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DESIGN OF CAUSTIC WASH SYSTEM FOR LIGHT HYDROCARBONS SUCH AS LPG , NGL AND NAPHTHA

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Abstract. *Impurities such as* H_2S *and RSH in light hydrocarbons usually causes bad odor, corrosion problem and air pollution after combustion . Therefore, elimination of these impurities is very important.*

One of the processes for removing these components is " Caustic Wash Process " that is applied in refineries and petrochemical plants for extraction of H_2S *and RSH and organic acids from hydrocarbons. This process is safe, economic and performance effective which is also safe for environment.*

In this article we try to present the design principles of caustic wash system which is based on modified extraction method. For design of semi batch process, a mathematical relation between extraction coefficient and published experimental data has been used.

By applying this relation and material balance over the system, the differential equations is solved which is based on a computer program. The flow chart of this program and the two applied examples are presented in this article. One of these examples is the caustic wash system which is designed for Kharg Petrochemical Co. of Iran.

Key words: *caustic wash, extraction, demercaptanization, sweetining,* H_2S*, mercaptane*

Introduction

One of the impurities which usually is found in oil fractions is sulfur compounds. In light hydrocarbon fractions, sulfur is usually in the form of hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptan (RSH).

These sulfur contaminates not only make odor in oil fractions but also during the combustion they will be oxidized and make the air polluted.

Furthermore, corrosion problems of these compounds are important and have undesirable effects on down stream catalysts. Such as methyl mercaptan which is very corrosive and toxic.

Sulfur compounds of oil fractions are:

1. LPG, contains of hydrogen sulfide (usually at high concentration) and methyl and ethyl mercaptans.
2. NGL, contains of H_2S and methyl and ethyl mercaptans and some times may have CS_2 and COS.
3. Gasoline, contains of H_2S plus light and heavy mercaptans, and even Butyl mercaptan concerning of different oil fractions.

For example hydrogenated and debutanized light gasoline have trace H_2S and /or produced gasoline from hydrocracking has also trace H_2S and a considerable amount of mercaptans.

Among different methods for removing sulfur compounds of hydrocarbons , caustic wash method is more economical (safe and simple) than the other methods. (e.g. absorption by Amine solutions.)

Caustic Wash

5-15 w% aqueous caustic solution is usually used. (for mercaptans with high boiling point, caustic concentration may be over 15-20 w%). The following reactions occur during washing stage:

$$H_2S + NaOH \rightarrow NaSH + H_2O$$

$$NaSH + NaOH \rightarrow Na_2S + H_2O$$

$$CH_3SH + NaOH \rightarrow CH_3SNa + H_2O$$

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

Where R indicates other hydrocarbon radicals.

This process can be done batch wise (concerning of the caustic phase) or continuous by counter current streams. In the counter current process, the rate of mass transfer of acid to caustic solution, is controlled with resistance of gas phase for high soluble gases and by resistance of liquid phase for low soluble gases.

Absorption of hydrogen sulfide is done like other acidic compounds with chemical, relations in the liquid phase, so the rate of absorption is controlled only by resistance of mass transfer in the gas phase.

In most refineries, caustic wash is done in a batch system. This system includes:

Mixer, settler, and pump for caustic circulation.

A process flow diagram of a two caustic wash stages system has been shown in Figure 1.

As shown the mixer in this process is a mixing valve. Sometimes static mixer can be used instead of mixing valve. In this system caustic is consumed and its concentration is diluted (because of water production in the process). Therefore it is necessary that a portion of spent caustic to be drained and fresh caustic with high concentration added to regulate Caustic concentration to apply again.

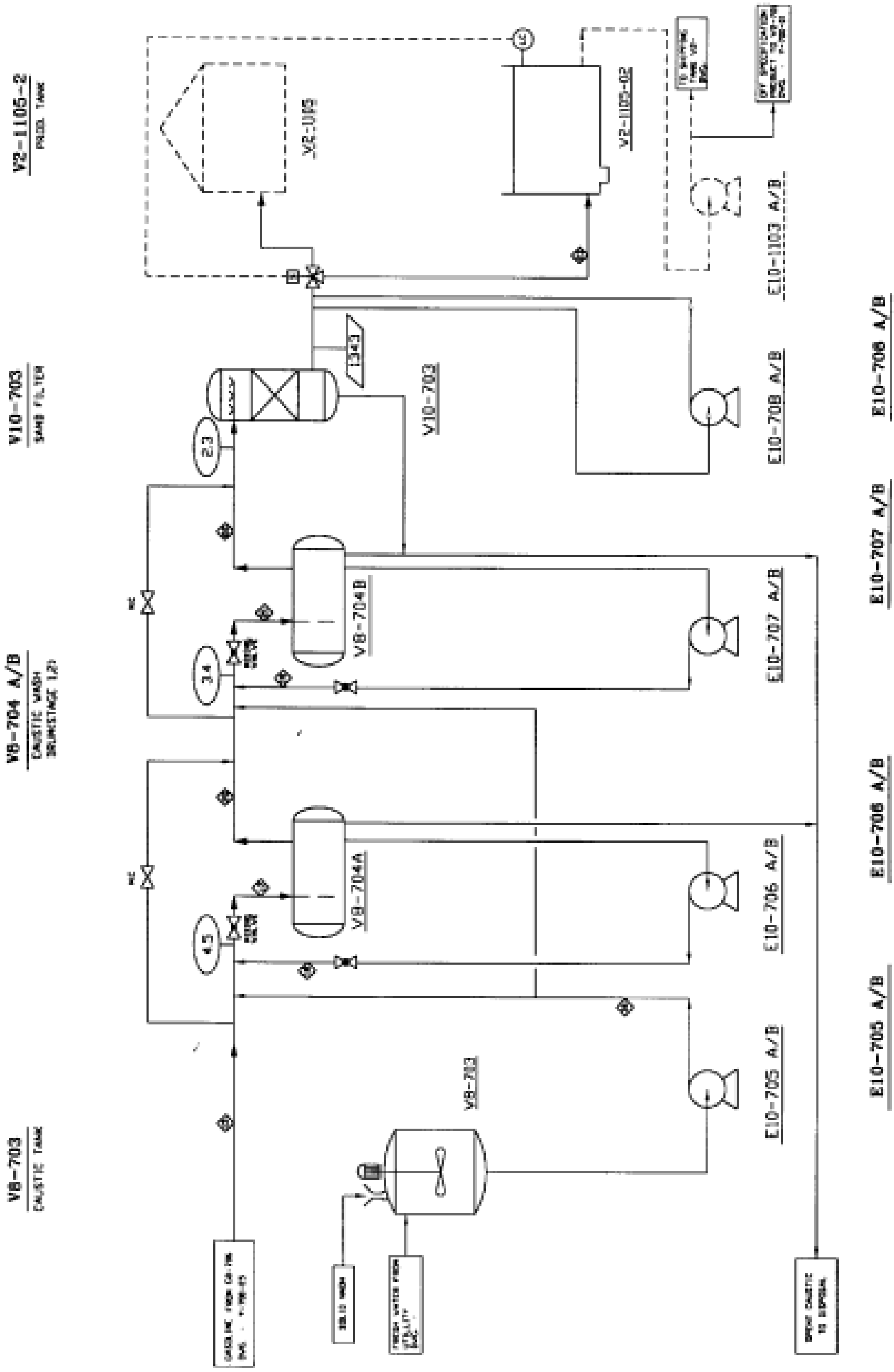

Figure 1. Sem+i batch process flow diagram of two stage caustic wash

Design Method

A design method for a unit, with using a continuous and counter current system has been presented by Yabroff, in which hydrocarbon fractions and caustic solution flow continuously with a specific ratio and a low percentage of caustic solution. In this condition it can be assumed that the extraction coefficient is constant and is a function of fresh caustic molarity.

This assumption is valid when caustic solution consumption is negligible however this is not true for a batch and counter current unit.

Another method has been presented by Beychok [2] for a semi batch and single stage unit that its calculations contain different stages and the results only presents the average concentration of outlet stream. This paper uses a logarithmic mean for extraction coefficient that can present real concentration of sulfuric compounds in outlet stream in a batch system. Also this paper presents an equation which indicates relation between the extraction coefficient of each acidic sulfur compound and molarity of caustic using the experimental data.

Extraction Coefficient

An acidic compound (i) has extraction coefficient (k_i) which is a ratio of the weight of acidic compound in a volumetric unit of caustic solution to the weight of acidic compound in a volumetric unit of hydrocarbon.

This extraction coefficient is a function of caustic molarity. The experimental data can be replaced in the following equation:

$$k_i = A_i(m_i)^{Bi}$$

A_i and B_i are experimental constants of each acidic component. These constants for different sulfur compounds have been presented in Table (1).

Table 1. Experimental Extraction Coefficient for sulfur compounds

Sulfur compound	Ai	Bi
H_2S	801678.1	1.084
CH_3SH	549.5	0.674
C_2H_5SH	100.9	0.727
C_3H_7SH	20.0	0.552
C_4H_9SH	3.8	0.543

As the molarity of caustic changes during the time therefore, a logarithmic mean has been calculated which is assumed constant within the process.

1. $k_i l_m = \dfrac{k_{if} - k_{it}}{k_{if} / k_{it}}$

2. $k_{if} = A_i[m_f(1-s_f)]^{B_i}$

3. $k_{it} = A_i[m_f(1-s_t)]^{B_i}$

4. $M = M_f(1-s)$

In these equations, s, is the mass fraction of caustic, also according to the extraction coefficient:

$$k_i = \frac{w_i}{x_i}$$

w_i, x_i are the weight of acidic compound in the volumeteric unit of caustic solution and in the volumeteric unit of hydrocarbon stream respectively.

Calculations

In a semi batch single stage process, the weight of removed acidic compound from the hydrocarbons is equal to the absorbed acid by the caustic solution:

$$F(x_{if} - x_{it})dt = vdw$$

F = Hydrocarbon flowrate.

V = Caustic solution volume

Based on extraction coefficient definition , compute as follows :

$$X_{it} = \frac{W_{it}}{K_{it}} = \frac{W_{it}}{K_{iLM}}$$

$$\mathrm{F}\,(X_{if} - \frac{W_{it}}{K_{iLM}})dt = Vd\,W_{it}$$

$$\frac{F}{K_{iLM}V}dt = \frac{dW_{it}}{k_{iLM}\;X_{if} - W_{it}}$$

$$\frac{Ft}{K_{iLM}V} = -\ln(K_{iLM}X_{if} - W_{it})\Big|_{W_{if}}^{W_{it}}$$

$$\frac{-Ft}{K_{iLM}V} = \ln\left(K_{iLM}X_{if} - W_{it}\right) - \ln\left(K_{iLM}X_{if} - W_{if}\right)$$

$$\frac{-Ft}{K_{iLM}V} = \ln\frac{K_{iLM}X_{if} - W_{it}}{K_{iLM}X_{if} - W_{if}}$$

$$K_{iLM}X_{if} - W_{it} = (K_{iLM}X_{if} - W_{if})\exp(-{}^{Ft}\!/_{K_{iLM}V})$$

$$W_{it} = K_{iLM}X_{if} - K_{iLM}X_{if}\exp(-{}^{Ft}\!/_{K_{iML}V}) + W_{if}\exp(-{}^{Ft}\!/_{K_{iML}V})$$

$$W_{it} = K_i X_{if}[1-\exp(-a_i t)] + W_{if}\exp(-a_i t) \quad , \qquad a_i = \frac{F}{K_i V}$$

$$W_{it} = S_{it}M_f M_{wi/120}$$

$$W_{if} = S_{if}M_f M_{wi/120}$$

$$S_{it} = \frac{120K_i X_{if}}{M_f M_{wi}}[1-\exp(-a_i t)] + S_{if}\exp(-a_i t)$$

$$Z_i = \frac{120\,K_i X_{if}}{M_f M_{wi}}$$

$$S_{it} = Z_i[1-\exp(-a_i t)] + S_{if}\exp(-a_i t)$$

$$S_{it} = Z_i[1-\exp(-a_i t)]$$

$$S_t = \sum Sit \quad = \sum Zi[1-\exp(-a_i t)]$$

Computer Program and Solutions

Computer program algorithm has been shown in Figure 2. In this program w_{it} and x_{if} are calculated through equation 12 and 5 respectively.

This flow chart is just for a single stage and can not show the program completely.

If caustic solution enters to the first stage from the second stage, the program will consist of 3 1oops, the main 1oop and 2 internal 1oops. The internal 1oops check the S_t of the first and second stages, however the main 1oop compares the s_{if} of the first stage with the S_{it} of the second stage, also x_{if} of second stage with x_{if} of the first stage in each iteration.

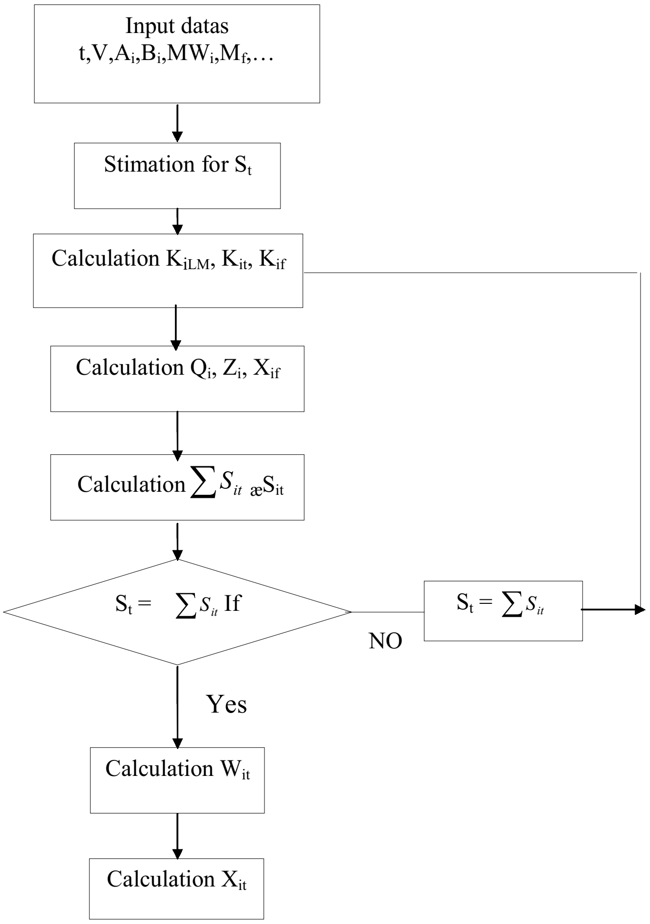

Figure 2. computer program flowchart

Case Studies

1. The flow of LPG is washed with caustic solution in two stages. Feed specification and process conditions have been presented in Table 2. The main purpose of this process is that the maximum concentration of sulfur compounds in this stream decreases to 20 ppm. Instead of the concentration regulation, caustic solution from the second stage is replaced with the first stage and the caustic solution from the first stage is conducted to the disposal system, With using the above mentioned, the results are as the following:

-After 72 hours about 15% of caustic solution from the first stage is consumed and the total H_2S will be removed. Also the concentration of methyl mercaptan and Ethyl mercaptans in outlet line will be 24.6 ppm and 66.8 ppm respectively. Then LPG enters to the second stage. In this stage after 72 hours, about 1.5% of caustic solution will be consumed and the concentration of methyl mercaptan and Ethyl mercaptan in outlet line will be reduced about 1.3 ppm and 15.9 ppm respectively.

Table 2. Feed Characteristics and LPG process specification

Flow rate kg/hr	11000
Density kg/m^3	510
Sulfur compounds	ppm
H_2S	60
CH_3SH	432
C_2H_5SH	217
Caustic volume (gal)	6840
Fresh caustic weight percent	10.6

2. Gasoline flow enters to two stages of caustic-washing system. Feed specifications and process conditions have been presented in the table 3. The maximum concentration of sulfur compounds in this process will be decreased to about 400 ppm. After using the software , the results are:

- After 36 hours, 16% of caustic solution from the first stage is consumed and the total H_2S will be eliminated. Also the concentration of methyl mercaptan and ethyl mercaptan and plopyl mercaptan in outlet line, Will be 13.2 ppm, 86.6 ppm and 402.1 ppm respectively. Then this gasoline stream enters to the second stage.

-After 36 hours 15% of caustic in second stage is consumed and the concentration of methyl mercaptan, ethyl mercaptan and plopyl mercaptan will be reached to 0.8 ppm, 24 ppm and 359.2 ppm respectively.

Table 3. Feed characteristics and process specification
of kharg Gasoline

Flow rate Kg/hr	5405
Density kg/m^3	652.47
Sulfur compound	ppm
H_2S	75
CH_3SH	200
C_2H_5SH	300
C_3H_7SH	446
Caustic volume in vessels (m^3)	2.5
Fresh caustic weight percent	20

This example is a case study of Kharg Petrochemical Co.. For over design consideration the maximum duration of each stage of design is 24 hours, which is under construction.

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