World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:5, No:7, 2011

Role and Effect of Temperature on LPG Sweetening Process

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***Abstract*—**In the gas refineries of Iran's South Pars Gas Complex, Sulfrex demercaptanization process is used to remove volatile and corrosive mercaptans from liquefied petroleum gases by caustic solution. This process consists of two steps. Removing low molecular weight mercaptans and regeneration exhaust caustic. Some parameters such as LPG feed temperature, caustic concentration and feed's mercaptan in extraction step and sodium mercaptide content in caustic, catalyst concentration, caustic temperature, air injection rate in regeneration step are effective factors. In this paper was focused on temperature factor that play key role in mercaptans extraction and caustic regeneration. The experimental results demonstrated by optimization of temperature, sodium mercaptide content in caustic because of good oxidation minimized and sulfur impurities in product reduced.

***Keywords*—** Caustic regeneration, demercaptanization, LPG sweetening, mercaptan extraction, temperature.

I. Introduction

LPG is one of the top products of South Pars Gas Complex refineries and consists of a mixture of low molecular weight hydrocarbon compounds. Some common sulfur compounds in LPG are H2S, Methyl mercaptan, Ethyl mercaptan and carbonyl sulfide (COS). These impurities are naturally present in natural gas or are formed by decomposition of higher sulfur compounds during distillation and cracking operations. In these refineries, H2S content in propane and butane feedstock is trace but Methyl and Ethyl mercaptan and carbonyl sulfide content is about 551, 31, 120 and 840, 4800, Trace for propane and butane, respectably.

II. SULFREX PROCESS DESCRIPTION

The AXENS Sulfrex extraction process was selected to remove sulfur compound from the C3 cut and the C4 cut. The process uses caustic soda solution as extractive medium, the low molecular weight mercaptans in the propane or butane cuts are very soluble in the caustic solution so when hydrocarbon and caustic phases are intimately contacted they are adsorbed in the caustic solution. Then rich caustic solution regenerated by means of a catalytic oxidation due to the presence of the sulfonated cobalt phthalocyanine as a catalyst and produced DSO routed to storage [1,2]. In overall Sulfrex Process consist of two stages that presented as below:

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A. Extraction Stage

In this stage, the outlet hydrocarbon stream from NGL fractionation is routed to the extraction step and light mercaptan components (C1-C2) and COS are eliminated by 12-15 wt% caustic solution [5,6]. In this step, the main reaction known as mercaptans with caustic soda (sodium hydroxide) is:

$$RSH + NaOH \longleftrightarrow RSNa + H_2O \quad (1)$$

In this reaction mercaptan is transformed to mercaptide anion by a base sodium hydroxide. Caustic Regeneration Stage: In this stage, in the presence of Sulfonated Cobalt Phthalocyanine as a catalyst and oxygen, mercaptide is oxidized and converted to disulfide by the following reaction:

$$2RSNa + \frac{1}{2}O_2 + H_2O \xrightarrow{Cat} RSSR + 2NaOH \quad (2)$$

In the oxidation step, the mercaptides (RS^-) in the solution move to the catalyst side and the reaction from mercaptides to free radicals (RS•) is taken place under catalysis, then the produced free radicals move back to the solution and react to form disulfides [3,4]. These reactions were listed below [7]:

$$RSNa \longleftrightarrow RS^- + Na^+ \quad (3)$$

$$CoSPc + O_2 \longrightarrow (CoSPc) \quad (4)$$

$$(CoSPc...O2) + RS^- \longrightarrow RS^0 + CoSPc + O_2^{0-} \quad (5)$$

$$RS^0 + RS^0 \longrightarrow RSSR \quad (6)$$

$$O_2 + H_2O \longrightarrow 2OH^- + \tfrac{1}{2} O_2 \quad (7)$$

$$OH^- + NA^+ \longrightarrow NaOH \quad (8)$$

Mercaptide is oxidized to disulfide via the formation of a ternary complex involving CoPcS, mercaptide anion and molecular oxygen (1).Then, the regenerated caustic is returned to the extraction stage.

III. RESULTS AND DISCUSSION

A. Effect of Temperature on the Mercaptan Extraction

As previously described, reaction of mercaptans with caustic soda (sodium hydroxide) to form sodium mercaptide in

extraction stage was occurred and mercaptan extraction is favored by lower temperatures because enhance extraction efficiency. According to AXENS advise, the upper temperature range is 40°C, because above this temperature mercaptan extraction will become increasingly poorer and lowest practical hydrocarbon feed temperature for extraction is about 20°C, because below this temperature, caustic entrainment by hydrocarbon may occur [1,2]. Also may be sodium sulfide and carbonate salts precipitate out of caustic solution and cause plugging problems. Although these range presented by AXENS and refineries of Iran's South Pars Gas Complex designed under Sulfrex license, but the basic information necessary to optimize the extraction temperature was not clear. Because wide range between minimum and maximum points of range has been considered and it may cause significant change in the product impurities (Total Sulfur).To explain this reason, there are two points. Ionization constant of mercaptans that decreases with temperature fall and extraction coefficient that enhances with temperature decrease because hydrolysis constant decreases [4]. For more understanding a series of experiments were tested with the different temperatures. The results of these experiments were shown in table I and figures 1, 2.

TABLE I
Operational temperature and impurities content on the product

Mercaptan in Sour C3/C4(ppm)	Extraction temperature° C	Mercaptan in Sweet C_3/C_4(ppm)	%Conversion In C_3/C_4
189-1195	31	30-34	84-97
149-1630	32	23-47	84.5-97.1
188-1425	33	28-41	85.1-97.1
223-1718	34	27-38	87.8-97.7
179-1355	35	21.5-31	87.9-97.7
219-1480	36	26-39	88.1-97.3
279-1222	37	33-36	88.1-97
235-1180	38	29-40.5	87.6-96.5
175-1250	39	24-48	86.2-96.1

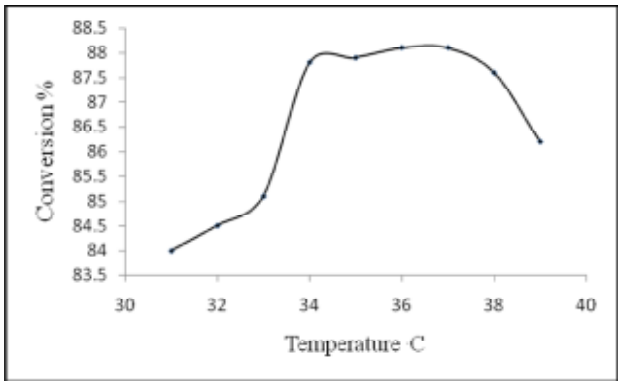

Fig. 1 %Conversion of Mercaptans into propane as a function of Temperature

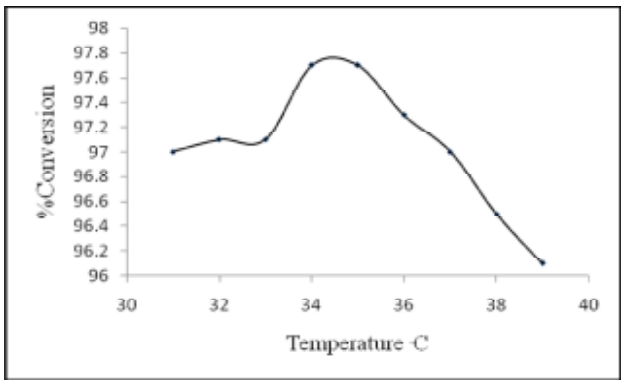

Fig. 2 %Conversion of Mercaptans into butane as a function of Temperature

In previous results were considered that caustic concentration is 14.2%wt and propane and butane extractors' pressure is 30.5 and 10.5 bar, respectably. Also propane and butane feed flow rate is 80 m3 and 55 m3.

As shown figures 1 and 2, variety temperature was studied from 31 to 39 °C. Because below 30°C is not accessible in normal operational process. So it can be found from figures and table, since temperature of sour propane and butane coming from the NGL fractionation unit are 55°C and 40°C respectively, the optimum temperature of 36-37°C for propane extractor and 34-35°C are recommended in order to have lowest mercaptan concentration in product.

B. Effect of Temperature on the Mercaptide Oxidation

Temperature is one of the most important factors that influence on mercaptide reaction. This reaction is exothermic and favored by higher temperature [5,6]. This temperature (oxidizer temperature) set in function of catalyst solution activity and of the mercaptans content in the C3 and C4 feeds [1,2]. By the other hand, the oxidizer temperature should always be kept as low as possible considering catalyst activity while still maintaining the desired degree of mercaptans regeneration. This temperature is normally kept within the range 38-45°C.Occasionally, it may be necessary to increase the oxidizer temperature to 48°C.In any event, oxidizer temperature should not exceed 55°C, because it's absolute maximum temperature and above 55°C,there are risk of stress corrosion embrittlement, and also possibility of decomposing disulfide oils to sulfonic acids [2,4].Furthermore at this temperature, the catalyst would start to be decomposed. In order to show the influence of the oxidizer temperature on the reaction of mercaptide to disulfide and obtain optimum temperature for regeneration reaction, a series of experiments were tested in different temperatures. The results of these experiments were shown in figure 3.

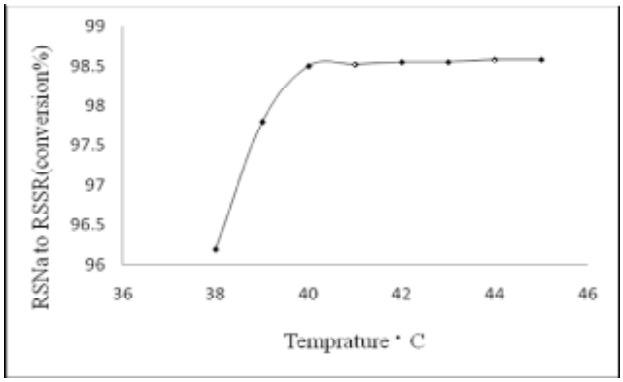

Fig. 3 %Conversion of mercaptides to disulfide oil as a function of temperature

In tests, were considered caustic concentration is 14%wt, Air injection rate to oxidizer is 65kg/h, Amount of Catalyst in alkaline solution is 100 wt ppm and also caustic solution containing about 7500 mg/L mercaptide. Laboratory results show that up to 41°C the conversion of mercaptides to disulfide oil will reach to 98.5%, thereafter the conversion from mercaptides to disulfide oil is changed unremarkably and temperature rising just uses more steam .Thus the optimum temperature of 40-41°C for oxidizer temperature is recommended in order to have 70-150 mg/L RSNa in lean caustic. Also since the sodium mercaptide content in caustic inlet to the reactor is 7500mg/L, reactor top and bottom optimum temperature would be around 45°C and 50°C respectively.

IV. CONCLUSIONS

The above presented results shown that temperature of 36-37°C for propane extractor and 34-35°C for butane extractor and oxidizer inlet temperature equal to 40-41°Cfor current situation of the plant (7500mg/L) sodium mercaptide at the inlet of the oxidizer are optimum values. In overall, these results are important to the industrial operation of LPG sweetening and it is concluded from the results that low impurity propane and butane products will be achieved in SPGC's Phases, if operating temperatures are adjusted as discussed in this paper.

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