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Deep desulfurization of petroleum streams: Novel technologies and approaches to construction of new plants and upgrading existing facilities

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ABSTRACT

Some main features of new generations of the POLF (presaturated-one-liquid-flow) technology developed originally in Russia (1995) with respect to hydrotreating are considered. It is shown a possibility of the construction and upgrading of hydrodesulfurization facilities with the purposes of decreasing the investment and operating costs, improving the process performance and safety.

1. Introduction

In refinery, catalytic hydrodesulfurization (HDS) is the most widely applied process technology, the role of which is continuously increased due to new, strengthening legislative norms imposed on transportation and other fuels, a demand on the higher yield of refinery products and a growing share in low-quality crude used for processing.

Despite the fact that a great number of new chemical and adsorptive procedures for the sulfur reduction have been developed last time, they are not and, apparently, will not be able to compete with the traditional desulfurization method—hydrotreating, which do and will dominate in industry.

This communication shortly presents some new approaches to deep HDS, which can be considered a powerful alternative to the conventional HDS technique with the gas recirculation. Our new methods are characterized not only by lower investment and operation costs, but also a possibility of upgrading the existing HDS units in order to cut the production costs and improve the process performance.

2. Conventional HDS

Although HDS units differ from each other with respect to a refinery stream to be treated or to particular technical embodiments, most of them have the similar process flow. Fig. 1 represents a typical technological scheme of HDS process.

The oil to be hydrodesulfurized is fed into the system by pump 8 and mixed with the hydrogen-rich gas recycled by compressor 5. The two-phase gas–liquid mixture goes through recuperative heat exchanger 3, where it is partly heated by the gas–liquid flow leaving reactor 1. (In the real HDS processes, more recuperators are installed in the loop. This recuperating network serves for the heat utilization not only in the HDS system itself as shown in Fig. 1, but also in the following stripping process.)

After recuperator 3, the gas–liquid flux is additionally heated in fired heater 2 up to 320–400 °C and then led to reactor 1, where it is uniformly dispensed by a liquid–gas distributor over a fixed-bed catalyst.

The fresh make-up gas containing hydrogen for the reaction is supplied by make-up compressor 7 keeping the constant pressure in the reactor.

In the reactor, the reaction between organosulfur species and hydrogen takes place on the catalyst surface, in the course of which hydrogen sulfide is formed. Over the HDS catalyst, other reactions can also occur in the presence of hydrogen as, for exam-

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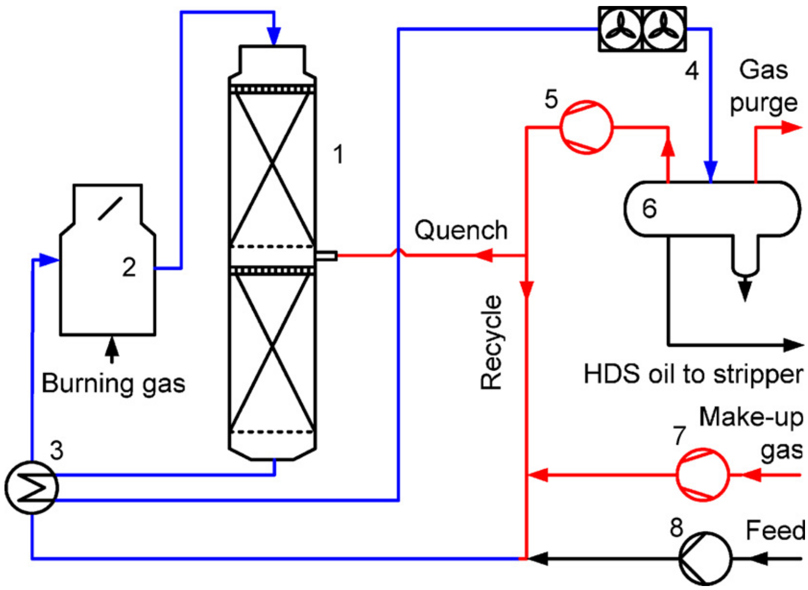

Fig. 1. Conventional catalytic hydrodesulfurizer. (1) Reactor; (2) fired heater; (3) recuperative heat exchangers; (4) cooler; (5) recycle compressor; (6) phase separator; (7) make-up compressor; (8) feed pump; indication for streams: red—gas; black—liquid; blue—two-phase flow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ple, hydrogenation of unsaturated compounds, hydrodenitration, hydrocracking, etc.

After the reactor, the gas–liquid mixture, which is heated by 20–40 °C in the course of the reaction, is consequently cooled in recuperator 3 and finally in cooler 4 down to 50 °C. The cooled two-phase flow enters the gas–liquid separator 6, from which hydrodesulfurized oil is directed to a stripper for removing any remaining hydrogen sulfide and light ends. The main part of the separated gas is returned into the reactor by recycle compressor 5 while another part is taken away for the withdrawal of generated hydrogen sulfide.

Because of the exothermic nature of the HDS reactions (approximately 63 $\mathrm{kJ/mol_{H2}}$ or 77 $\mathrm{MJ/m^3_{oil}}$), an enormous quantity of the hydrogen-content gas should be recycled through the catalyst bed in order to provide the demanded temperature level in the reactor. For the better temperature control, the catalyst bed is often divided in two (or more) sections, between which the cooled gas can be injected.

It should be underlined that the maximum pressure drop in the system cannot exceed 20–25 bar as this value corresponds to the uttermost pressure increment that can be overcome by the gas recycle compressors used in industry.

From a thermodynamic point of view (see analysis given in [1,2]), one of the main drawbacks of the conventional HDS technologies is the bad process arrangement, which accounts for high operation costs and complicated embodiments.

Really, since the recycle compressors can only operate under mild temperatures that are significantly less than those in the reactor, the recuperative heat exchangers should be used on the gas loop. It implies the necessity of the long-distance pipework (sometimes about 200 m) for transportation of the two-phase mixture to the reactor and from it. It is not surprising that about 95–97% of the pressure increment produced by the gas recycle compressor falls on the pipework while the reactor accounts for only 3–5% of the pressure drop.

The same distribution is true for the energy spent for carrying out the HDS process. Thermodynamically it means that from 100% of the energy delivered by the gas recycle compressor in the system, only 3–5% of the energy is spent for the process purposes, namely, for ensuring the acceptable gas–liquid–solid mass transfer in the catalyst bed and heat removal. The rest 95–97% of the energy input is consumed by the pipework and numerous recuperators and can be regarded as a non-productive loss.

Taking into account a great number of HDS units in a typical refinery, it is not surprising that 20% of the whole energy consumption in oil processing is spent in hydrotreating [3].

Apart from the very low energy efficiency, other disadvantages of the conventional HDS reactors should also be pointed out.

The HDS units are distinguished by complex equipment and control systems and characterized by a significant demand on energy and hydrogen consumption (see Table 2), which, therefore, results in the high operating costs.

The catalyst bed can suffer from the uneven wetting, which leads to catalyst fouling and the appearance of “hot spots”.

The HDS facilities are strongly sensitive to any attempt to increase the reactor productivity since it requires the higher rate of the gas recirculation for the heat removal, which cannot be achieved by gas recycle compressors. This limitation lying in the pressure drop causes every time the same problem if a new oil with a higher demand on hydrogen and, hence, greater heat evolution should be treated.

Finally, despite the novel advanced catalysts, the potential of operating HDS reactors for the further elimination of sulfur is almost exhausted so that new reactor installations are needed to meet the challenge towards ultra-clean fuels [4].

3. POLF technology and approaches to construction and revamping operating reactors

The description and scientific approaches to the first generation of the POLF (presaturated-one-liquid-flow) technology destined for HDS and other exothermic processes can be found elsewhere (e.g. in [1,2,5–8,10]).

Contrary to the conventional HDS technologies where two-phase gas–liquid flow with low energy efficiency enables the heat removal as well as gas–liquid and liquid–solid mass transfer, the POLF processes utilize the energy of the single liquid flow. The main technological “trick” of this process is carrying out gas–liquid mass transfer not in the catalyst bed, but outside the reactor in a special

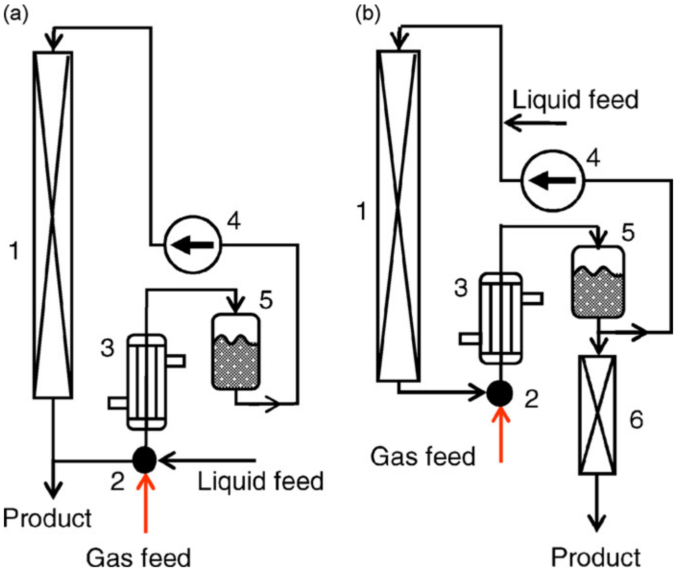

Fig. 2. One-stage (a) and two-stage (b) POLF processes of the first generation. (1) Reactor; (2) MPCP device; (3) heat exchanger; (4) recycle pump; (5) phase separator; (6) second reactor; indication for streams: red—gas; black—liquid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

appliance of extreme intensity called MPCP device. That allows one to pump through the reactor only the liquid phase (with dissolved gas), which eminently enhances liquid–solid mass transfer and, as a result, increases the concentration of hydrogen on the catalyst surface.

The simplified flow diagrams of the first generation of POLF reactors are shown in Fig. 2.

One part of the treated stream after the reactor enters MPCP's device 2 where it is combined with the gas feed. In the MPCP device, the liquid gets saturated. The liquid flow with the gas in the dissolved form is taken by recycle pump 4 and then led to the reactor.

Proceeding from the specific feature of the chemical reaction, the liquid feed can be brought into the system either just before the MPCP device or after it. It is also possible to direct the feed straight to the device as shown in Fig. 2a.

The liquid phase at the inlet of reactor 1 represents the mixture of the product, dissolved gaseous compound and initial liquid reactant. The latter is converted into the product by contacting the catalyst. After the reactor, one part of the product with the flow rate equal to that of the feed is taken away by means of a level regulator installed in small vessel 5 and another part is recycled through MPCP's device 2.

The pressure in the system is kept constant by a pressure regulator on the gas feed line, which automatically supplies the reactor with the fresh gas as it is consumed in the course of the reaction.

Since only the single liquid phase is pumped through the catalyst bed, heat exchanger 3 and pipework, the pressure drop that pump 4 should overcome is insignificant as well as the energy spent for liquid pumping. As a result, the flow velocity through the catalyst can be increased and/or small catalyst particles can be used. It incredibly enhances liquid–solid mass transfer or, in other words, it facilitates by far the higher reactor productivity.

Although the POLF reactors demonstrate much greater productivity, the temperature raise does not go beyond 10–30 °C since the solubility of nearly all the industrially important gases, including hydrogen, is low. Also, the POLF process has no problem with the heat removal, which is carried out in external heat exchanger 3.

The recycle rate is determined by the gas solubility and can be calculated as given, for instance, in [1,2].

The first generation of the POLF technology has several modifications suitable for all possible industrial applications. The direction of the liquid flow the reactor can be arranged both upwards and downwards and has, to some extent, no effect on the process efficiency. In many cases, it is preferable to use the two-stage POLF process (Fig. 2b), which can be combined in one reactor with two catalyst beds and where second reactor 6 (or second separate catalyst bed) is destined for further deep conversion.

The second generation of the POLF process as pertaining to HDS is shown in Fig. 3. In comparison to the POLF processes shown in Fig. 2, this modified POLF technology is still more universal and flexible and has higher productivity and better selectivity.

The oil to be treated is supplied to the system by feed pump 7 through recuperative heat exchanger(s) 3 and fired heater 2. Being preheating, the oil enters modified MPCPs device 5, where it is combined with the make-up gas. The MPCP device is a small-size multifunction apparatus. It provides the intensive dissolution of gas in liquid, the purging of gas from the reactor if it is needed for the process, and the recirculation of liquid through the chosen catalyst bed (as shown in Fig. 3) or through the whole reactor.

From the MPCP device, the oil with saturated hydrogen is led to reactor 1. After passing the first catalyst bed, the liquid stream is divided into two parts. One part is withdrawn by MPCP device 5 from the catalyst bed and recycled through recuperative cooler 4, where the reaction heat is removed. Another part equal to the liquid feed is forwarded through the second catalyst bed for deep hydrodesulfurization. After the second catalyst bed, the hydrodesulfurized oil gives up the reaction heat to the entering feed and is then automatically delivered to a stripper by means of a controller installed in the MPCP device.

The modified POLF process possesses the flexible arrangements for any practical applications. Proceeding from the technological tasks, the catalyst bed participating in the liquid loop can be situated in the top part of the reactor (as shown in Fig. 3) or in the bottom. In both catalyst sections, the direction of the liquid motion can be set either up- or downwards.

The main advantages of the POLF technology are presented in Table 1. It is necessary to point out additionally that the POLF technology ensures the catalyst activation without gas recycling.

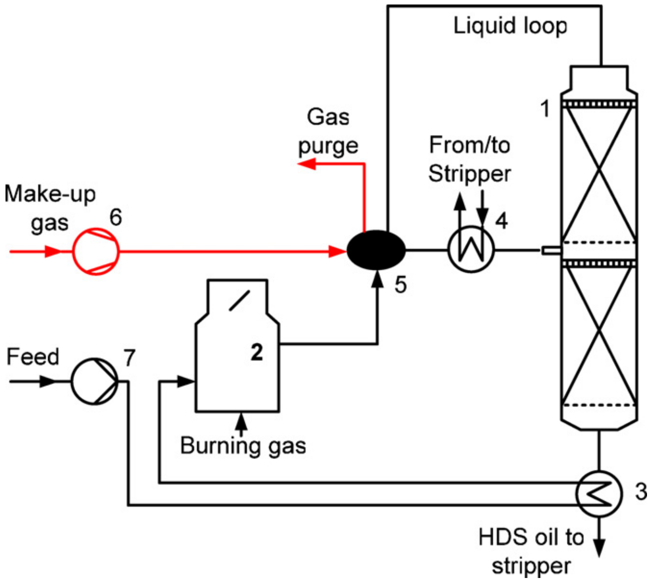

Fig. 3. POLF process of the second generation. (1) Reactor; (2) fired heater; (3) recuperative heat exchanger; (4) cooler; (5) MPCP device; (6) make-up compressor; (7) feed pump; indication for streams: red—gas; black—liquid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
Conventional technologies vs. MPCP processes.

Features	Conventional reactors	POLF reactors
Productivity enhancement	Impossible	Possible
Gas recirculation	Yes	No
Pressure drop	Problematic	Not problematic
Safety	Problematic	Absolute safe
Reactor, equipment and control systems	Complicated	Uncomplicated
Use of small catalyst particles	Impossible	Possible
Investment and operation costs	High	Lower
Possibility of revamping the operating units	No	Yes

The introduction of the POLF process permits to solve a lot of problems encountered in industry.

In the case of HDS, for example, a lower grade of the fouling in the fired heater can be expected since the liquid permanently washes the heated surface. (In the conventional embodiments (see Fig. 1), the liquid and gas phases contacts the hot surface of the heater tube alternating. While the gas phase bubble touches the tube wall, the local heat transfer becomes difficult because only the thin film of oil remains on the surface. This film subjected to the considerable overheating forms the indelible deposition, which lessens the tube diameter and, hence, increases the pressure drop. In turn, it worsens the heat transfer and promotes the further deposition.)

As there is no gas recirculation in the POLF HDS processes, the fired heater demands less energy. Furthermore, the rate of the purging gas can be decreased significantly or even eliminated at all.

The most important advantage of the POLF system is the simplification of the heat recuperation since there is no problem to pump the hot oil at 320–450 °C.

Since the difference between maximum and minimum temperature in the liquid loop is just about 20–40 °C, there is no need in the numerous recuperative heat exchangers, with which the conventional HDS plant is furnished. It reduces not only the investment costs of the HDS reactor, but also simplifies the following stripper system.

Actually, contrary to the POLF technologies, in the conventional HDS system with gas recycling, such a temperature difference in the gas loop is about 300 °C. In order to arrange the management of all heat fluxes, a common network of recuperators combines a conventional HDS reactor and a following stripper unit, which increases not only investment costs, but also energy expenses for transpiration of a gas–liquid mixture through extremely long pipework connecting these two units.

On the basis of the POLF technology, the existing HDS facilities can be upgraded so that nearly all old apparatuses, equipment and control systems can be adopted by the new process. Moreover, to exclude any risk, the old scheme can be retained undistorted in order that it can always take up the process if necessary.

The retrenchments, which could be achieved after revamping the HDS operating unit of 100 tons of middle distillate per hour, is shown in Table 2.

Table 2
Savings brought by upgrading the conventional HDS units according to the POLF technology.

Parameter	Conventional HDS	The same reactor after upgrading
Energy for fired heater, MJ/m^3_{oil}	260	220 (15% less)
Electric energy, MJ/m^3_{oil}	17	5 (70% less)
Demand on make-up gas (H_2-content ~20% mass or ~80% Vol.), kg/m^3_{oil}	21.3	17.5 (18% less)

Fig. 4. POLF-HDS pilot-plant unit. The reactor position is at an angle of 45°.

4. Pilot-plant test of HDS process

Fig. 4 represents the POLF-HDS pilot-plant unit manufactured by MPCP GmbH in the cooperation with the Institute for Energy Research – Fuel Cells (IEF-3) of the Forschungszentrum Jülich GmbH.

The reactor contains 3 dm^3 of a commercial HDS catalyst and can operate under maximum pressure and temperature up to 70 bar and 400 °C, respectively.

The shown unit is designed for much harder examinations than it can be demanded for the refinery industry because the pilot plant is intended for simulation of on-board applications. For these purposes, the reactor has to function at different angles between horizontal and vertical with the hydrogen-lean make-up gas containing plenty of carbon dioxide and monoxide and without any gas purging.

The conditions of the day-and-night pilot-plat test carried out during 240 h are given in Table 3.

Over the whole period of the trial, no change in the catalyst activity was detected. The concentration of sulfur in hydrodesulfurized

Table 3
Pilot-plant test conditions.

Liquid feed—Jet A1	
Sulfur content, ppm	717
Gas feed—mixture of gases in vol.%	
H_2	39.5
N_2	39.6
CO_2	20.2
CO	0.5
CH_4	0.2
Reaction conditions	
Temperature, °C	390
Total pressure, bar	50
Flow rate of liquid feed, dm^3_{oil}/h	2
LHSV, h^{-1}	0.7
Gas purging	Absence

Table 4
Typical statements and questions posed by industrial and scientific community.

N	Statement or question	Explanation
1	Contrary to trickle-bed and bubble column reactors with gas (e.g. hydrogen) recycling, the catalyst in the POLF reactor falls under the deficit of the gaseous compound, which causes: (i) lower productivity; (ii) worse selectivity and faster catalyst deactivation.	Despite the fact that in the conventional reactors, a reacting gas (e.g. hydrogen) presents in the gaseous form everywhere around catalyst particles, the catalyst in these reactors runs under the extremely low gas concentration in the first part of the catalyst bed and comparatively high concentration at the reactor outlet [1,2]. In the POLF processes (Fig. 2), the gas concentration gradually becomes less passing the reactor. In the modified POLF reactors (Fig. 3), the gas concentration can remain equal to the maximal possible value (equilibrium concentration) throughout the catalyst bed. In both POLF technologies, the average gas concentration on the catalyst surface is higher than that in the conventional reactors. That results in (i) much higher productivity (sometimes 100-fold); (ii) better selectivity and longer "catalyst life" not only because of the higher gas concentration, but also because of the fully wetted catalyst (no "hot spots").
2	The POLF technology should malfunction if a gas feed is a mixture of several gases.	The POLF technology does not change the chemical nature of the process, but improves the reaction performance even if the partial pressure of the reacting gas is lower (see Section 3 above).
3	Can the POLF reactor really work without liquid distributors or redistributors?	The POLF reactor does not need liquid (re)distributors. The existing gas–liquid distributors in reactors designated for revamping can be left because they do not disturb the POLF process.
4	Significant reduction or even elimination of purging leads to reaction fading.	Apart from the reaction with the considerable evolution of by-gases, the flow rate of the off-gas nearly in all industrial applications can be reduced to zero.
5	The R&D department of our refinery failed to reproduce the POLF process. Does it mean that the technology is wrong and cannot function?	Although the POLF technologies are comparatively simple, the profound knowledge of physical and chemical particularities is of great importance for technical realizations. The POLF processes are uncomplicated, but demands sophisticated arrangements and "tricks" adjusted to each specific application.

oil made up about 1 ppm when the hydrogen sulfide formed by the reaction was completely removed before the analysis versus 9 ppm in the sample directly taken after the stripper installed in the pilot-plant unit. As was found out, this difference in 8 ppm derived from hydrogen sulfide remaining in the product because it was not completely removed by stripping. The more detailed information concerning the pilot-plant test can be found in [9].

As the laboratory and pilot-plant tests demonstrate, the POF technology can be considered the powerful alternative to conventional HDS reactors with gas recycling.

5. Typical misunderstandings concerning the POLF process

Although the scientific principles of the POLF processes are widely elucidated in academic and patent literature, the questions related to the process performance in the POLF reactors are often posed by industrial engineers and researches. The answers to frequently asked questions are given in Table 4.

6. Conclusion

The POLF technology suggests the best options if a new HDS facility is planed to be built. The POLF unit allows a refinery not only to save expenses for equipment and construction work, but also to cut the future operating costs.

The upgrading of the existing HDS units is also a good opportunity to cut production costs, improve the process safety, and increase the output.

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