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EXPERIMENTAL INVESTIGATION ON DIFFERENT PARAMETERS IN DEMERCAPTANIZATION OF GAS CONDENSATE IN PILOT PLANT SCALE

Maryam Ghaedian, Mansoor Bazmi, Zahra Rabiei, Morteza Tajerian, Ashraf Dehghani

Petroleum Refining Technology Development Division, Research Institute of Petroleum Industry, Tehran, Iran. E-mail: ghaedianm@ripi.ir

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Abstract

Hydrogen sulfide and mercaptans in hydrocarbon streams cause environmental pollution and corrosion problems in pipelines and storage tanks.Thus Demercaptanization of hydrocarbon streams is recognized as an important refining process. DMC process has been developed as a proper sweetening method. A pilot plant of DMC with 15 BPD capacity is designed and constructed. In this article, experimental result of pilot test run for a sour gas condensate is presented. Also optimum quantity of effective operation conditions is determined. Long term pilot plant test results proved the adequacy of DMC process.

Key words: gas condensate; hydrogen sulfide; mercaptan; demercaptanization; DMC process.

1. Introduction

Production rates and processing of oils and gas condensates which contain a great amount of mercaptans and hydrogen sulfid has been grown in all over the world during the recent years. Hydrogen sulfide and low molecular weight mercaptans (C_1-C_3) are toxic and volatile, they have irritant odour and high corrosivity. For a ecological and technological safe storage, transportation and processing, these crude oils and gas condensates should be treated for removing hydrogen sulfide and low molecular weight mercaptans.

Most of the known methods for extraction of mercaptan from oil and gas condensates involve their treatment with an aqueous solution of an alkali metal hydroxide or ethylalcohol, ketone, formaldehyde, sodium salt of arylsulfinnic acid. Also there are some other demercaptanization methods for petroleum distillates which involve the oxidation of mercaptans using the oxygen of the air in the presence of a base and heterogeneous catalyst.

Essential deficiencies of these methods are insufficiently mercaptan extraction or oxidation of feed, the necessity of consuming significant quantities of the alkali or other substances, and the low stability of catalytic activity in heterogeneous catalyst systems.

DMC process has been developed as a proper sweetening method for petroleum and gas condensate. In this process using caustic solutions, light mercaptans , H_2S, COS, and CS_2 are removed from crude and gas condensate. Also corrosive and active heavy mercaptans are converted into disulfides.

Advantages of this process comparing with similar methods are higher degree of demercaptanization, higher stability of catalyst activity and more economical aspect of the process.

2. DMC process description

In the first stage of the process (Pre-wash) hydrogen sulfide, the main quantity of low molecular weight mercaptans C_1-C_2 and naphthenic acids are extracted by circulating alkaline solution. In the second stage (Extraction) removal of C_2-C_3 mercaptans and a part of C_4 mercaptans is performed by using regenerated alkaline catalytic solution, which will be routed to the first stage of extraction afterwards. The third stage (Oxidation) of the process provides deep oxidative demercaptanization of feed in oxidation reactor in the presence of air, enriched with oxygen, and homogeneous IVKAZ catalyst. Mercaptans C_4^+, which could not be removed during extraction stages, will be converted to non-toxic dialkyl disulfides in the oxidation stage, and remain in treated condensate.

The regeneration (Caustic Regeneration Stage) of the alkaline catalyst complex solution (CC) is carried out by catalytic oxidation of sodium sulfide and mercaptides in the presence air oxygen over homogeneous IVKAZ catalyst. Dialkyl disulfides, formed during mercaptide oxidation, dissolve in the condensate afterwards.

3. Chemistry of Process

3.1 Stage 1 and 2: Extraction of hydrogen sulfide and mercaptans C_1-C_3

Chemistry of condensate treatment for hydrogen sulfide and light mercaptans C_1-C_3 is based on their extraction by using aqueous sodium hydroxide solution in the form of mercaptides and sodium sulfide as the following reactions [3,4]:

$$H_2S + 2\ NaOH \rightarrow Na_2S + 2\ H_2O \tag{1}$$

$$RCOOH + NaOH \rightarrow RCOONa + H_2O \tag{2}$$

$$RSH + NaOH \leftrightarrow RSNa + H_2O \tag{3}$$

Three reactions proceed at high excess rate of sodium hydroxide at a temperature of 20-70°C. Reactions 1 and 2 are irreversible and exothermic. Reaction 3 is reversible and exothermic and at a temperature higher than 90°C the reaction equilibrium shifts to the left, i.e. to the side of mercaptan formation.

3.2 Stage 3: Oxidation of mercaptans C_{4+}

Heavy mercaptans (C_4^+) are oxidized over homogeneous phthalocyanine catalyst IVKAZ with oxygen of air to form disulfides by the following reaction at a temperature of 50-70 °C:

$$2\ RSH + 0.5\ O_2 \xrightarrow{\text{Catalyst , NaOH}} RSSR + H_2O \tag{4}$$

The reaction is irreversible, exothermic and is accelerated by increasing reactor temperature and pressure, and catalyst supply.

3.3 Stage 4: Regeneration stage of the caustic solution

Regeneration of alkaline solution, containing sodium mercaptides and sulfide, proceed over homogeneous catalyst solution IVKAZ by oxidizing sodium sulfide and sodium mercaptides with oxygen of air by the following reactions: [5,6]

$$2\ RSNa + 0.5\ O_2 + H_2O \xrightarrow{\text{Catalyst,}} RSSR + 2\ NaOH \tag{5}$$

$$3\ Na_2S + 4\ O_2 + H_2O \xrightarrow{\text{Catalyst, , T}} Na_2S_2O_3 + Na_2SO_4 + 2NaOH \tag{6}$$

The reactions are catalytic, exothermic and are accelerated by increasing temperature, pressure, air and catalyst quantities.

3.4.DMC pilot plant

Following laboratory studying of demercaptanization concept, it was necessary to prove the process in pilot plant scale. Basic and detailed designs, construction and installation of demercaptanization pilot plant (DMC) are done. Nominal capacity of the pilot plant is taken equal to 100 l/hr. The plant can operate in the range of capacity from 20 to 120 l/hr.

3.5 Feed composition for DMC process

An Iranian stabilized gas condensate of South Pars gas field was chosen as feed for the pilot designing. Table 1 shows the feed specification.

Table 1 Specification of condensate feed

Specification	Quantity
Total sulfur, wt %	0.22
Hydrogen sulfide, ppm wt, max.	15
Mercaptan sulfur, ppm wt	1620
Density , kg/m3	756
Acid number, mg KOH/g sample	0,05

Table 2 shows individual mercaptan content in the feed (ppm as S) and estimated values of treatment stages of process.

After treatment, gas condensate should meet the following requirement:

- mass fraction of hydrogen sulfide, 2 ppm, max.
- mass fraction of mercaptan sulfur, 50 ppm, max.

Table 2 Mercaptan composition of DMC pilot feed and stage wise products

Components (as ppm S)	In feed	After extraction	After oxidation
Methyl mercaptan	20	0	0
Ethyl mercaptan	350	0	0
Isopropyl mercaptan	250	0	0
t-butyl mercaptan	10	10	8
n-propyl mercaptan	100	5	0
2-butyl mercaptan	210	50	0
i-butyl mercaptan	10	0	0
n-butyl mercaptan	100	0	0
∑ mercaptans C1-C4	1050	65	8
High molecular weight RSH	570	570	40

3.6. DMC process flow diagram (PFD)

Figure 1 shows PFD of condensate demercaptanization process (DMC) pilot plant.

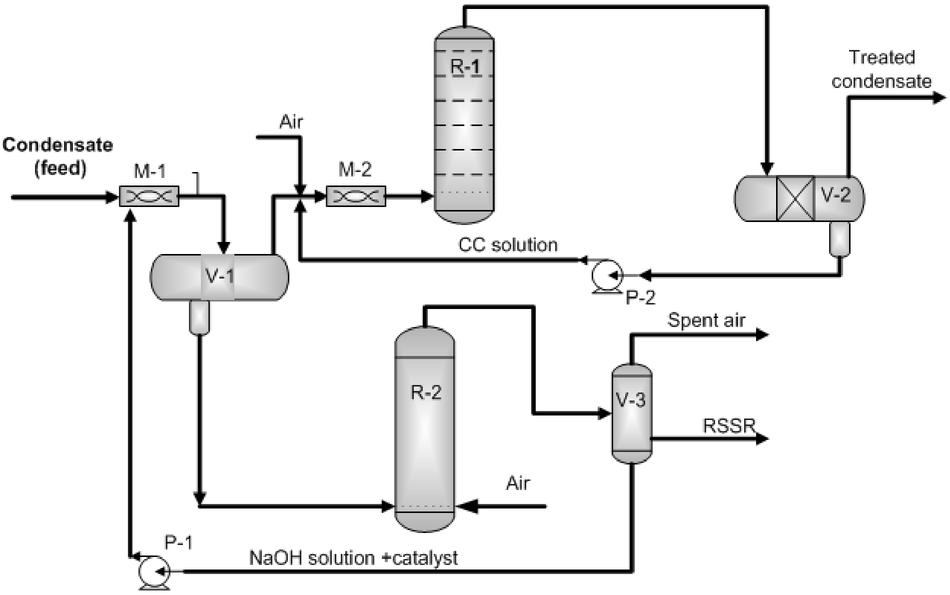

Fig. 1. Simplified PFD of DMC pilot plant

4. Results and discussion

4.1 The effect of various parameters on the process

The most important parameters which influence the reactions of the process are temperature and entrance air flow rate (oxygen) to two reactors: oxidation and regeneration. The criteria for choosing the optimum values are mercaptan content of outlet condensate for oxidation column and mercaptide content of outlet caustic solution for regeneration column.

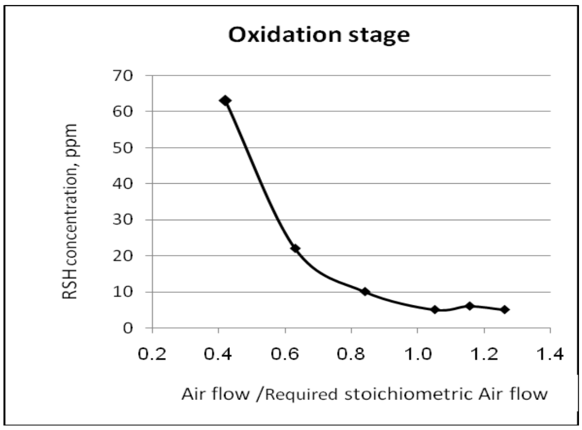

Fig. 2 The effect of air flow rate on demercaptanization in oxidation stage

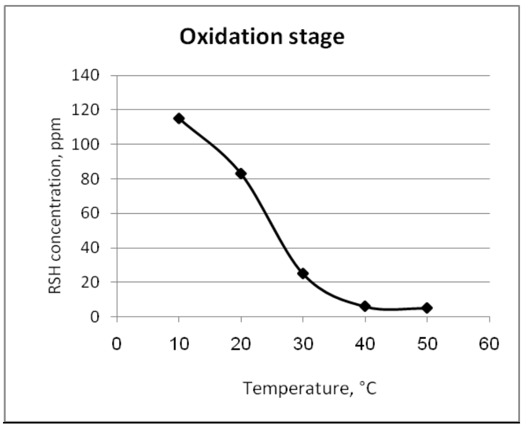

Fig. 3 Temperature effect on oxidation stage reactions

For determination optimum values of these key factors, some set of pilot plant runs have been designed and done. Figures 2, 3 and 4 illustrate the results of these test runs.

Increasing air flow rate in oxidation column, increases demercaptanization with a sharp gradient and as it is shown in Fig. 2 required stoichiometric oxygen is enough for completing the reactions. Both oxidation and regeneration column have the best performance at 40-50°C (Fig. 3, 4).

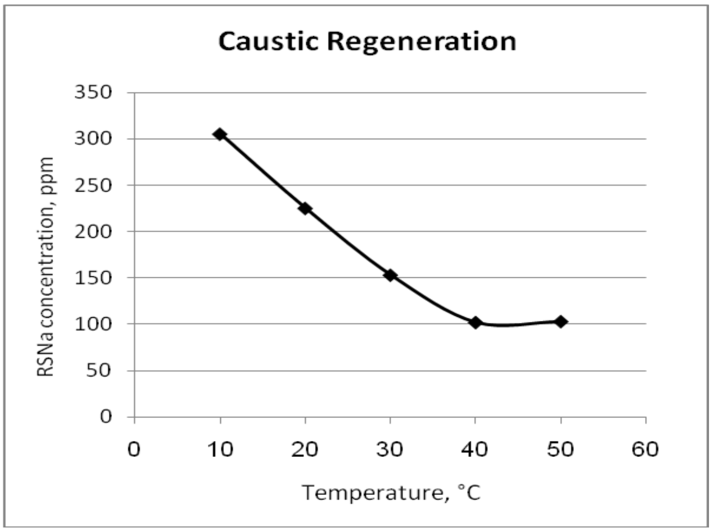

Fig. 4 Temperature effect on caustic regeneration stage reactions

4.2 Long Term Pilot Test

In DMC process light mercaptans are removed in extraction section and heavier mercaptans converted to disulfides in oxidation section. In both sections mercaptan content of treated product is the criteria for checking the performance of the process. In this study pilot plant was run for 10 days and two samples were taken from outlet of extraction and oxidation columns three times a day. Laboratory test results of samples' mercaptan content are illustrated in Figures 5, 6.

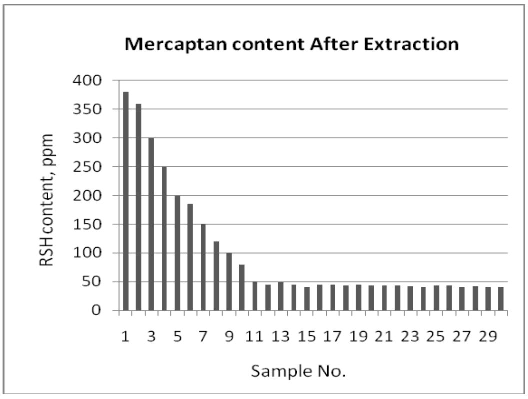

Fig. 5 Light mercaptan content of condensate feed after extraction

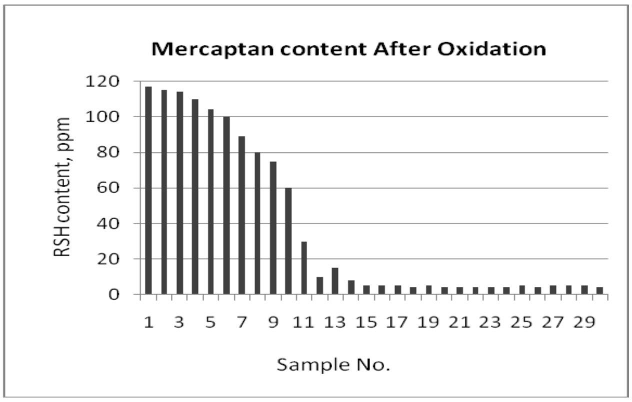

Fig. 6 Light mercaptan content of condensate product after oxidation

After four days pilot was reached to steady state condition and thus mercaptan content of product remained constant. As it were expected (Table 2), light mercaptan content of product reached to less than 50 and 15 after extraction and oxidation stages, respectively.

The results of pilot test runs show that DMC is a proper process for demercaptanization of gas condensate and the pilot plant is designed and constructed correctly and had an acceptable performance.

5. Conclusions

Laboratory experiments of DMC proved its capability for removing H_2S and mercaptans of crude oil and gas condensate up to world standard levels. Basic and detailed designs for a pilot plant with 15BPD capacity were accomplished based on a sour gas condensate as feed. After construction and starting up of pilot, effect of key factor variations such as air flow rate and temperature, in oxidation and regeneration columns were investigated based on analysis of their outlet (RSH and RSNa content, respectively). In both stages optimum reactions temperature was 40-50°C.Stochiometric air flow to the oxidation reactor is adequate for completion the reactions (based on equation 4). By applying optimum parameters, long term tests in DMC pilot plant performed. In steady state condition, light mercaptan content of feed after extraction stage decreased to less than 50 ppm and final product (demercaptanized condensate) had less than 5 ppm of light mercaptan content.

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