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Odorant production based on the development of Demercaptanization process

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Abstract

Regarding to the importance of applying odorants and other odour materials in gas industry, which is increasing today, this article subjects to odorant production in order to reach to the pure mercaptans in a pilot plant scale. Huge gas sources in Iran, the necessity of exploration, and safety problems of natural gas applications make us to apply proper methods to produce odorant. Our method is not a synthetic method, however it based on the development of demercaptanization process. The pilot operation including two parts, making caustic feed (contain sodium mercaptide) and reactive distillation, has been investigated. Also the results of odorant analysis has been examined in this article.

Key words: mercaptide, odorant, caustic, desulfurization.

Introduction

Odorants are consumed as odour materials in gas industry. Since the natural gas is odourless, using these materials helps us to diagnose, if there is any natural gas leakage, and increases the safety factors of the operating environment. Toxicity and non-recoverability after burning are the weak points of odour materials. So attention to the amount of odorant consumption & its proper dosage are important items[1].

Alkyl mercaptanes are the odour materials, which are widely used for gas streams. Tertiary Butyl Mercaptane (T.B.M) and Iso Propyl Mercaptane (IPM) are the most important of all[2].

Alkyl mercaptanes are so stable during storage time up to mixing with gases, also they have low freezing point & high volatility. Not any waste and ash after vaporization and burning are the significant specifications of these materials.

Autofina, Hansa, Ubichem are the most important companies of all odorant producers in the world[3,4,5].

In our investigated method, this article, the primary feed for odorant production is provided from demercaptanization process. So at first, caustic solution containing sodium mercaptide with a proper concentration is provided. Then through reactive distillation, odorant including pure mercaptane is produced.

Testing method

To provide the feed of odorant pilot which is caustic solution consuming in demercaptanization process, DMD demercaptanization pilot plant was installed using feed of shiraz refinery (LSRG), naphtha containing 1140 ppm mercaptan and the flow rate of about 80 lit/hr[6].
This operation consists of two stages, extraction & oxidization. Exiting caustic from extraction stage is reversed to the extraction stage without any reduction. This operation is done in some batch systems. When the concentration of sodium mercaptide in the caustic solution increases to a considerable amount, of about 5000 ppm, the operation will be stopped. Then consumed caustic is discharged to the spent caustic tank which is the feed of odorant pilot plant. In continuation, caustic saturation process to provide the feed of odorant pilot plant and odorant production have been explained.

A. Caustic saturation

The feed of odorant pilot plant will be provided from extraction stage of demercaptanization pilot which is explained below[7].

In this stage light mercaptans (C_1-C_3) are extracted from naphtha. Naphtha feed is pumped from storage tank to the bottom of extraction column. This feed is heated before entering the column. The solution of about 8-10W% of NaOH is extracted from top of the column. In this stage light mercaptans convert to sodium mercaptide through the following reaction & enter to the caustic solution from gasoline phase:

$$RSH + NaOH \rightarrow RSNa + H_2O$$

purified gasoline leaving the top of the extraction column, after a separator & purification from droplets of residual caustic is sent to oxidization stage. From the bottom of the extraction column, caustic solution containing sodium mercaptide is returned to the top of the extraction column through a pump. In this stage, the system is batch regarding to caustic phase and caustic solution will be recycled until the concentration of sodium mercaptide increases to about 4000-5000 ppm. After this operation, caustic solution containing sodium mercaptide is discharged to the storage tank which is the tank of feed of odorant pilot. The flow scheme of this section has been shown in figure 1.

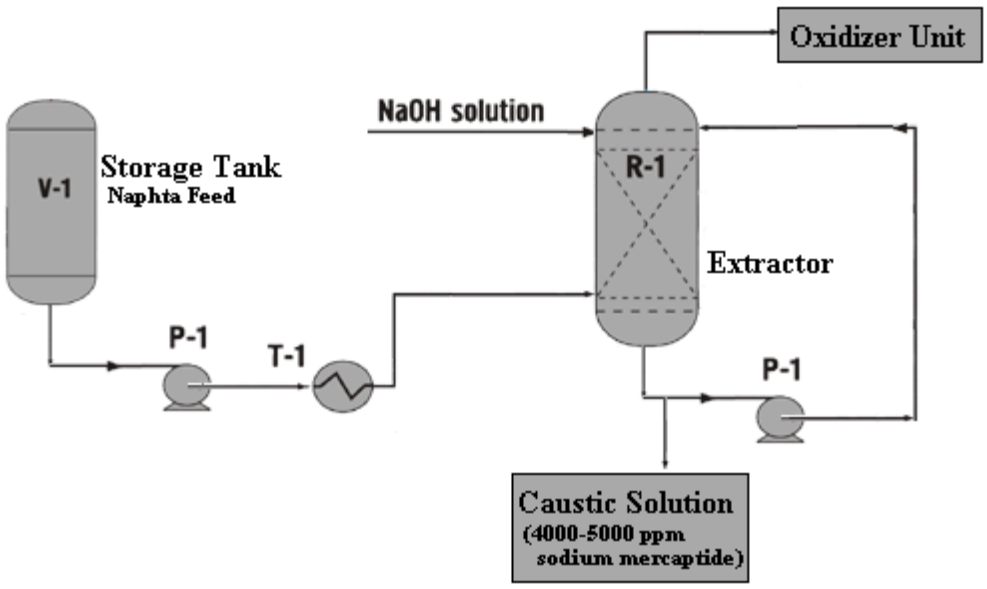

Fig.1-Flow Scheme of Caustic Saturation

B. Odorant production:

In this process, at first odorant feed is diluted by water 20V% then is pumped to the bottom of the heat reduction column, which is a batch distillation column. Caustic solution containing sodium mercaptide is heated to about 80-90ºC before entering to the column. Finally its temperature will reach to about 110ºC by steam injection.

So the caustic solution will be vaporized and as a result the mercaptides will be hydrolyzed and separated from caustic by conversion to mercaptan[8]. Hydrolyzation reaction follows this equation:

$$RSNa + H_2O \rightarrow RSH + NaOH$$

Mercaptans accompanied by steam leaving top of the reduction column, enters to the condenser-cooler. At last it enters to a separator to separate the megatons phase from water. Water phase exiting the reflux drum is pumped to the top to the reduction column as a reflux stream. The mercaptan phase formed in the reflux drum is collected as the product. The flow scheme of this process has been shown in fig 2.

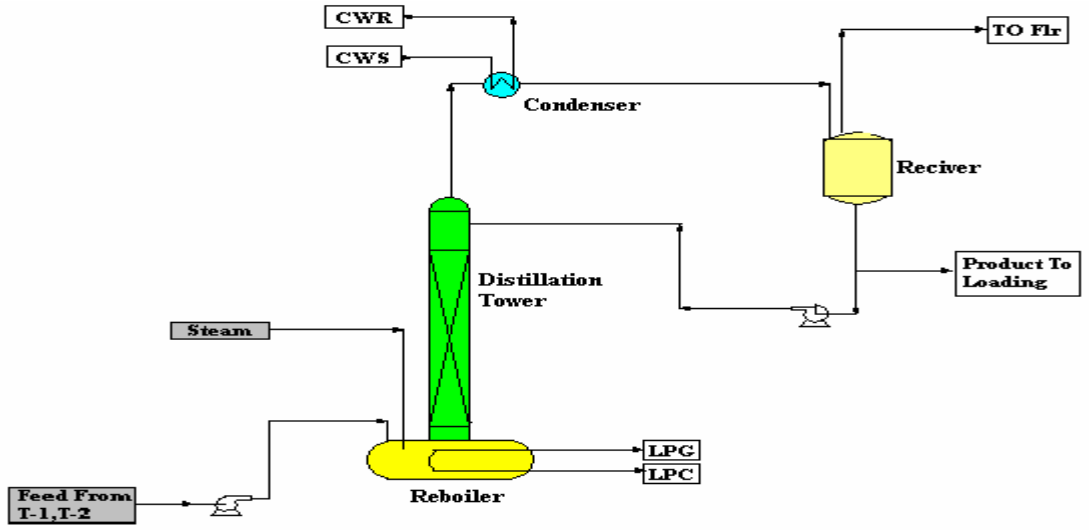

Fig 2-Flow Scheme of Odorant Production

Results and experimental data

During the caustic saturation operation and in the defined times, sample has been taken from two different points of pilot for analysis which is explained below:

1. Exiting naphtha form extraction stage: for residual mercaptane analysis.
2. Exiting caustic from extraction stage: to analyze exiting sodium mercaptide in the recycled caustic solution.

The analysis has been proceeded by using potentiometric method.

It must be mentioned that the caustic saturation process has been operated in 5 batches. The results of different sample analyses in each batch have been given in table (1).

Table 1-Results of saturation process analysis

Batch no.	Feed rate (lit/hr)	% NaOH	(ppm) RSH concentration		RSNa concentration in circulating caustic (ppm)
			Feed	After extraction	
1	123	5	1140	914	5067
2	80	8	1140	214	4700
3	80	9	1140	595	5645
4	80	7	1140	533	4832

Analysis method

To determine the amounts of mercaptans in the product of odorant process, two different methods are applied, [9,10] which are explained briefly:

1. Titration

In this method the amount of mercaptans in the product of odorant process is determined by titration and potentiometer. The solution using in the potentiometer is an ammonia solution containing $AgNO_3$.
To prepare the sample, product is diluted by alcohole because of high mercaptan concentration in the product.

Through two following equations we can calculate the mercaptane percentage:

$V= V_n+[(\Delta E_{max}-\Delta E)\Delta V]/[2\Delta E_{max}- (\Delta E_1+\Delta E_2)]$ (1)
Mercaptan percentage based on sulfur $=V*T*100/W$ (2)
Applied parameters in these two equations mean:
V_n : Consumed volume of ammonia solution containing $AgNO_3$ up to equivalent point (cm3).
ΔE_{max} : Maximum differential potential between two measurments.
ΔE_1 : Differential potential before equivalent.
ΔE_2 : Differential potential after equivalent.
ΔV : Added volume in each step.
T: Concentration of sulfur mercaptids equal to titration solution (gr/cm3).
W: consumed weight of analyzed sample.

2. GC analysis

Using gas chromatography apparatus, we can analyze the product of odorant pilot plant. Needed GC apparatus with the name of Crystalux has been provided from Metacrom Company of Meriel Republic of Russia. This apparatus includes two columns: Tceplo 10% , Odpn 2% and two detectors: FPD , FID.

Information obtained from GC, enters to the computer via hardware key and is processed by Netchrom v1.5 software. The results are shown in a group or individually and based on the different concentration units such as ppm. The results of analysis of odorant production process of two different batches lave been given in table 2.

Table 2- Calculated weight percentage of mercaptans based on two different analyses for the first & second batch.

Analysis method	weight percentage of mercaptan	
	First batch	Second batch
Titration	82%	83.79%
GC	83.4%	85%

Results and conclusion

In this section, it must be recalled that odorant plant is a part of demer-captanization pilot pant and it is not an independent pilot. Since the feed of odorant pilot is provided from demer-captanization process, we have to re-operate demercaptanization pilot. The results show that the product of odorant pilot is a mixture of pure mercaptans shich are mostly Ethyl mercaptan and Isopropyl mercaptane. Also it must be mentioned that Methyl mecaptan is not hydrolyzed and remains in the caustic solution[11].

Investigation of odorant production process gives these results:

- P^H in exhaust of the condenser must be arranged less than 9 to prevent caustic carry over.
- There must not be any oxygen in the reflux drum to prevent mercaptan oxidation & disulfide production. For this reason, reflux drum is purged using N_2 gas before operation
- There must not be any naphthenic acid in the system.

If there is any naphthenic acid in the process stream, a layer of viscous oil will

form on top of the water in reflux stage. So a prewash stage is neces-sary during caustic saturation.

Variations of sodium mercaptide concentration in the caustic solution versus time of operation in 4 batches and equal temperature and pressure conditions have been shown in fig 3. As shown, increasing of consumed caustic concentration in caustic saturation stage leads to increasing of time of caustic saturation. Also increasing of flow rate of feed in demercaptanization pilot decreases the time of caustic saturation.

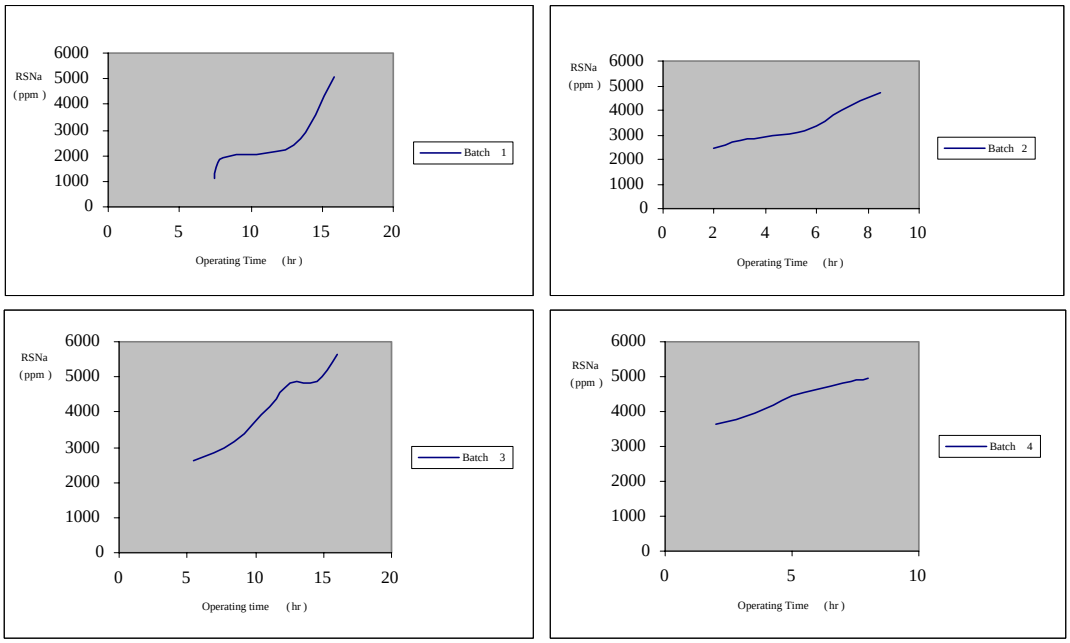

Fig 3-Variation of Sodium Mercaptide Concentration in Caustic solution versus time in 4 batches

Suggestions:

In general desulfurization process (DMD) not only have the ability of mercaptane separation of hydrocarbon feed but also can provide the possibility of pure mercaptane production as a by product. Results lead us to these solutions for tow oil and gas industries of the country in the future:

1- installation of an odorant production plant can provid the total demand of the country.
2- Odorant production plant is not an independent plant however is a part of demercaptanization plant (DMD). So beside each demercaptanization plant, the caustic reduction section can produce odorant.
3- Installation of DMD plant, which is equipped with odorant production section, is possible for sour hydrocarbon feed with high concentration of mercaptane.
4- Based on the experiences obtained from DMD process, it seems that the investment cost of a odorant production plant can easily be provided during about 2 years in the case of not any imports as a economized condition.
5- It must be mentioned that the product of odorant pilot has heed confirmed by the expert group of national Iranian gas company.

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