Natural Gas Odorant Production from Sour Condensate-
Increasing Added Value & Decreasing Environmental Problems

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Abstract

Treated Natural Gas (NG) is a colorless gas without any smell. Odorant is added to natural gas to provide a distinctive odor, thus allowing any potentially hazardous leakage to be detected or realized by smelling. Due to very strong smell, Light mercaptans are quite common for this purpose. Existing vast sources of sour gas condensate in south pars field has led RIPI to extraction natural mercaptans for this aim. The offered method not only reduced sulfur content of gas condensate but also has not any problems of DSO production and caustic treatment units which are faced in demercaptanization processes.

Introduction

In 1880's, Nitrobenzene and Ethyl mercaptan had been utilized as an odorant which used to be added to blue water gas, in order to indicate the presence of carbon monoxide. NG odorization started in US, in 1930's in consequence of the New London's disaster. After the World War II, low molecular weight synthetic chemicals, such as mercaptans and sulfides, are being used vastly, for odorizing of natural gas in form of pure or blended with other synthetic chemicals.

The history of using mercaptan as an odorant in Iran, refer to the first experience of NG to residential application in 1960s. By developing of gas distribution network and increasing of natural gas consumption up to 80 bcm per year just in residential sector, the NG odorant consumption reaches to 600 ton/y in Iran.

Today, the most part of demanding mercaptans are produced in synthetic methods, under catalytic reactions. But mercaptans can be extracted from natural hydrocarbon sources, which

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is a good opportunity for putting to use of a waste and hazard material. Remarkable amount of sour gas condensate in Iran, are available sources for producing odorant. Natural mercaptans exist as a severe impurity in sour gas or crude oil

Problem

Production, transportation, storage and processing of crude and gas condensate with high content of hydrogen sulfide and mercaptans are connected with serious ecological and technological problems. Light Mercaptans are toxic, volatile and corrosive, they have strong odor.

During gas treatment processes or oil refining, mercaptan should be removed and the amount of these compounds would not be more than a specific limit, based on a product specification or standard and their effect on downstream processes and catalysts.

Wastes and by products of these processes cause environmental impacts and more ecological treatment should be considered.

Research Institute of Petroleum Industry (RIPI) has developed demercaptanization process of gas condensate and produced odorant in pilot scale. The pilot plan was consist of demercaptanization of sour naphtha (DMD process) and reactive distillation of spent caustic solution from that process[1].

Pilot plant results had made RIPI to continue the idea and plan industrial odorant production unit.

Light Mercaptan Removal

Extraction with alkaline solution is mainly commercial method for removing light mercaptans from hydrocarbons.

The most rational and economically efficient process of mercaptan extraction from hydrocarbon cuts and gas condensates with high sulfur content is their extraction with alkaline solutions by mercaptan conversion into alkaline metal mercaptides, which are soluble in alkaline solutions and non-soluble in hydrocarbons following reaction:

$$RSH + NaOH \rightarrow RSNa + H2O + q \quad (1)$$

At the same time hydrocarbons are treated for mercaptan sulfur, which is an impurity in hydrocarbon feed. The alkaline process based on mercaptan capability to react with alkalies forming mercaptides following reaction (1) is one of the first commercial processes of treating liquid and gaseous hydrocarbons for mercaptans.

In commercial practice of mercaptan extraction from hydrocarbons a less costly and more available sodium hydroxide is usually used as an alkali mainly in a form of 10-20% aqueous solution.

Regeneration of alkaline solution, containing sodium mercaptides and sulfide, proceed over homogeneous catalyst solution by oxidizing sodium sulfide and sodium mercaptides with oxygen of air by the following reactions: [2, 3]

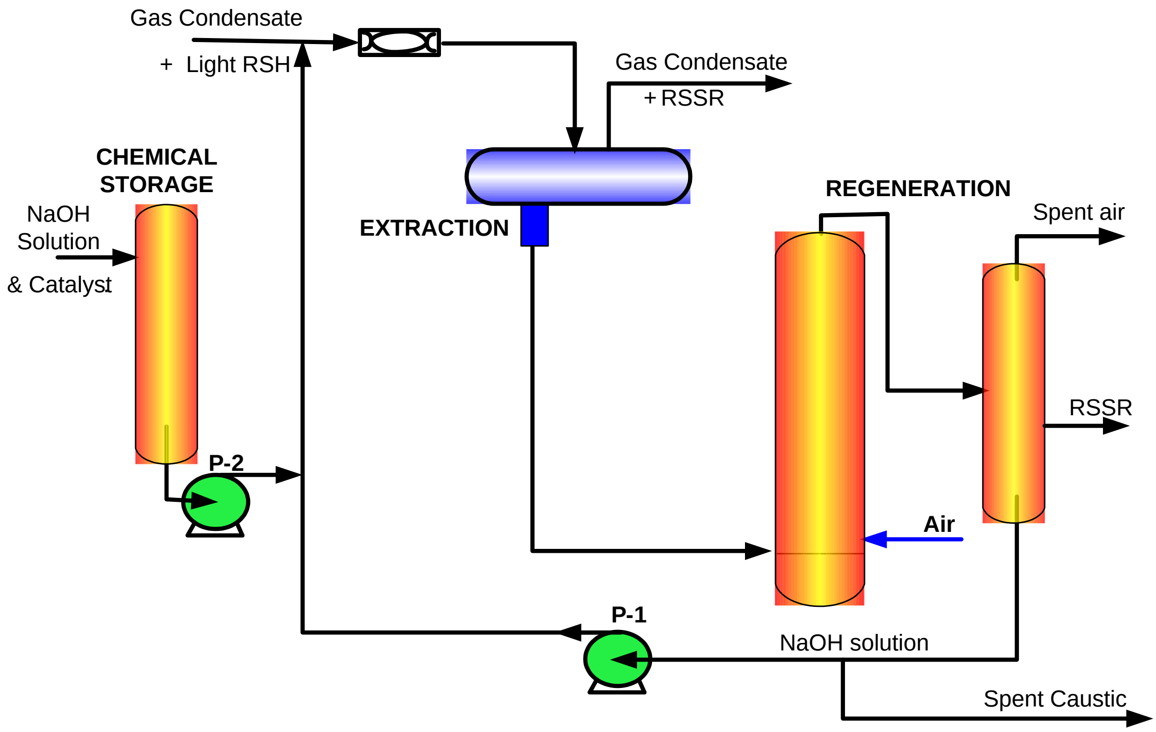
$2\ RSNa + 0.5\ O_2 + H_2O \rightarrow RSSR + 2\ NaOH$ (2)

$3\ Na_2S + 4\ O_2 + H_2O + q \rightarrow Na_2S_2O_3 + Na_2SO_4 + 2NaOH$ (3)

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

The schema of gas Condensate Demercaptanization unit (DMC unit) is shown in Fig.1.

Fig.1- DMC Unit Schema



Toxic sulfur-alkaline waste waters are produced crude oil and gas condensate sweetening process. Disulfides (RSSR) are produced in alkaline regeneration cycle and pollute waste water and spent air from this process causes environmental impacts and more ecological treatment should be considered.

Typical composition of these streams are listed in table no.1.

Table 1- Composition of DMC Waste Streams

Spent Caustic Composition, % mass	
- NaOH	2
- Na_2CO_3	0.07
- $Na_2S_2O_3$	0.67
- Na_2SO_4	0.6
- RSNa	traces
- RCOONa	4.4
- RSSR	traces
- Catalyst	traces
- H_2O	balance
Density, kg/ m^3	~1100
pH	14
Odor	of sulfur compounds
Spent air Composition, % mass	
- Hydrocarbons	up to 0.1
- Water	1.5
- Disulfides, below	1.8

Light Mercaptan Separation

It's possible to avoid producing disulfides and to reduce waste water environmental impacts by separation of mercaptans in alkaline regeneration section. Separation suitable mercaptan as natural and liquefied gas odorant provides against pollution of water sources and air and increases value of inlet Hydrocarbon (as feed) via sweetening and deodorizing of it.

Reaction (1) is reversible and during heating the equilibrium can shift substantially to the left:

$$RSNa + H2O + q \rightarrow RSH + NaOH \qquad (4)$$

The process of mercaptan extraction and thermal regeneration of spent mercaptidealkaline solutions is based just on this feature of the reaction [4].

Industrial Odorant Production

Pilot plant results had made RIPI to continue the idea and plan industrial odorant production unit.

The unit has been designed and installed for separation aliphatic mercaptans from gas condensate in south pars by NIGC (National Iranian Gas Co.) investment and will be started up in near future. Products of this unit are deodorized gas condensate and Odorant for natural gas.

Following stage had been considered for design and construction of industrial plant.

Feed Selection**:** The first step of design industrial plan is selection feed sources, based on product specification and annular demand rate. The feed properties are as following:

Total sulfur, wt %	0.375
Hydrogen sulfide, ppm wt, max.	10
Mercaptan sulfur, ppm wt	2029
Density , kg/m3	752
Σ mercaptans C1-C4SH	1450

The plant capacity for feed (gas condensate) is 15 000 BPSD The plant capacity for salable product (odorant) is 800 t/hr (100 kg/hr).

Odorant properties: Product specification is as following based on Iranian gas standard no. IGS-M-CH-038:

H2S ppmwt	Less than1
Methyl mercaptan ppmwt	Less than 1
Ethyl mercaptan wt%	Less than 1
Σ C3–C4 mercaptans wt%	95
Free Water ppmwt	Less than1

South Pars sour gas condensate is suitable source for this aim by considering above product's specification. Gas condensate of 4 phases had been studied and suitable feed was selected.

Plant Location**:** following items had been reviewed for selection plant location

1) Nearest to feed source and consumer
2) Availability of utilities
3) Availability of infrastructures

Process design**:** The process of gas condensate treating and odorant production consists of the following stages. Schema of unit is illustrated in Fig.2.

- Feed pre-alkalization for removal of hydrogen sulfide and carbon dioxide.
- Mercaptan extraction from the feed with 10% aqueous caustic solution.
- Caustic solution thermal regeneration.
- Odorant separation from a mixture of low-boiling C1-C4SH.

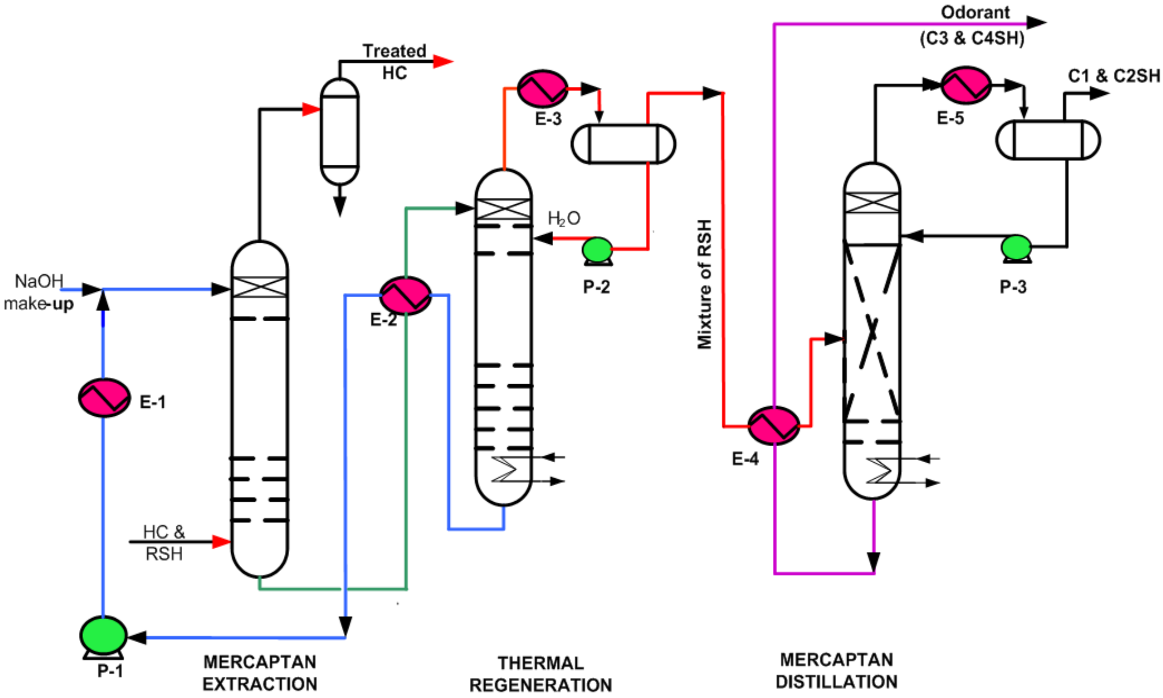
By-Products**:** The by-products of process are treated gas condensate and C1-C2SH which are valuable byproducts. The price of deodorized gas condensate is about 2$/Bbl more that untreated material.

Treated gas condensate has following specifications:

Hydrogen sulfide content, ppm wt	Nil
C1,C2SH ppmWt as Sulfur	Less than 20

C1-C2SH will be distillate and separate. These mercaptans could be used as feedstock of medical industries after more purification.

Fig.2- Odorant Production Unit Schema



Conclusion

Undesirable affects of Caustic regeneration will be reduced in demercaptanization processes via thermal regeneration of caustic solution and removal light mercaptans. Natural light mercaptans will be used as finished product as "Odorant".

References

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