PROJECT 2 OF THE CAREER

INTRODUCTION

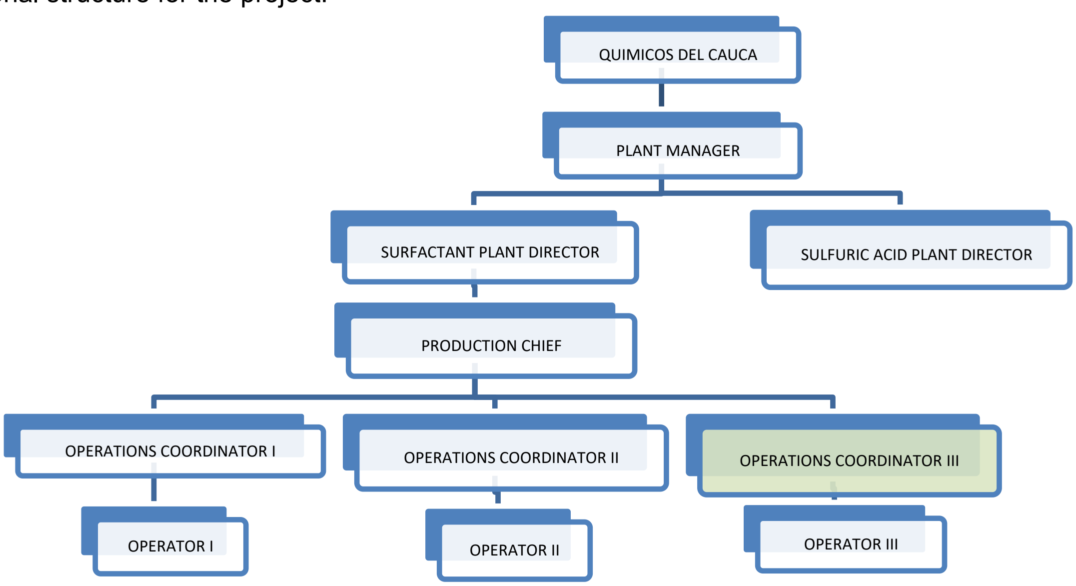
2.1 **Project:** Management of the operational parameters of the sulphated alcohol plant for the multinational Unilever.
Company: Químicos del Cauca SAS.
Name: Miguel Angel Paz Rosero.
Job position: Operations Coordinator.
Location: Caloto, Cauca – Colombia.
Date: September 7, 2017 - July 24, 2020.

BACKGROUND

2.2 This project involved parameterising the processes in the sulphated alcohol plant, oriented towards start-up, to produce Sodium Lauryl Ether Sulphate of 1 mol (SLES 1EO) as a raw material with the quality specifications required by Unilever for its portfolio of personal care products.

2.3 Químicos del Cauca is a company that manufactures and markets surfactants for home care, personal care, and agrochemical applications. The sulfonic acid production plant commenced operations in March 2002. In May 2015, it inaugurated the sulphated alcohol production plant, which has supplied companies such as Colgate, Unilever, Reckitt, Dersa, Belleza Express, and others.

2.4 Organisational structure for the project:



2.5 The project was born in response to a globalised market of personal care products and the need to expand the parameterisation of the operation, control and monitoring of the sulphated alcohol production plant. This is achieved by means of changes in operational parameters (lauryl alcohol/sulphur trioxide flow ratio, use of lauryl alcohol of different ethoxylations (1, 2 or 3 mol), dosing of neutralisation inputs, valve opening set-point. This involves increasing production and optimising the parameters from the current operation to the new one.

2.6 As Operations Coordinator, my responsibilities were:

- Operate, control and monitor the operation of the sulfonic acid and sulphated alcohols production plant; comply with the requirements of production, quality, environmental control and safety requirements.
- Analyse process variables to inform decision-making in product quality and meet established standards.

- Lead the production work group in the two sulfonation and sulfation plants.

PERSONAL ENGINEERING ACTIVITY

2.7 The sulfation process generates mass consumption products in home and personal care, which consist of adding an SO_3 molecule (sulfuric anhydride) to an organic molecule to form a sulphur-carbon bridge, in this case, a lauryl alcohol ethoxylate. This process involves the conversion of lauryl alcohol to sodium lauryl ether sulphate (SLES), an ingredient in shampoos, toothpastes and dishwashing detergents. SLES is a surfactant that reduces the surface tension of water, allowing it to remove dirt and oil. The dirt removal efficiency is based on the number of moles of ethoxylated alcohol; the higher it is, the less aggressive it will be in generating irritation during use, but less effective in its removal. The most commonly used is lauryl alcohol, specifically 3-mol (3EO), followed by 2EO and 1EO.

2.8 In 2019, Unilever requested Químicos del Cauca's product SLES 1EO for inclusion in its portfolio in response to a globalised market of personal care products and the need to expand the parameterisation of the operation, control and monitoring of the sulphated alcohol production plant. For this, I assumed responsibility for the project and requested the client's specifications:

Buen día Hoover y Pedro,

Espero se encuentren muy bien.

A continuación les envío las especificaciones del SLES 1EO para Unilever y la especificación deseada:

	Especificación	**Especificación deseada**
Materia Activa (%)	68.5 – 71.5	Min 70
pH (4%)	6 – 8.5	6.5 – 7.5
Material no sulfatado (%)	1.3 – 3	2- 3
Contenido de sólidos	70.3 – 76.3	Asegurar un activo mayor a 70%
Sulfatos (%)	< 1	
Color APHA 20%	**Max 70** (max 40 klett 20%)	
Peróxido de hidrogeno	Max 20ppm	
Buffer	0.5% ácido cítrico	

Con el fin de asegurar un material no sulfatado entre el 2 y 3% el rango de valor ácido sugerido es de **174 – 177 mg KOH/g.**

Quedo atenta a cualquier inquietud,

Cordialmente,

Laura María

Figure 1. Unilever email to surfactant plant director and production chief on SLES 1EO specifications.

I established the project scope, which consisted of parameterising the processes in the sulphated alcohol plant, oriented towards start-up, to produce Sodium Lauryl Ether Sulphate of 1 mol (SLES 1EO) as a raw material with the quality specifications required by Unilever for its portfolio of personal care products, replacing imports from other countries with a domestic solution. I selected the work team for the implementation of LESS 1EO, including the operator coordinator, plant assistants, and auxiliaries, under my supervision and validated by the production manager. In order to achieve a contract with this company and a huge profit for Químicos del Cauca S.A.S.

2.9 I established the stages of the **sulfation** process to perform the parameterisation, starting from the reaction to form an alkyl pyrosulfuric acid, followed by a slower reaction to generate alkyl sulfuric acid:

$$R - EO_{\mathrm{n}} - OH + 2SO_3 \rightarrow R - EO_{\mathrm{n}} - O - SO_2 - O - SO_2 - OH$$
$$R - EO_{\mathrm{n}} - O - SO_2 - O - SO_2 - OH + R - EO_{\mathrm{n}} - OH \rightarrow 2R - O - SO_2 - OH$$

Formula 1. Sulfation reaction with lauryl alcohol ethoxylate.

This acid is thermally unstable, so I avoided high sulfation temperatures and neutralised it. This process is done by means of the SO_3 stream that comes from the sulfuric acid plant (QBC - Química Básica Colombiana) at a concentration between 5-8%, and diluted with ultra-dry air (***Figure 2***), to reduce it to 3-5% and that enters the 37 tube reactor for the reaction. See ***Figure 3***:

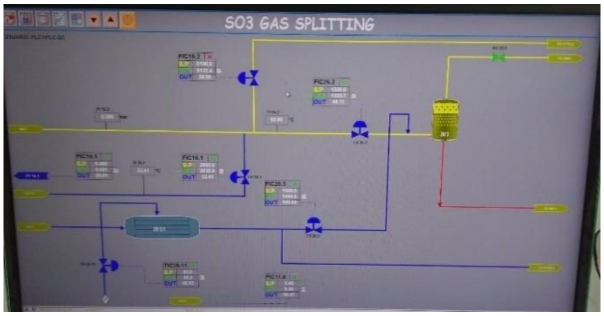


Figure 2. SO_3 flow distribution lines – SO_3 flow lines, dry and ultra-dry air to sulfonation and sulfation

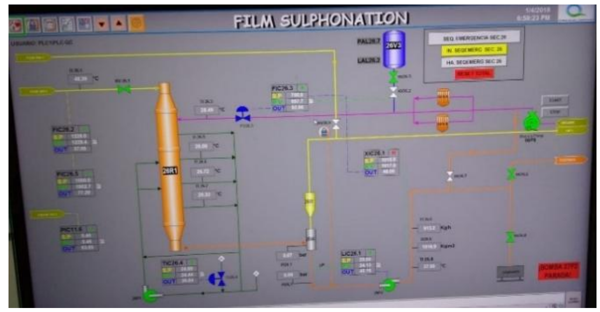


Figure 3. Sulfation - Tubular Reactor

I compared the current process (lauryl alcohol 3EO) with the information in ***Figure 1***. In addition, I researched lauric alcohol 1EO and compared it with the current 3EO in terms of hydroxyl number, molecular weight, and acid value in sulfation in order to understand the parameters that need to be changed. This information was provided by the company's quality department, which was conducting tests with different types of lauryl alcohol ethoxylate, obtaining:

Table 1. Acid value for each type of lauryl alcohol

Alcohol	Hydroxyl number (N°-OH)	Molecular weight (g/mol)	Acid value (mg KOH/g)
3 mol	165-170	330-340	152-158
1 mol	231-240	233-243	174-177

I required a higher flow rate of SO_3 to obtain SLES 1EO, and a higher flow rate of dry air to avoid the formation of 1,4-dioxane. To establish the parameters for SLES 1EO production, I considered:

Table 2. Comparison of operating conditions SLES 3EO vs. SLES 1EO

Operating conditions SLES 3EO	Operating conditions SLES 1EO
- Molar ratio SO_3/alcohol = 1.01-1.02	-1.02-1.03
- SO_3 required = 3-5% molar	- 3% molar maximum
- Organic temperature = 25°C	- 25°C
- Sulfation temperature = 35-40°C	- 38-45°C
- Dry air flow rate/SO_3 flow rate ratio = 1.20-1.25	-1.40-1.45

2.10 **Neutralisation.** The acid from the previous stage is volatile and can undergo a reversible reaction; therefore, it must be neutralised with 32% sodium hydroxide. The neutralisation pH must be between 9 and 11, avoiding low pH points that favour the hydrolysis of the product, which generates H_2SO_4 and therefore produces an unrecoverable product and corrosive byproduct. This process is done with a double-step neutralisation, which consists of the addition of water and NaOH to lauryl ether sulphate acid in a mixer to obtain SLES with the appropriate active material. See ***Figure 4***.

I deduced that the acid produced has a lower pH when using lauryl alcohol 1EO than when using lauryl alcohol 3EO, resulting in a greater requirement for sodium hydroxide in the process. To establish the parameters for the production of SLES 1EO, I considered the following conditions with SLES 3EO:

- Maximum time to neutralise acid = 1.5 minutes.
- Maximum pressure in the neutralisation loop = 4.8 bar (SLES 70%) and 2.5 bar (SLES 28%)
- Neutralization temperature = 38°C
- Pump piston position of neutralisation SLES 70% = A: 0% (water), B: 8% (water), C: 31% (NaOH) and D: 80% (NaOH)

- Pump piston position of neutralisation SLES 28% = A: 40% (water), B: 15% (water), C: 31% (NaOH) and D: 80% (NaOH)

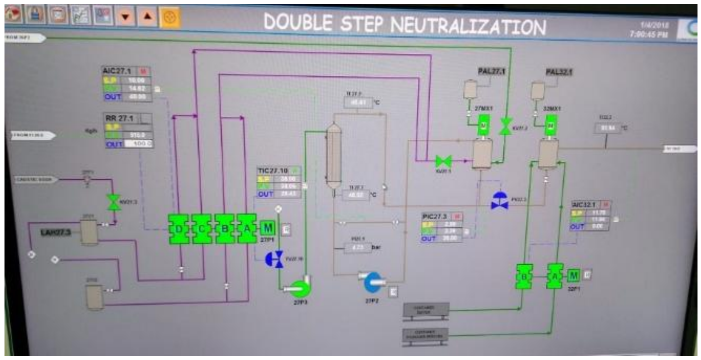


Figure 4. Neutralisation - Double Pass (use of two mixers)

I established the following operating conditions for production SLES 1EO:
- Maximum time to neutralise acid = 1 minute
- Maximum pressure in the neutralisation loop = 5 bar (SLES 70%) and 3 bar (SLES 28%)
- Neutralisation temperature with cooling = 40°C
- Pump piston position of neutralisation SLES 70% = A: 0% (water), B: 4% (water), C: 40% (NaOH) and D: 100% (NaOH)
- Pump piston position of neutralisation SLES 28% = A: 35% (water), B: 5% (water), C: 40% (NaOH) and D: 100% (NaOH)

2.11 Homogenisation

The SLES from step one has an alkalinity greater than 0.2 and must be neutralised to achieve a pH of 7.0. In step two, the alkaline SLES is passed to another mixer with citric acid at 50% and hydrogen peroxide at 15% for homogenisation, see ***Figure 4***:

- ❖ Citric acid neutralises and forms sodium citrate, a buffer that stabilises the pH of the SLES.
- ❖ Hydrogen peroxide bleaches the SLES by breaking conjugated carbon-carbon bonds (C=C) to prevent the formation of opaque products.

Neutralisation, being a reaction that requires more sodium hydroxide in SLES 1EO compared to SLES 3EO, necessitates an increased dosage. Additionally, since its sulfation process requires a higher acid value, its reversible reaction forms an opaquer acid that will require more hydrogen peroxide in SLES 1EO compared to SLES 3EO. To establish the parameters for the production of SLES 1EO, I considered the following conditions with SLES 3EO:

Pump piston position of additive = A: 40% (citric), B% 10% (peroxide)

I established the following operating conditions for production SLES 1EO:

Pump piston position of additive = A: 55% (citric), B% 15% (peroxide)

2.12 Deaeration

The product generated is a white fluffy SLES, which is taken to the adjustment tanks of the production batch, adjusting with:

- ❖ SLES 70%: Sodium hydroxide and/or citric acid, to reach the desired pH (from 6.5 to 8.5); hydrogen peroxide (Max 20 colour on Klett scale) and chlorinated water for the adjustment of the active material (from 69.5 to 71.5).
- ❖ SLES 28%: Sodium hydroxide and/or citric acid equal to SLES 70%, additional phosphoric acid to form sodium phosphate (pH balancing buffer); hydrogen peroxide (Max 20 colour on Klett scale), chlorinated water for active material adjustment (from 27.5 to 29.0), formaldehyde to avoid formation

of microorganisms (more than 60% water content) and, in some clients, salt and/or excess lauryl alcohol ethoxylate. The SLES 1EO is processed at this stage as the SLES 3EO.

Once adjusted (***Figure 5***), it is deaerated using a vacuum pump to improve the appearance of the paste, decrease its viscosity, facilitate pumping and storage:

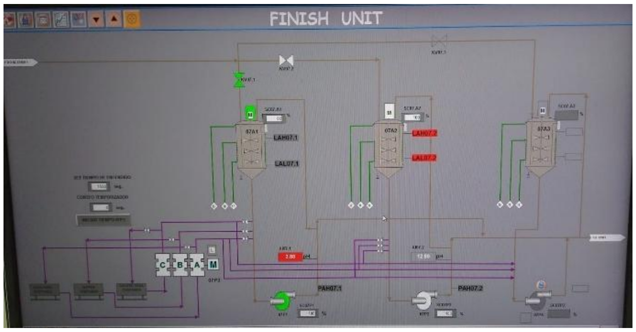


Figure 5. Adjustment tanks SLES

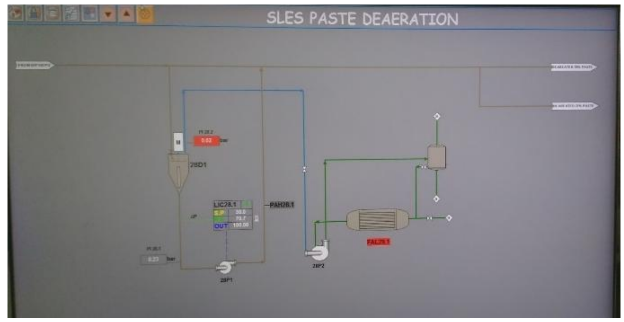


Figure 6. Vacuum system for SLES deaeration

2.13 **Gas treatment**

It consists of reacting residual SO_2 and SO_3 to convert to sulphates using oxygen:

$$1.)\ SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$
$$2.)\ SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$
$$3.)\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

Formula 2. Formation reaction of sulphite and sodium sulphate.

A *scrubber* recirculates the water and sodium hydroxide with a pH between 6 and 7 (***Figure 7***). This mixture captures SO_2 and SO_3, and reacts to form sulphites and sulphates. The drop in pH forms sodium bisulphite:

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

Formula 3. Formation reaction of sodium bisulphite (pH 4.5-5.0)

Figure 7. Gas scrubbing - Sulfonation and Sulfation

I established the following operating conditions for production SLES 1EO:

- Sulphite and sulphate formation time = 60 minutes and sodium bisulfited = 40 minutes.

2.14 I compiled information on operating conditions at each stage of LESS 3EO production to generate operating conditions at each stage of LESS 1EO production, taking into account the limitations of the current plant for its start-up with the new product. I established the following comparative table for the output of the SLES 1EO, referring to 3EO, emphasising the differentiating elements, and the identical ones referred to as “Idem”:

Table 3. Aspects to consider at key moments of the SLES 3EO vs. SLES 1EO process

Moment of the process	*Aspects to monitor, frequency*	*Operating aspects Sulphex 3EO*	*Operating aspects Sulphex 1EO*
Start-up	**Before**: - Identify gas concentration from QBC by looking at the behaviour of the sulfonic acid line and achieve faster stabilisation of the acid value. **During**: - Sample at reactor outlet 26R1 for acid value. **After**: - Check pH 27MX1 and 32MX1 with phenolphthalein.	**Before**: - Reduce the cyclone level to 25%. - Verify the pump piston position. **During**: - Secure the piston of the pump 32P1 at a 40% hydrogen peroxide flow rate for 20 minutes and reduce it to 10%.	**Before**: - Reduce the cyclone level to 20%. - Idem. **During**: - Secure the piston of the pump 32P1 at a 60% hydrogen peroxide flow rate for 20 minutes,
Adjust with citric acid.	**Sulphex 70%**: - Maintain an alkalinity of the product at the outlet of the 32MX1 between 0.09% and 0.1%. **Sulphex 28%**: - Maintain an alkalinity between 0.2% and 0.3%.	**Sulphex 70%**: - Set piston C initially at 20% of pump 27P1 and adjust as required. - Add citric acid according to the calculation for 13500 Kg of Sulphex and the given alkalinity. **Sulphex 28%**: - If the alkalinity is higher than 0.2, add all the phosphoric acid necessary for 16500 Kg, stir and recirculate for 30 minutes.	**Sulphex 70%**: - Set piston C initially at 35%... - Idem. **Sulphex 28%**: - If the alkalinity is higher than 0.25... - If the alkalinity is SLES, then 0.25...
Adjustment of active material.	**Sulphex 70%**: - Maintain the product active material at the outlet of the 32MX1 for Sulphex 70% between 70% and 70.5%.	**Sulphex 70%**: - Add the amount of water to achieve an active 70% for a Sulphex quantityof 13000 kg. **Sulphex 28%**: - For a Sulphex quantity of 16500 kg.	**Sulphex 70%**: - Add the amount of water to achieve an active 70.5%... **Sulphex 28%**: - Idem.
Homogenis ation	- Check pH 60 minutes after addition for Sulphex 70% and 30 minutes for Sulphex 28%. - Take a sample for lab analysis after 30 minutes of filling the tank. - Take a sample for laboratory analysis every 25 minutes.	- Activate recirculation and agitation, respecting the times of each activity.	- Sulphex 70% agitate at least 60 minutes after each addition. Sulphex 28% agitate and recirculate for 20 minutes.

Note: Sulphex is the trade name for SLES, as designated by Químicos del Cauca SAS.

SUMMARY

2.15 The start-up of the sulfation plant for the production of SLES 1EO was a project that I led to increase the market share of mass consumer products for personal care using raw materials manufactured in Colombia, thereby achieving a significant increase in the company's growth. It was possible by making the analogy of the current production of SLES 3EO, and a valuable human resource that I selected. My experience in production processes and teamwork was key to securing this contract, and I successfully delivered the product as specified by Unilever, the client. My background in chemical engineering and the application of physical and chemical concepts in the industry, particularly in process controls, allowed me to plan and implement a new product. I presented the information I established for the production of SLES 1EO to the surfactant plant director and production chief, who agreed with my analysis and the parameters I established, whose test was a success.