Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 48 (3), 68-73, 2006

CONSTRUCTION OF DMD PILOT PLANT AND ITS SCALE UP TO INDUSTRIAL UNITS

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Received October 18, 2006; accepted November 24, 2006

ABSTRACT:
Demercaptanization of oil cuts is regarded as an important refining process and in particular the DMD process. Following the technology transfer of this process to RIPI and construction of 20BPD pilot based on the acquired know-how, pilot tests with LSRG feed from Shiraz refinery and naphtha from Kharg Petrochemical Complex were carried out respectively and successful results were obtained. Following the tests, process scale up was carried out and then basic and detailed designs of 3 industrial units for propane, butane and naphtha feeds were accomplished. At present, these industrial units are under installation. We intend to investigate and analyze the results obtained and describe the effects of important parameters on this process.

Keywords: Demercaptanization, sweetening, DMD process

1. Introduction

With regards to increasing exploitation of crude oil from reservoirs with enhanced sulfur contents and also increasing exploitation from sour reservoirs cause gradual increase of sulfur contents of refinery feeds throughout the country. This phenomena causes an increase in mercaptan content in middle distillate fractions. Hence RIPI as a leading R&D center in petroleum industry in Iran acted upon technology transferring of DMD process from a Russian company called VNIIUS. The technology transfer was achieved in following phases:

1. Laboratory tests at bench scale which were already presented in the previous article published in this journal [1].
2. Basic and detailed designs, construction, installation of a pilot plant with 20 BPD capacity.
3. Commissioning and pilot tests with selected feeds to obtain design data.
4. Pilot scale up and design of industrial units to be implemented in one of the petrochemical complexes in Iran.

In this work, we first describe the DMD process and investigate its advantages compared to similar processes and then we will be assessing the effect of various parameters on this process with regards to pilot results obtained.

2. DMD Process Description

DMD desulfurization process consists of the following stages:

a) Pre-wash Stage: In this stage, light sulfur components like H_2S and a part of COS are eliminated via caustic solution (1-2 wt%)
b) Extraction Stage: In this stage, the outlet hydrocarbon stream from pre-wash stage is sent to the extraction stage and light mercaptan components (C_1-C_3) and COS are eliminated by 10-15 wt% caustic solution. In this stage, as a result of produced water, caustic concentration is gradually reduced and within the specific and calculated periods a part of diluted caustic solution is drained and equally, fresh caustic with high concentration is injected to the system to keep the hold up and concentration constant.
c) Oxidation Stage: this stage is only used for rather heavy hydrocarbon streams such as gasoline that contains heavier mercaptans than C_4 (In the case of LPG, since there are no heavy

mercaptans, this stage is eliminated). In this stage, in the presence of IVKAZ catalyst and oxygen, heavy mercaptans in a packed bed, oxidized and converted to disulfide by the following reaction:

$$2RSH + 0.5O_2 \rightarrow RSSR + H_2O$$

d) Caustic Regeneration Stage: In this stage, the outlet caustic solution from extraction stage which contains sodium mercaptide, in presence of IVKAZ catalyst which is soluble in caustic, is oxidized by the following reaction and fresh caustic is obtained:

$$RSNa + H_2O + 0.5\,O_2 \rightarrow RSSR + 2NaOH$$

Then, the regenerated caustic is returned to the extraction stage.

DMD Process Advantages Compared to Similar Processes

In this regard, similar processes are used in the refining industry in the world which generally have the same PFD [2]. The advantages of DMD process compared to similar ones are outlined as follows:

1) Enhanced capability of eliminating COS and CS_2 by this process versus to other processes.
2) Utilizing IVKAZ activator catalyst compared to similar catalysts. This particular catalyst was replaced for the old catalyst used in shiraz refinery for three months and the results obtained indicated that not only catalyst consumption rate was reduced in comparison, but also reaction efficiency was enhanced [3].
3) Possibility of rising temperature of regeneration reaction due to high stability of catalyst regarding degradation with respect to temperature. According to design criteria in similar units, regenerator temperature should not exceed 50^{o}C where as in a DMD process, the temperature can be raised up to 60^{o}C causing an increase in the rate of regeneration reaction.
4) This process is more economical in comparison with similar processes.

3. Feed Selection for Pilot Tests

Following technology transfer, basic and detailed designs, construction and installation of demercaptanization pilot plant at RIPI was another step which is carried out pilot operations by using refinery feeds.

For this purpose, one of the sourest feeds for demercaptanization by Gachsaran oil fields which is supposed to produced the sourest crude oil in Iran whose cuts contains various sulfur contents.

Therefore, at first LSRG from Shiraz refinery was used as feed in this project and continuous operation was carried out for 3 months with online analysis of product. Following completion of this task, naphtha feed from Kharg Petrochemicals was used in this pilot for two months [4] .

4. Pilot Test Results

1. LSRG feed from Shiraz refinery has H_2S content about 100 ppm and mercaptan content about 700-1200 ppm and total sulfur content about 1600-1800 ppm. Feed and product analysis are shown in figure (1).
2. The results show that pilot performance has been extremely well and the mercaptan in product is lower than 5 ppm which has conformity with world standard.

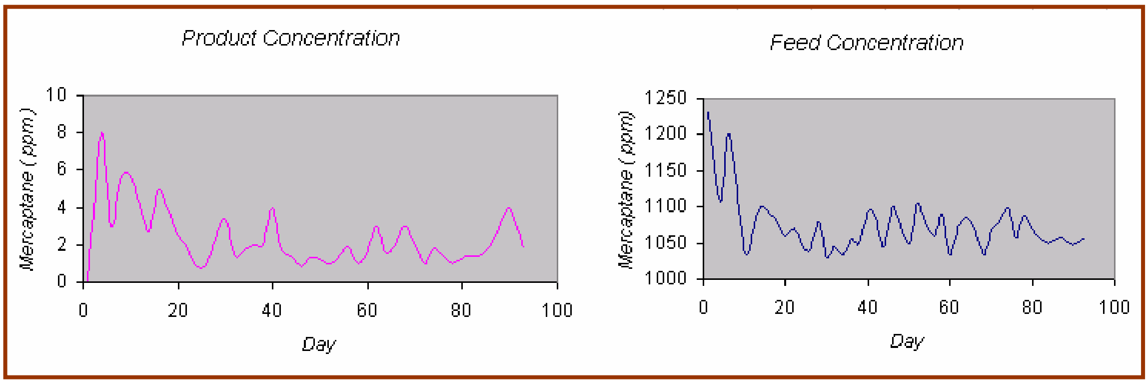


Figure (1): Analysis of LSRG feed from Shiraz refinery and pilot product.

3. Naphtha feed from Kharg Petrochemicals has H2S content less than 10 ppm and mercaptan content about 600-700 ppm. The mercaptan content of product in most cases was reported to be less than 5 ppm. The analysis of feeds and products are shown in figure (2).

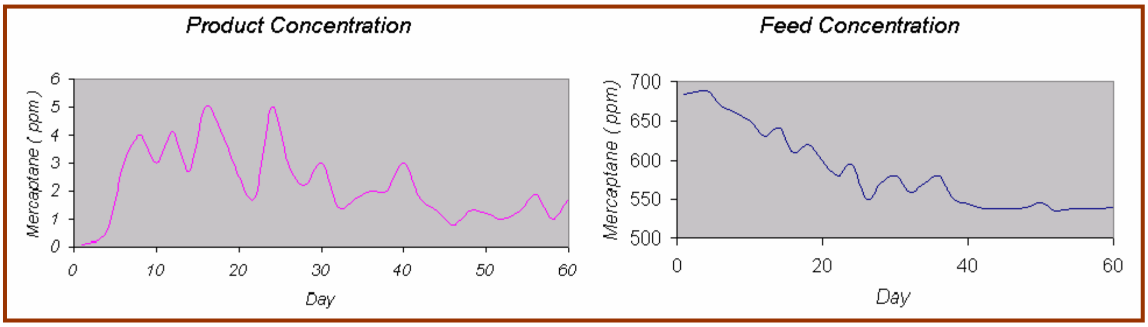
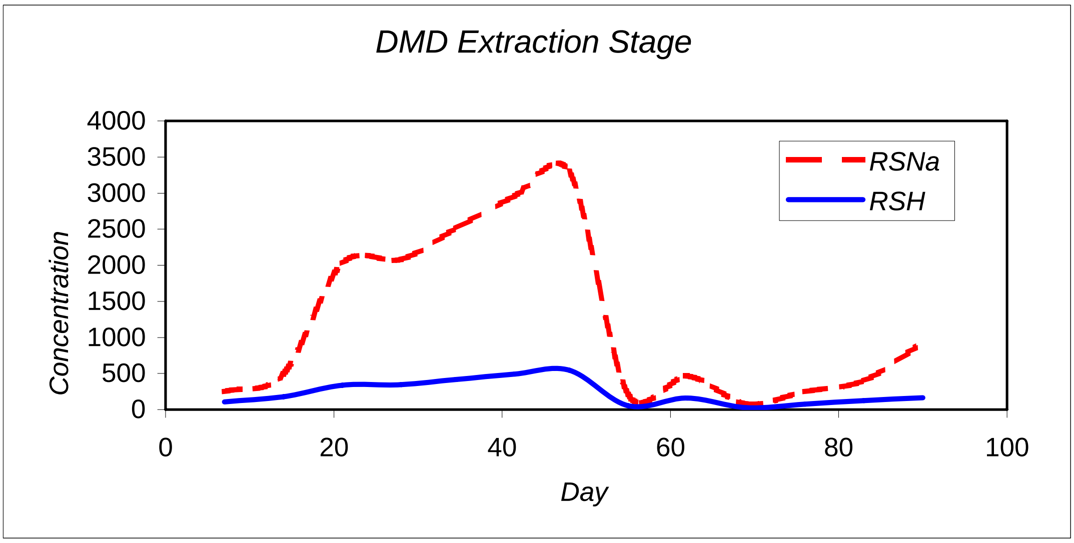


Figure (2): Analysis of Naphtha feed from Kharg Petrochemicals and pilot product.

4.1 The Effect of Various Parameters on the Process

1) Optimized extraction and minimization of mercaptans in this stage: The best contact between caustic and hydrocarbon phases at extraction tower is the effective factor of light mercaptan elimination from oil cut. Therefore key parameters such as optimization of size of length and diameter, suitable packing selection, caustic temperature, sodium mercaptide content in caustic and also feed's mercaptan play an important role in extraction operation. In figure (3) variations of mercaptan content in extraction tower outlet within 3 months of pilot work is shown.

Figure (3): Analysis of caustic and oil cut outlet from extraction stage.



2) Optimized regeneration and keeping low sodium mercaptide concentration in caustic: In catalytic regeneration tower some key parameters are very important; the rate of injected air to the tower, tower temperature, maximum sodium mercaptide content and concentration of catalyst which is solved in caustic. As known, by optimization of injected air and catalyst and keeping tower temperature at its maximum permissible value, sodium mercaptide can be kept at its lowest level. Also it is known that the lowest concentration of this substance in the caustic, causes the greater mercaptan absorption by the caustic. In figure (3), the variations of sodium mercaptide content at outlet of regeneration tower is shown within 3 months. It can be seen that with reducing RSNa value, better absorption takes place in extraction tower and mercaptan content is lowered in the extraction tower.
3) Pressure increasing in oxidation tower: Oxidation reaction of heavy mercaptans is catalytic and the role of following parameters in this reaction are of great importance:
   i. Injection of dilute caustic into oxidizer column for a small amount.
   ii. Injection of optimized air for oxidation.
   iii. Suitable pressure and temperature for assumed reaction.

It is known that for endothermic reactions on the LHS of stochiometric equation, as a result of gas presence, a rise in pressure and temperature, increase rate of the reaction.

4) Optimized separation of disulfide from the caustic: the produced disulfide in regeneration tower enters the separator with the caustic and is collected in the form of a layer and separated at the top of the caustic. It should be mentioned that disulfide and caustic densities are very close to each other. Therefore, the separation was done with some difficulties that led to outlet caustic to carry some disulfide in the extraction tower which eventually caused an increase in total sulfur of product. Thus two methods were employed to improve the separation process:

iv. Injection of naphtha or an oil hydrocarbon in the inlet caustic stream into the separator for mixing with disulfide and alleviating the organic phase.

v. The use of antracite to coagulate small particles of disulfide which is dispersed in the caustic.

4.2. Scale up and Industrial Design

Following the completion of third phase of this project and getting acceptable results from the pilot, all the required data for industrial design and scale up were taken. Then, RIPI carried out the implementation of industrial project for designing and construction of three desulfurization units at one of the Iranian Petrochemical Complexes. In this work, naphtha, propane and butane products were desulfurized independently with the following capacities and their final products will be exported.

- Butane desulfurization unit: 500 tons / day
- Propane desulfurization unit: 500 tons / day
- Naphtha desulfurization unit: 4000 BPSD

It should be mentioned that basic and detailed designs and procurement of equipments of these units are completed and now the project is in installation phase.

PFD'S for these units are shown in fig. (4), (5) and (6) for butane, propane and naphtha respectively. The total sulfur content for naphtha , propane and butane in these industrial units are 950 ppm, 450 ppm and 1110 ppm respectively. During the process, products with the following specifications are obtained:

Table (1): Specification of products

Composition	Specification (ppm)
H_2S	≤ 1
COS	≤ 1
CS_2	≤ 5
RSH	≤ 5
Total sulfur: naphtha	≤ 51
Total sulfur: butane & propane	≤ 35

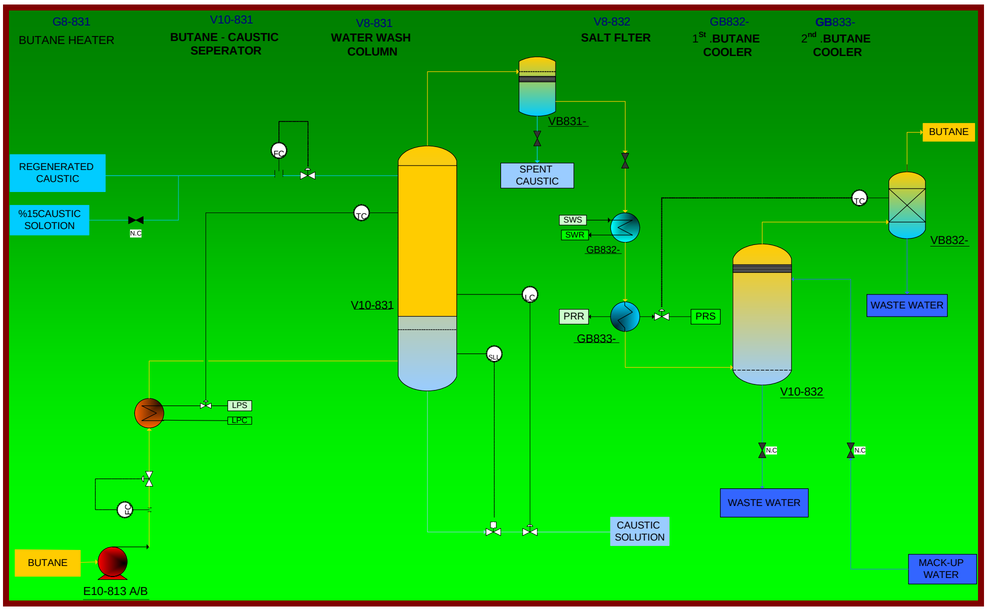


Figure (4): Desulfurization process flow diagram for butane feed.

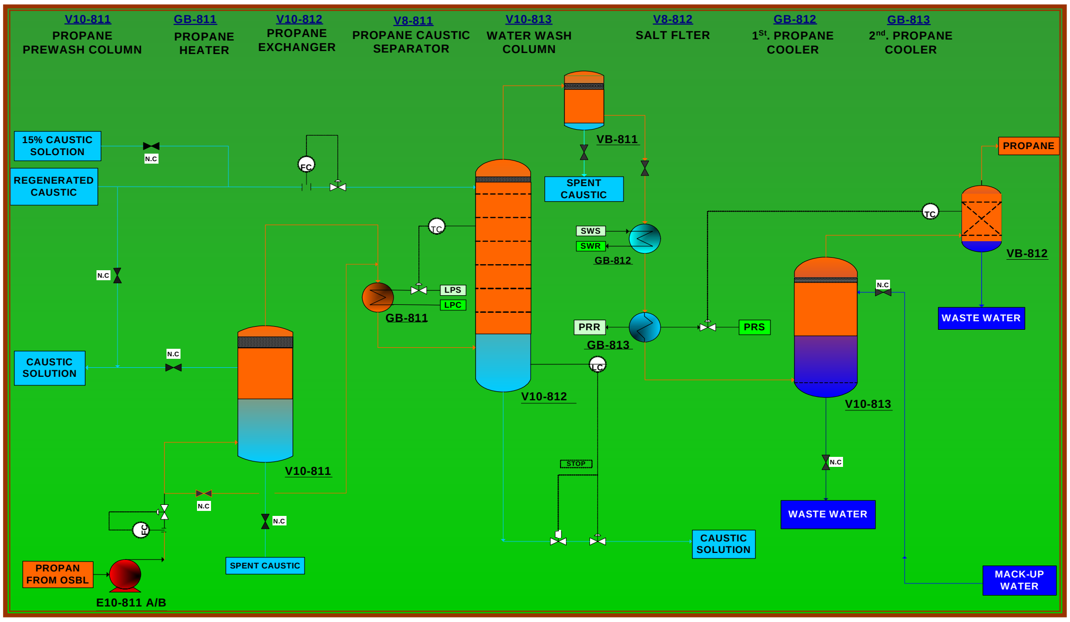


Figure (5) Desulfurization process flow diagram for propane feed.

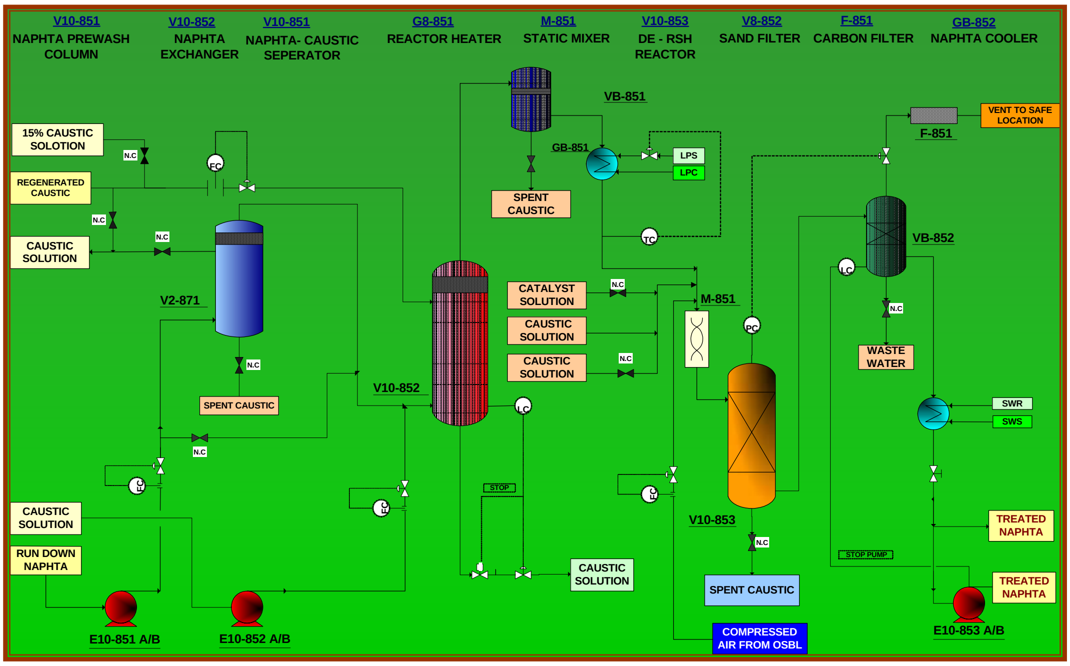


Figure (6): Desulfurization process flow diagram for naphtha feed.

5. Discussion

Following long term tests on industrial feeds in the pilot plant and investigation on optimizing the process condition to obtain better results, the significance of following findings were identified:

1. Suitable air injection both in oxidation and regeneration towers based on analysis of outlet off gas must be performed because during the process due to various fluctuations in RSNa or RSH content, one can not rely on default design data for air injection. Therefore for acute conditions, it is necessary to find out how much air should be injected into the system by oxygen analysis of off gas outlet.
2. Suitable time to inject the catalyst into the caustic based on RSNa analysis in the caustic outlet may be determined.

3. It is necessary to enhance the circulation caustic flow rate over time where mercaptan content of feed is increased for any reason. By performing this task, the increase in the outlet mercaptan content from the extraction tower, can be prevented.

6. Conclusions

With respect to DMD process advantages compared to similar ones introduced in this article, it was chosen as the first option for technology transferring. Preliminary evaluation of DMD at laboratory scale proved that it is capable for eliminating mercaptans at world standard levels. Following the construction and commissioning of a pilot plant using industrial feeds confirmed the preliminary findings. The design data for industrial scale were obtained. Then basic and detailed designs for 3 industrial units were accomplished. Another important finding in the DMD process is environmental friendly. Unlike similar processes, not only the poisonous Na_2S produced by H_2S removing, does not enter the environment but also it is converted to harmless sulphates and thiosulphates. This phenomena is vitally important where H_2S content in feed is high [5].

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