

Sodium Sulfate Production from Sulfidic Spent Caustic

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Abstract: Sodium sulfate is produced from naturally occurring brine or crystalline mineral sources and as a product from various chemical processes. These processes for sodium sulfate production are all costly but for first time we would like to introduce a new chemical process from LPG (Liquefied Petroleum Gas) process waste called sulfidic spent caustic, on the other hand spent caustic is known as one of the most hazardous waste, by using this method this waste from LPG Units can be considered as a valuable raw material in a very economical process to produce sodium sulfate with high quality confirmed by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) tests. This process is not only inexpensive for producing a valuable industrial salt but also it comes from a waste that its treatment was very costly and difficult according to its refractory pollutant. The waste also could be treated much easier as a majority of sulfide Ions turn to sulfate.

Keywords: Desulfurization, LPG Process, Sodium Sulfate, Spent Caustic, Neutralization

1. Introduction

1.1. Liquefied Petroleum Gas (LPG)

Liquefied Petroleum Gas (LPG) consist mainly of commercial propane and commercial butane mixtures. Having both saturated and unsaturated hydrocarbons. It is produced as a by- product of Natural gas processing. Figure 1.

Propane feed contains mainly COS and methyl mercaptans and the butane feed contain mainly ethyl mercaptans as impurities, therefore desulfurization process is required.

Maximum sulfur compounds and mercaptan removal from propane and butane cut are necessary because these hydrocarbons need to comply with commercial grade LPG specification.

Desulfurization process is based on the use of caustic soda wash process with caustic regeneration. The low molecular weight mercaptans in the propane and butane cuts are very soluble in the caustic solution so when hydrocarbon and caustic phases are intimately contacted they are absorbed in the caustic solution.

This caustic which is called rich caustic need to be regenerated by oxidation with air in the presence of a liquid catalyst, it is important to reuse this regenerated caustic to the maximum extent to save on operating costs and to stay within product specifications. [1]



Figure 1. Gas Processing Refinery and LPG treatment Unit.

Following reactions describe the process:

- (1). R-SH +NaOH \rightarrow RSNa + H₂O
- (2). $4RSNa + O_2 + 2H_2O \rightarrow 2RSSR + H_2O$

Where R-SH is mercaptan, RSNa called Mercaptide and RSSR is Disulfide Oil (DSO) which is a by-product and will be sent to storage after passing a three phase separator. Figure 2. In case of existence of acidic gases; hydrogen sulfide (H_2S) and Carbon Dioxide (CO₂) react with caustic

under following competing reactions:

- (1). $H_2S + 2NaOH \rightarrow Na_2S + 2H_2O$
- (2). $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$
- These secondary reactions cause several problems:
- (1). Caustic is irreversibly consumed and must be replaced.
- (2). The presence of sodium salts in caustic solution will reduce its property to absorb mercaptans
- (3). Salt accumulation can cause precipitates



Figure 2. Caustic regeneration unit in LPG process.

According to above explanation a part of caustic soda need to be removed from DSO separators to be replaced by new fresh caustic to keep the operation efficient.

The removed portion is full of refractory pollutant like salts and sulfur compounds as described. This waste is known Sulfidic spent caustic (SSC) which is classified by RCRA (US Resource Conservation and Recovery Act) as hazardous waste [12].

1.2. Sulfidic Spent Caustic Characteristics

Without treatment, SSC stream may cause environmental problems because of their alkalinity (pH>12), salinity (Sodium of 5-12% wt) and high Sulfidic S⁻² level exceeding (2-3% wt.). [2]. this stream has a high content of chemical oxygen demand (COD) and biological oxygen demand (BOD). Current levels of removal of the pollutants from wastewater which can be achieved using the conventional water treatment technologies are often not sufficient; especially when wastewater streams contains significant amounts of hardly biodegradable chemicals [4]. Spent caustic characteristics can greatly vary from refinery to refinery; it may contain high concentration of sulfides, disulfides, mercaptans, phenolic compounds, amines, hydroxides and other hydrocarbons depending upon its origin [5]. several efforts have been made in recent decades to develop a better option to treat spent caustic [6], mostly all efforts were based on convert sulfides to elemental sulfur or sulfate that are preferred finishing product as it does not represent COD and may be allowed to be discharged into the environment [3].

According to hierarchical approach for solving pollution problems. At the base is pollution prevention /waste minimization, which is and should be most preferred approach [7].

Note that considering spent caustic as a raw material for producing a chemical could be the best way for waste minimization and pollution prevention as a result beside of benefit of its product.

1.3. Sodium Sulfate Salt

Sodium sulfate is used mostly in detergents but also finds use in sodium sulfide production and glass, pulping, and textile applications. Detergent applications have shown steady growth, especially in developing countries; in 2016, detergent uses account for about 39% of global consumption. Sodium sulfide production accounts for 19% of total sodium sulfate consumption in 2016; this market is almost exclusively in China, where sodium sulfide is still produced by reduction of sodium sulfate with powdered coal. Glass is the third-largest use for sodium sulfate, and is also the market most impacted by economic conditions (especially for construction markets and automobile production) [13].

Although data on mine production for natural sodium sulfate is estimated to be about 6 million tons. Total word production of byproduct sodium sulfate is estimated be between 1.5 and 2 million tons [14].

2. Materials and Methods

The process of sodium sulfate production from Spent Sulfidic caustic is consisting of following steps:

2.1. DSO Removal

As mentioned before spent sulfidic caustic would be separated from DSO separator, therefore DSO contamination is possible.

DSO Removal could be done easily by separators or hydro cyclones depending upon the cost and rate.

If retention time in separator is acceptable based on feed/time, then using separators and skimming are preferable, because of difference in density of oil and aqueous solution.

2.2. Filtering

According to the method of spent caustic collecting, there are a majority of suspended solids waste inside the liquid, a simple filtering make it clean enough for entering next stage.

2.3. Advance Neutralization

This stage is the most important part and divided into 3 sections

- (1). Reducing the pH down to 2.8 by using Sulfuric acid
- (2). Leave the sample for 72 hrs. for growing the sodium sulfate crystals (after 8 hrs. crystal growing start and may continue to 72 hrs.)
- (3). Adding droplets of NaOH (1N) to adjust the pH on 7.

We call it advance Neutralization because in conventional neutralization which is common in gas refineries we got no result but consuming too much acid. The volume of consumed acid vs. pH changing is shown in Figure 3. It shows the difference amount of acid for changing pH from 7 to 2.8 is not so much and the whole of required acid is 6.5% of sample when using H₂SO₄ with concentration of 95-97% and in case of using higher concentration the consumed volume may reduce. In this stage the crystals of sodium sulfate is growing by time and after 72 hrs. It will occupy nearly half of the volume of sample beaker Figure 4.

Acid Consumption vs. pH value



2.4. Final Filtering

The bulk could be removed easily and for more efficiency a 30 µm filter is proper choice. Figure 5.



Figure 4. Sodium sulfate before filtering.



Figure 5. Extracted salt after filtering.

3. Results and Discussion

3.1. Sodium Sulfate as a by Product of LPG Process

Sodium sulfate occurs in nature as the minerals mirabilite and thenardite while thenardite is the anhydrous form of Na₂SO₄.10H₂O.

Sodium sulfate is one of the most important sodium salts. The decahydrate, commonly known as the Glauber's salt, was first prepared by Johann Glauber in the seventeen century as a byproduct in making hydrochloric acid from sulfuric acid and sodium chloride [8]. It is produced from naturally occurring sodium sulfate –bearing brines or crystalline evaporate deposits and as a byproduct from different chemical process.

Byproduct sodium sulfate recovery has been derived from primary production of ascorbic acid, cellulose, flue gas desulfurization, hydrochloric acid, lithium carbonate, rayon, resorcinol, silica and sodium dichromate manufacture. Virtually all the locations are in the Midwest, south and the east.

Sodium sulfate has been recovered as a waste product from these manufacturing processes and has competed with sodium sulfate produced from natural sources [9]. As mentioned earlier spent caustic is a waste from LPG sweetening process and when sodium sulfate is obtaining from spent caustic we may claim sodium sulfate is a byproduct of LPG sweetening process but more efficient and much easier to produce.

3.2. Analysis of Obtained Sodium Sulfate

3.2.1. X-Ray Diffraction (XRD)

X-Ray diffraction is a non-destructive technique for analyzing the structure of materials, primarily at the atomic or molecular level it works best for materials that are crystalline or partially crystalline (i.e., that have periodic structural order) but is also used to study non-crystalline materials. XRD relies on the fact that X-Rays are a form of light, with wavelengths on the order of nanometers. When X-Rays scatter from a substance, with structure at that length scale, interference can take place, resulting in a pattern of higher level intensities.

This is qualitatively similar to the colorful patterns produced by soap bubbles in which different colors are viewed in different direction [10].

3.2.2. X-Ray Fluorescence (XRF)

XRF is an analytical method to determine the chemical composition of all kinds of materials; the materials can be in solid, liquid, powder, filtered or other form.

XRF can also sometimes be used to determine the thickness and composition of layers and coating, the method is fast, accurate and non-destructive and usually requires only a minimum of sample preparation, the precision and reproducibility of XRF is very high. Very accurate results are possible when good standard specimens are available, but also in applications where no specific standards can be found [11].

X-Ray fluorescence (XRF) and X-Ray diffraction (XRD) analyzers provide qualitative and quantitative material characterization for detection, identification and analysis. We have needed both analyses to identify the obtained crystal as well as its purity; these are shown in table 1 and 2 respectively and Figure 6 shows the X-Ray diffraction pattern of Na_2SO_4 .

Table 1. Sodium Sulfate XRD Result (Test by Razi Metallurgical Centre.

XRD Test				
Certified under ISO/IEC17025	Sample: Sodium Sulfate			
Humidity: 30%	T: 25°C Ref: ASTM E 1621-13			
Current: 30 mA	/ Voltage: 40 KV Anode: Cu			
20: 4-70°C	Step Size: 0.05	counting time: 0.5 Sec.		
XRD Result for Sample:				
1.	Thenardite	Na ₂ SO ₄		
2.	Mirabillite	Na ₂ SO ₄ .10H ₂ O		

Table 2. Sodium Sulfate XRF Result (Test by Razi Metallurgical Centre).

XRF Test				
Certified under ISO/IEC17025	Sample: Sodium Sulfate			
Humidity: 30%	T: 25°C	Ref: ASTM E 1621-13		
Quantity and Quality Analysis				
wt. %	Comp.			
0.1	K ₂ O			
52.11	SO ₃			
1.9	MgO			
40.09	Na ₂ O			
89%	Na ₂ SO ₄			
9%	Na ₂ SO ₄ .10H ₂ O			
< 1	La&Lu			
5.8	L.O.I			

*L.O.I measured in 950°C for 1.5 hrs.



Figure 6. X-Ray diffraction pattern of Na₂SO₄.

It is noticeable that this crystal is taken from beaker directly and no more purification has been done on that. It is obviously that the purity could be improved. This is not a simple acid and base reaction, this is not sulfuric acid and soda reaction which is known since 1830, we have to emphasis on that because could make a big misunderstanding and invalid our research consequently. We are not talking about aqueous sodium sulfate in solution, but a crystalline sodium sulfate which can be extracted easily in solid phase. Figure 7 and Figure 8.



Figure 7. Right sample is spent caustic and left one is NaOH solution (9.5%wt).

To prove that spent Sulfidic caustic is the raw material for producing sodium sulfate we need to check other probable reaction.

The first reaction which can produce sodium sulfate theoretically is

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

To understand how reaction of our first guess could be involved in producing sodium sulfate, following test has been implemented. First a sodium hydroxide solution with concentration of 9.5% prepared. This is the same concentration of NaOH in spent Sulfidic caustic, and then same advance neutralization has been done for both samples. i.e. the same amount of Acid consumed and final pH were near to each other Figure 7, crystallization in spent caustic was occurred while no change in fresh caustic happened sodium sulfate in fresh caustic is in aqua phase. Therefore the first guess could not be involved in sodium sulfate formation.

The second attempt was studying about effectiveness of Na_2S by using 2 different solutions of Na_2S and compare them with spent Sulfidic caustic see table 3.



Figure 8. Sodium sulfate extracted from Spent caustic.

	Table 3. Study on Na2S Solution	n effectiveness in	sodium sulfate production	
-			-	

Sample Tag.	TS1	TS2	TS3
Identity	Spent Caustic	Na ₂ S.sol. (100 mg/l)	Na ₂ S.sol. (Wt. 1%)
pH _{Initial}	12.18	10.46	12.13
pH _{Final}	2.8	2.84	2.93
Acid Consumption	15 ml.	1 droplet	40 droplets
Crystallization	Yes	NO	NO

As crystal obtained in TS1 and noting happened in TS2 and TS3 it may show that individual Na₂S cannot be the reason for sodium sulfate production.

These experimental tests are shown that artificial spent caustic cannot be known as raw material of producingsodium sulfate and several complicated reactions might be involved with producing sodium sulfate as a final product.

4. Conclusions

Spent caustic as araw material for producing a chemical could be the best way for waste Minimization and pollution prevention as a result beside of benefit of producing a valuable industrial salt. XRD and XRF tests both confirmed that this could be an acceptable raw material for producing sodium sulfate which is done for first time. Therefore Sulfidic spent caustic could be known as a byproduct of LPG process units and no more called as a hazardous waste, the remain filtrate is clear, odorless and ready for reuse or other treatment activity.

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