinetic Monte Carlo (kMC) method. However, few papers were published concerning the model of the whole technology as well as providing different process alternatives.

The aim of the present work was to prepare a techno-economic analysis for quality improvement of heavy gas oil to be done in one and two steps ways.

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2. Experimental and Methodology

First step of the study was to determine the advantageous process parameters (temperature, pressure and Liquid Hourly Space Velocity in the following LHSV) for producing gas oil blending components of sulphur content lower than 10 mg/kg for both cases. Heavy gas oil was selected as feed for the experiments to model the gas oil fractions to be obtained from heavy crude oils. Its important properties are summarized in Table 1. Properties of feed and products were determined by standard measurements.

Commercial type $NiMo/Al_2O_3$ catalyst promoted with phosphorus (Ni/(Ni+Mo) atomic ratio 0.274, surface area 182 m^2/g and pore volume 0.55 cm^3/g) was used in the one step process as well as in the first step of two steps process. The catalyst was pre-treated as recommended by the supplier. In the second step of two steps process, a PtPd/USY-zeolite catalyst was applied containing 0.6% Pd and 0.3% Pt (SiO_2/Al_2O_3 ratio 33.5, total and mesopore surface areas 592.5 m^2/g and 51 m^2/g, metal dispersion 0.48), which is applicable for feed containing sulphur until 200 mg/kg.

Hydrotreating of the selected gas oil was investigated in wide process parameter range considering the industrial practice. In case of one stage hydroprocessing they were as follows: temperature 300-380°C, total pressure 50-80 bar, LHSV 1.0-3.0 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3. In the first step of two stages hydrotreatment they were as follows: temperature 360°C, total pressure 60 bar, LHSV 1.5 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3. In the second step they were as follows: temperature 280-340°C, total pressure 60 bar, LHSV 1.5 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3.

After carrying out the experiments model of hydrotreating units were prepared based on the advantageous operation parameters to be determined using a commercial type process engineering software (ProII from Invensys). The model contained all of equipments are applied in a hydrotreating plant e.g. distillation and absorption columns, heat exchangers, pumps etc. Reactor was not included in the model instead of the mass balance obtained at the catalytic experiments was applied for both cases.

After obtaining the heat and mass balance of the process heat exchanger network analysis was accomplished to minimize the energy consumption and to maximize the energy efficiency. This was done by applying the so-called Pinch technique, which worked out by Linnhoff and co-workers, and published elsewhere (Kemp, 2007) and more recently (Klemeš et al., 2014)

In order to preparing a capital cost estimation for the investigated processes the main parameters of equipments were determined, for example height and diameter of towers, area of heat exchangers, power requirement of pumps, heat duty of fired heaters etc. Operating cost was calculated for every process, too.

3. Results and Discussion

3.1 Catalytic experiments

In order to determine the advantageous process parameters, yield and composition of products as well as properties of process streams catalytic experiments were done in wide parameter range.

Table 1: Important properties of heavy gas oil feed and the “Feed for 2nd step”

Parameter	Heavy gas oil	“Feed for 2nd step”
Density, @15°C, kg/m^3	860	847
Sulphur content, mg/kg	9910	187
Nitrogen content, mg/kg	286	24
Aromatic content		
mono	21.4	18.7
di	10.4	8.0
poly	4.1	-
total	35.4	26.7
Distillation, ASTM D86, °C		
Initial boiling point	190	180
10 vol.%	285	247
30 vol.%	310	282
50 vol.%	325	305
70 vol.%	335	324
90 vol.%	355	356
Final boiling point	375	372

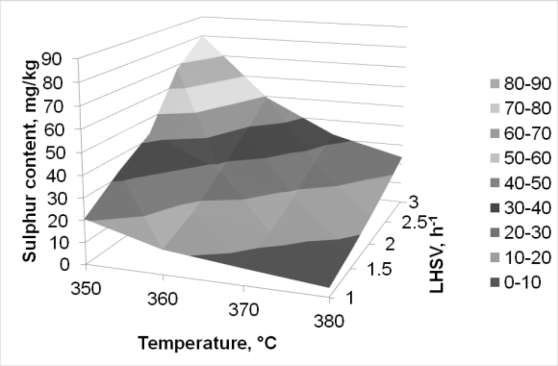

Figure 1: Change of the sulphur content of products in function of temperature and LHSV in case of one stage process (total pressure: 80 bar)

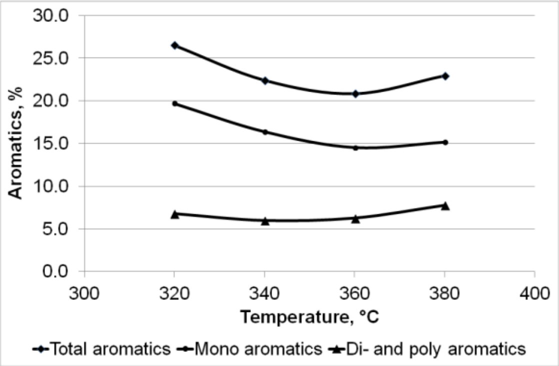

Figure 2: Change of the aromatic content of products in function of temperature in case of one stage process (total pressure: 80 bar, LHSV: 1.0 h^{-1})

Figure 1 shows the change of sulphur content of products in function of temperature and LHSV at pressure of 80 bar in case of one step process. Results show that products of sulphur content lower than 10 mg/kg can only be produced at high temperature (>370°C) and low LHSV (<1.5 h^{-1}) on the investigated NiMo/Al_2O_3 catalyst even relatively high pressure was applied.

Figure 2 displays the change of the aromatic content of products in function of temperature at pressure of 80 bar and LHSV of 1.0 h^{-1}. Results show that the total, mono, di- and poly aromatic contents were reduced in considerable extent at the applied process parameters.

However, it can also be shown that the change of aromatic content followed a minimum point curve, and products of lower total aromatic content were obtained at temperature of 360 °C.

In comparing the advantageous process parameters for the hydrodesulphurization and hydrodearomatization it can be stated that these values are not coincide on the investigated catalyst and in the applied process arrangement.

The strict operating conditions to be required to produce product of low sulphur content (<10 mg/kg) decrease the yield of valuable liquid products by increasing the rate of hydrocracking reactions, and shorten the lifetime of the catalyst. Additionally, the low LHSV reduces the productivity and the required high temperature increases the energy consumption, too.

In order to eliminate the disadvantages of the “one step process” the quality improvement of the heavy gas oil was performed in two consecutive steps, too. Firstly, partially hydrogenated gas oil fraction having sulphur content lower than 200 mg/kg was produced at lower pressure and at temperature to be advantageous for the aromatic reduction. The selected process parameters were the following temperature 360 °C, total pressure 60 bar, LHSV 1.5 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3.

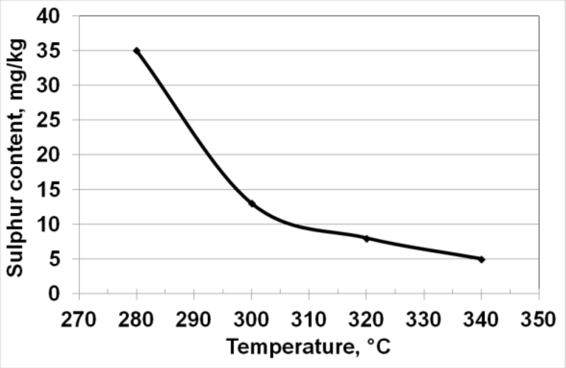

Figure 3: Change of the sulphur content of products in function of temperature at the second step of two stage process (total pressure: 60 bar, LHSV: 1.5 h^{-1})

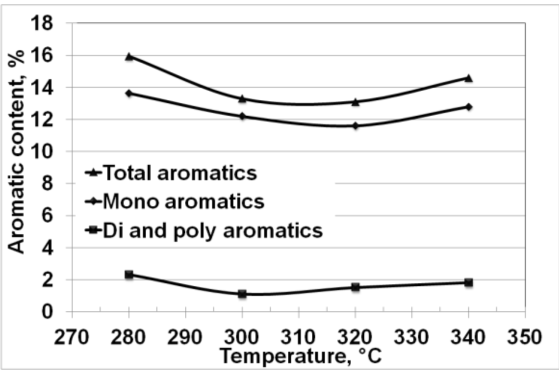

Figure 4: Change of the aromatic content of products in function of temperature at the second step of two stage process (total pressure: 60 bar, LHSV: 1.5 h^{-1})

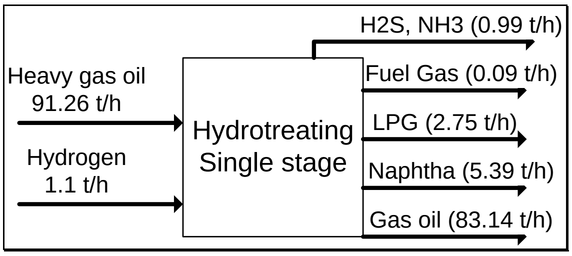

Figure 5: Simplified mass balance of one stage process

Most important properties of the obtained product are summarized in Table 1 named as "Feed for 2nd step". Then the product of first step was hydrogenated further on PtPd/USY catalyst to reduce its sulphur content below 10 mg/kg as well as its aromatic content below 14 %.

Figures 3 and 4 show the change of the sulphur and aromatic contents in function of temperature at pressure of 60 bar and LHSV of 1.5 h^{-1}, respectively. Based on the results it can be assessed that temperature of 320 °C is adequate to produce gas oil fraction of required qualities.

Based on the catalytic experiments the following process parameters were selected to prepare the model of the hydrotreating units:

- single stage unit – temperature: 380 °C, pressure: 80 bar, LHSV: 1.0 h^{-1}, H_2 to feed volume ratio 400 Nm^3/m^3
- two stage unit
  - first step – temperature: 360 °C, pressure: 60 bar, LHSV: 1.5 h^{-1}, H_2 to feed volume ratio 400 Nm^3/m^3
  - second step – temperature: 320 °C, pressure: 60 bar, LHSV: 1.5 h^{-1}, H_2 to feed volume ratio 400 Nm^3/m^3

3.2 Modelling of hydrotreating units

Based on the results of the catalytic experiments model for both types of hydrotreating unit were prepared for capacity of 800 kt/y heavy gas oil. Figures 5 and 6 show the simplified mass balance of both units. Comparing the data it can be seen that the two-stage process resulted more gas oil product, and less LPG and naphtha products with respect to the same feed quantity. It clearly shows that the milder operating parameters being applied at the two-stage process decreases the rate of hydrocracking reactions. It is advantageous from the aspect of the economy of the process because the diesel fuel is sold with higher margin than the motor gasoline is in the European fuel market.

Figures also show that hydrogen consumption of two-stage process was higher than that of one-stage process was. The reason of this was that the saturation of aromatic compounds took place in higher extent at the two-stage process resulting better product quality. However, the higher hydrogen consumption increases the operating costs, too.

After preparing the model for both alternatives containing all of equipments to be applied in an industrial hydrotreating plant (e.g. heat exchangers for feed preheating and product cooling, fired heaters, flash drums, distillation columns, pumps, make-up and recalculating hydrogen compressors, amine washing unit etc.) the heat exchanger network integration was prepared to maximize heat recovery for each units.

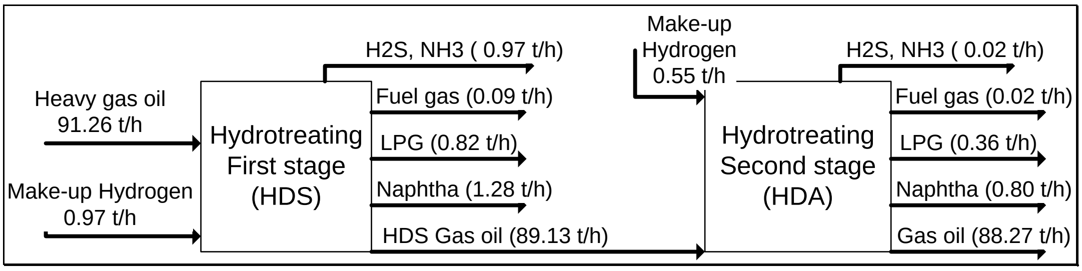

Figure 6: Simplified mass balance of two stage process

Table 2: Utility consumption and cost for the investigated alternatives

Utility	One stage process		Two stage process	
	Consumption	Cost, thousand $	Consumption	Cost, thousand $
Natural gas, thousand Nm^3/y	1,556	20,630	2,135	28,260
Steam, thousand t/y	46.7	2,140	44.6	2,040
Cooling water, thousand t/y	64,030	6,559	60,030	6,150
Electricity, MWh/y	14,790	1,515	21,445	2,197

Taking 20 °C minimal temperature approach the pinch temperature was 160 °C for one-stage while 110 °C for two-stage process.

Table 2 shows the utility consumption and cost considering the following data: natural gas: 13.26 $/GJ, steam 45.78 $/t, cooling water 0.102 $/t and electricity 102.45 $/MWh. It shows to operate the two-stage process 37% higher consumption in natural gas was required than in case of one stage process mainly due to the fact that the intermediate gas oil product should be cool down and reheat between the stages.

It can also be assessed that among the cost items to fire the furnaces was the highest for both cases showing the importance of the energy efficiency improvement.

The electricity consumption was also higher for the two stage process, which was not surprise since the hydrogen consumption was higher for this alternative meaning higher make-up gas volume, too. Additionally, the circulating hydrogen flow rate was also considerable higher for this case because the adequate hydrogen-to-hydrocarbon ratio had to be ensured both for the HDS and HDA reactors.

On the contrary the cooling water consumption was somewhat lower for the two stage process because less amount of naphtha was produced, which had to be cool down to lower temperature than the gas oil from safety reasons.

After preparing the modified heat exchanger network the parameters of main process equipments were determined in order to capital cost estimation can be done. The cost estimation was accomplished by applying the equations that are published in the open literature. The estimated purchase price of the equipments was corrected by the installation factor and updated to the year of 2013 using the CE Index published in the Chemical Engineering journal in monthly base.

The estimated total investment cost was $19.43\ 10^6$ $ for one step process and $25.67 \cdot 10^6$ $ for two stage process, respectively.

Distribution of the cost elements are displayed on Figure 7 and 8 for both investigated alternatives. Data show that the cost of heat exchangers (31.2 % and 33.6 %) and compressors (28.6 % and 27.6 %) exposes more than a half of the estimated investment expenses. Figures also demonstrate that there was not significant difference between the two alternative process routes in respect to the distribution of costs.

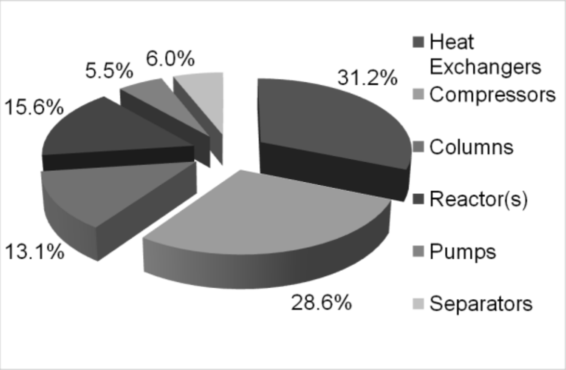

Figure 7: Distribution of the cost elements for one stage process

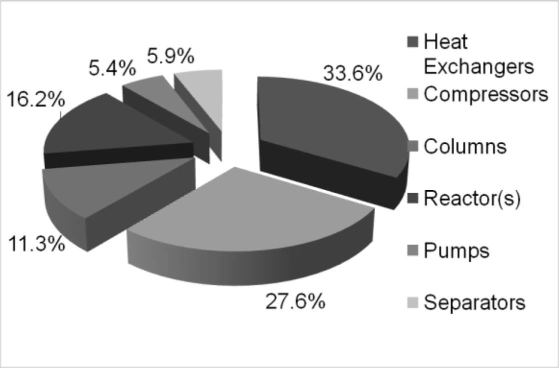

Figure 8: Distribution of the cost elements for two stage process

Despite the higher cost of the two-stage process it shows the following advantages.

- Higher yield of gas oil is in comparison to one-stage process.
- Better product quality which is made it possible to apply low value hydrocarbon streams in higher quantity at the blending.

- Two-stage process results gas oil products of lower density, and as the diesel fuels are sold on volume basis at the petrol stations it increases the profit, too.

4. Conclusions

Present paper summarizes the results of a complex study to be done to investigate the techno-economic feasibility of different hydrotreating processes to improve the quality of a heavy gas oil fraction. The selected technologies were one-stage and two-stage hydrotreating processes. In the first step the advantageous process conditions for producing gas oils of quality meeting the standard requirements were determined for both alternatives. Experimental results showed that the advantageous parameters for the hydrodesulphurization and aromatic content reduction did not coincide in case of one-stage process. Additionally, the strict process parameters required to obtain high quality product resulted yield loss, too.

Two-stage process provides high quality product in higher yield at milder process conditions but on the expense of higher hydrogen consumption. Based on the experimental results model of both hydrotreating technologies was prepared. Heat exchanger network analysis and detailed design of the main equipment were accomplished. Operating and investment costs were also estimated. Results showed that the two-stage process requires higher investment and operating costs, but the better product quality can offset it.

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