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RESEARCH ARTICLE

Industrial Manufacturing of Aqueous Solutions of Sodium Sulphydrate (NaHS 43%) in a Multi-Phase Reactor

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Abstract:

Background:

This research deals with the manufacture of sodium sulphides and sodium sulphydrate in an isothermal multiphase chemical reactor to produce concentrated aqueous solutions of sodium sulphydrate (greater than 43%) through Gas-Liquid-Solid reactions from hydrogen sulfide and hydroxide of sodium at 50%.

Methods:

A method is proposed that integrates the recovery of hydrogen sulfide from an industrial chemical process where the H₂S gas is generated as a sub product, the strategy of the developed process was integrated into a manufacturing plant of dithiophosphoric acids (ADTF) where it was possible to recover the hydrogen sulfide in the form of an aqueous solution of NaHS with a concentration higher than 43%.

Results:

The experimental tests showed that the biphasic reaction mixture formed by Na₂S, NaHS and H₂O with global compositions of 13.3%; 26.9% and 59.7% respectively, is appropriate to obtain 43% sodium sulphydrate in a stirred tank reactor, operated at temperatures ranging from 50°C to 55°C, where gaseous hydrogen sulfide is continually bubbled.

Conclusion:

Sodium sulfide (specifically Na₂S.5H₂O crystals) of the biphasic mixture is produced from a solution of sodium sulphydrate (43% NaHS) and aqueous sodium hydroxide (50% NaOH). The environmental problem generated by the H₂S was solved with a 90% recovery in the multiphase reactor and 5% in the safety absorber.

Keyword: Sodium hydrosulphide (NaHS), Multiphase reactors, Sodium sulphide and Hydrogen sulfide(H₂S), Reactivos Nacionales S.A.

Article History

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1. INTRODUCTION

Hydrogen sulfide is a highly toxic gas [1, 2, 3]; with an offensive odour reminiscent of rotten eggs [4, 5] it is readily water soluble [3]. One of the problems caused by hydrogen sulfide with respect to the health and safety of personnel is the time and concentration of exposure. If exposed to 100 ppm H₂S during 8 hours, people will hemorrhage and die. Concentrations above 600 ppm can be fatal if exposed between 3 and 5 minutes [6]. Exposure to H₂S is highly dangerous and the sequelae that can appear in people who survive acute pois-

oning are generally neurological post-anoxic. Chronic exposure can cause chronic bronchitis and neuro-psychic symptoms [7]. Industrial emissions that contain low concentrations of hydrogen sulfide (less than 1 ppm) have odor problems [8] that affect the environment, and exposure to high concentrations (greater than 100 ppm) has effects on people's health leading to fatal consequences, see www.osha.gov [9]. Chemical industries – especially those industries that generate high concentrations and volumes that affect the economy of the main process – are constantly searching for chemical control methods of these emissions and their final disposal. A method of chemical control of hydrogen sulfide gas consists of transforming it into stable substances with commercial value such as elemental sulfur [10, 11] or using processes that transform H₂S without

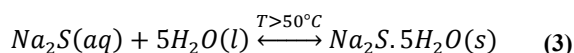
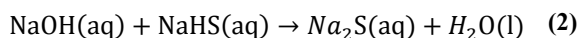
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production of inorganic salt byproducts and wastewater [12] and stable aqueous solutions of sodium sulphide and sodium sulfhydryte and other salts [13, 14]. In the oil and gas industry there are advanced treatment of acid gases (H_2S) where seven ways to remove H_2S from crude oil and gas are described [15]. Absorption is used in the oil & gas industry to remove H_2S and carbon dioxide from sour natural gas and refinery gas. This removal is called gas sweetening, which consists in the transfer of H_2S from the gas phase to the liquid phase [16]. Caustic scrubbing is a technology that has been used for the removal of H_2S from gases in variety of industries for many years. According to McIntosh, *et al.*, 2012 improvement in design and controls strategies, favorable prices for caustic compared with other non-regenerable H_2S scavenging chemicals, and the potential for sales value for the NaHS product have made caustic scrubbing an economic and viable option for many refinery streams [17]. Industrially the manufacture of the sulfhydryte of aqueous sodium is made by the chemical reaction of a solution of sodium hydroxide and hydrogen sulfide according to the following reaction [18].

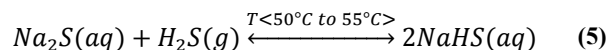
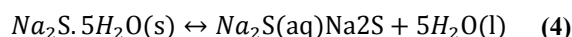


The chemical reaction is carried out in absorption towers (filling columns) that operate countercurrent and at temperatures around 70 °C, preferably at 90 °C. The manufacturing processes of sodium sulfhydryte are differentiated by the source of hydrogen sulfide [19]: Fosfoquim process when the H_2S coming from the reaction of H_2 and Sulfur, Akzo Nobel process if the H_2S coming from the manufacture of CS_2 and Tessenderlo Kerley if H_2S coming from the desulfurization of Natural Gas or Oil. These processes have the advantage of producing sodium sulfhydryte continuously and for this the process is provided with a series of auxiliary absorbers that allow to neutralize the H_2S that has not been absorbed in the main absorber due to its low solubility in the absorbent solution. These processes require working at temperatures close to 100 °C to avoid the crystallization of sodium sulphide inside the packing of the packed column and at the bottom of the tower [19]. In packed towers, the absorbent liquid may be aqueous sodium hydroxide or a pre-warmed sodium sulfide solution to avoid crystallization of sodium sulphides in the transfer lines [20]. Some absorbers are provided with stirred tanks in their lower part where it allows to prepare the sodium sulfide that will be recirculated in the absorption tower. The reactions in the process are exothermic (Eq. 9) [21], so the heat generated must be removed by means of water-cooled heat exchangers and by water jackets that are installed in the recirculation tank and in the absorption towers themselves.

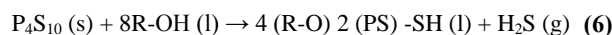
Formation of sodium sulfide crystals from NaOH:



Formation of sulfhydryte from sodium sulfide.

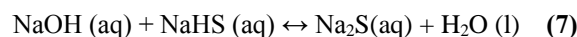


The industrial production of dithiophosphoric acids (ADTF) at Reactivos Nacionales S.A generates significant amounts of hydrogen sulfide (Eq 6), as an undesirable by-product has a high treatment cost, and its final disposal in aqueous solutions of 20% Na_2S affects the economy of the process principal of reactor established to maintain

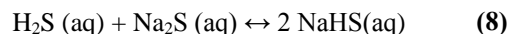


Where R-OH represents an alcohol typically isopropanol, isobutanol or isopentanol, and $P_4S_{10}(s)$ at phosphorus pentasulfide. The process of NaHS production in a multiphase reactor can be explained with the chemical Eqs. (7-9) whose heats of reaction are -4.51, -3.64 and -8.15 Kcal / mol respectively [22].

Stage 1:



Stage 2:



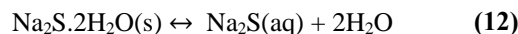
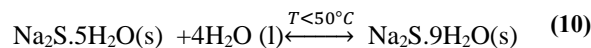
Global process:

In the scrubbing process, NaOH react with H_2S dissolved in aqueous solution to form NaHS or Sodium Sulfide [23].



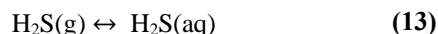
The reaction mechanism proposed in a first stage explains the formation of sodium sulphide (Na_2S) given by (Eq. 7), and crystals of sodium sulfide with the (Eq.3) that is favored if the temperature is higher than 50 °C.

At temperatures below 50 °C, the formation of $Na_2S \cdot 9H_2O$ crystals (s) explained with (Eq. 10) is favored. Dehydration of this crystal can occur at temperatures above 50 °C [24], which can be explained by the inverse process of (Eq. 10), when the temperature is higher (>83°C), the dehydration of the crystals of $Na_2S \cdot 5H_2O(s)$ can be given [24, 25, 26], and can be explained with Eqs. (11 and 12) [27]. There are also other forms of dehydration of $Na_2S \cdot 5H_2O$ crystals in species such as $Na_2S \cdot 0.5H_2O$ [28].

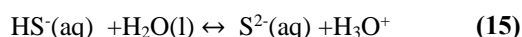
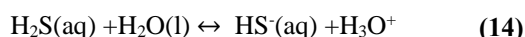


Stage 2 of this mechanism explains the formation of sodium sulfhydryte. Gaseous hydrogen sulfide is absorbed by

the aqueous solution [29]. H₂S absorption in the aqueous solution of sodium sulphide is high even in sodium hydroxide solutions [30] where it will finally dissociate in sulfur ions depending on the pH of the medium [31]. Under unfavorable conditions, the desorption of hydrogen sulfide can occur, transferring the H₂S from the aqueous solution to the gas phase [32] explained with (Eq.13).



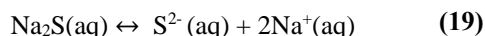
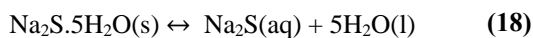
Hydrolysis of hydrogen sulphide generates disulphide ions (HS⁻) [2, 3, 33], which leads to a decrease in pH due to the presence of hydronium ions [34]. The balance between H₂S, HS⁻, and S²⁻ is explained with Eqs. (13-15).



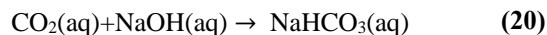
Hydrogen sulfide, dissolved in water, is a very weak acid that undergoes ionizations with pK₁ of 7, at 25 °C and pK₂ of 12.92 at 25 °C for Eqs. 15 and 16 respectively [35, 36]. For an advanced study of H₂S, HS⁻, and S²⁻ equilibria (in aqueous solutions), Petrucci and Moews propose several methods to calculate the concentrations of the species [37]. The formation of sodium sulfhydryte in an alkaline medium pH <10 is explained by taking into account that in the equilibrium there is a higher proportion of HS⁻ ions and the sulphurous ions are transformed into disulphide ions, explained with Eqs 16 and 17.



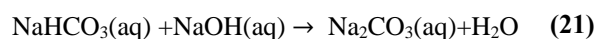
Due to the deficiency of sulfur ions in the reaction solution, the sodium sulfide crystals dissociate in sulfuric ions maintaining the concentration of S²⁻ and explained with Eqs (18 and 19).



The presence of CO₂ and O₂ in the gas stream leaving the ADTF reactor generates unwanted reactions when the gases are brought into contact with the sodium hydroxide (Eq 20) in the absorbers [20, 21]. CO₂ absorption causes unnecessary caustic usage, contamination of the NaHS product solution with carbonate salts (Eq. 21), and potential plugging and fouling of process equipment with carbonate salt solids [20].



On the other hand, the oxygen in the air reacts with NaHS and Na₂S to give undesired products such as Na₂CO₃, Na₂S₂, Na₂S₂O₃, and Na₂SO₄, this is observed in the pulp and paper industry [38]. CO₂ and O₂ come from the air, these can enter the reactor through the phosphorus pentasulfide feed system or through the reactor seals. During the industrial process the control of these gases is achieved by making a vacuum in the ADTF reactor. Fig. (1) shows the proposed mechanism where the presence of the three phases is observed as well as the species involved in the formation of sodium sulfhydryte. It shows the summary of the chemical processes that during the absorption of H₂S in a solution of sodium sulfhydryte saturated with sodium sulfide, where the presence of the three phases is observed. The mechanism presented is an extension of the Al-Tarazi model [39] of a liquid gas contactor for formation of crystal and aggregates.



The hydrolysis of NaHS can also occur to form H₂S, and can be appreciable and sensitive to small variations of pH of neutral aqueous solutions [40]. Multiphase reactors are widely used in chemical industries because they offer high flexibility and allow appropriate conditions according to the requirements of the chemical reaction [41]. To maintain the phases in contact, an efficient system [42] of agitation is necessary, which allows keeping balanced the amounts of the different substances in each phase [43, 44]. The wide range of agitation devices (and the variety of impellers) and geometric parameters of the system allows to select a precise combination for the intended application [41]. In these types of reactors, under the action of the impeller or liquid agitation device, it allows the suspension of solids [42] and the dispersion of the gas phase (entering through the bottom of the container and close to the impeller), in such a way that the contact between the three phases is favored [45]. According to the phase diagram (see Fig. 2) of the Na₂S-H₂O system, if the reactor will be worked in a system formed only by sodium sulfide and water, it can be seen that we have two regions where two phases are present, such as L + C1 and L + C2.

The objective of this research was to study the manufacture of sulphides, specifically sodium sulphides, in an isothermal multiphase chemical reactor to produce concentrated aqueous solutions of sodium sulfhydryte greater than 40% (NAHS 42-45%) from chemical reactions in a Ternary Gas-Liquid-Solid system, recovering the hydrogen sulfide (H₂S) generated during the industrial production of dithiophosphoric acids.

For which we propose to develop a more attractive process by reducing the temperature of the process with respect to the technologies currently used in this area.

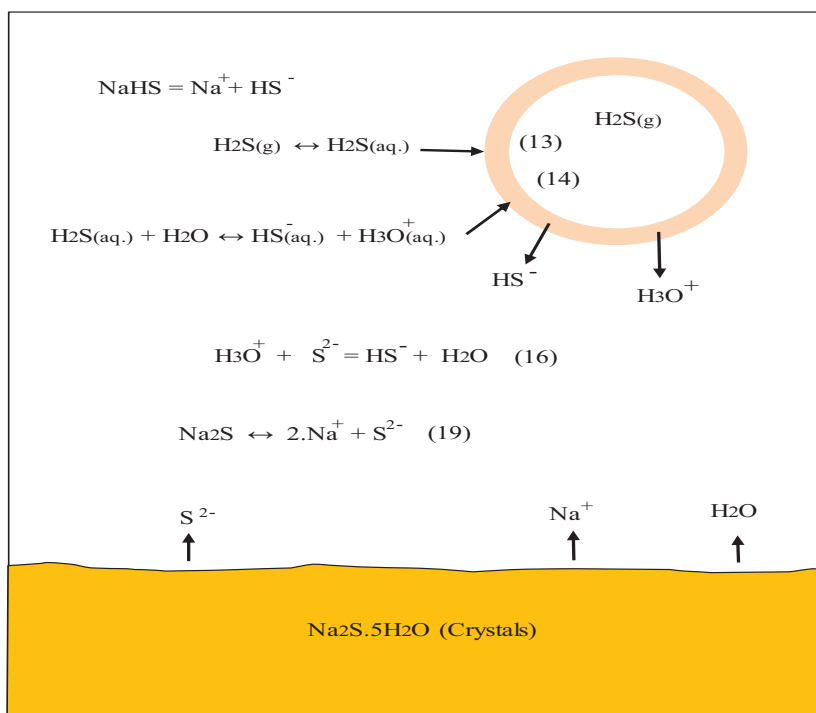


Fig. (1). Processes of absorption of H₂S in a solution of sodium sulphydrate saturated with sodium sulphide.

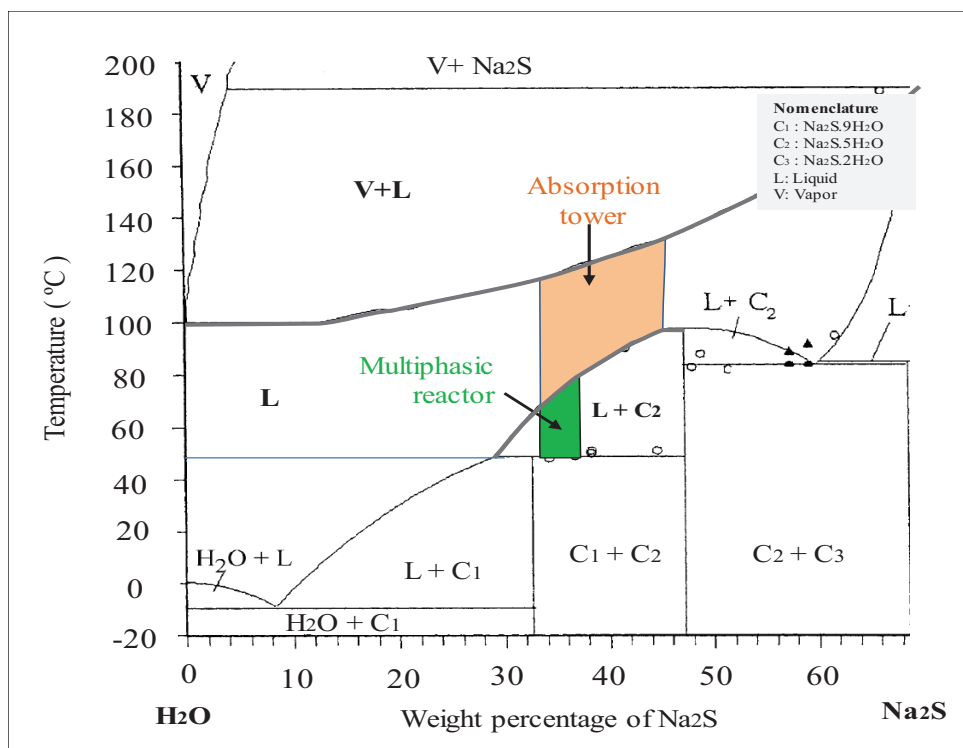


Fig. (2). Region of operation of a multiphase reactor starting only with aqueous solutions of Na₂S [25].

2. MATERIALS AND METHODS

2.1. H₂S and ADTF Production

Before indicating the characteristics of the reactor for this study, first we give the general guidelines of how hydrogen

sulfide is generated in the Reactivos Nacionales S.A Company, which is the main problem we are trying to solve. The production of dithiophosphoric acids (ADTF) is carried out in a stirred tank-type semicontinuous reactor, where the phosphorus pentasulfide and a specific alcohol mentioned above are

reacted. On alcohol at 90 ° C, the phosphorus pentasulfide is added, the chemical reaction produces the ADTF and H₂S. The reactor is maintained at a pressure of -20 mmH₂O (-196.14Pa), and a production batch takes 6 hours. Table 1 shows the production of H₂S depending on the alcohol used. The raw materials are industrial grade at 99% and theoretically generate 92 kg H₂S for each production batch, according to the production record of ADTF and the balance of material are recovered 90.4 kg H₂S, are recovered, which represents 98.3% recovery of the theoretic value. The H₂S (g) for its treatment is

bubbled in a stirred tank with a dilute solution of Na₂S-NaOH or sent to the scrubber where diluted solutions of sodium sulphide are obtained with a concentration by 20 to 25% weight. Faced with this problem, a technological alternative is sought that allows to dispose the residual H₂S in such a way that it improves the economy of the main process.

When monitoring the values recorded by the pressure transmitter it is common to find the following pressure patterns (see Fig. 3), H₂S flow (see Fig. 4) and the temperature and pH profiles (see Fig. 5) during the ADTF production process.

Table 1. Stoichiometric formulation for the production of ADTF.

| Products | Alcohol (kg) | P ₄ S ₁₀ (s) (kg) | ADTF (kg) | H ₂ S (kg) |
|-------------------------------|--------------|---|-----------|-----------------------|
| ADTF from isopropanol alcohol | 648.8 | 600 | 1156.8 | 92 |
| ADTF from isobutanol alcohol | 800.3 | 600 | 1308.3 | 92 |
| ADTF from isopentanol alcohol | 951.8 | 600 | 1459.8 | 92 |

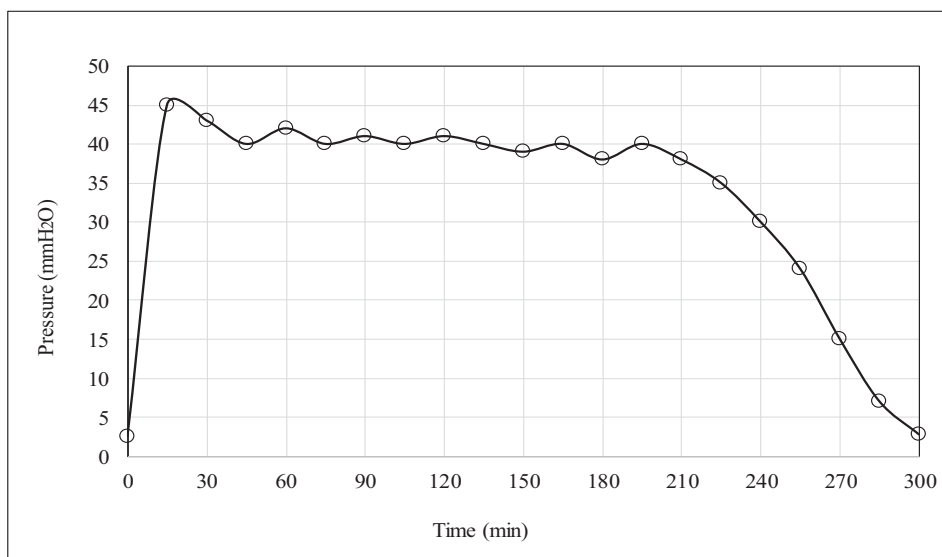


Fig. (3). Pressure pattern in the semicontinuous stirred tank industrial reactor during the production of ADTF (Reactivos Nacionales S.A., Lima Peru).

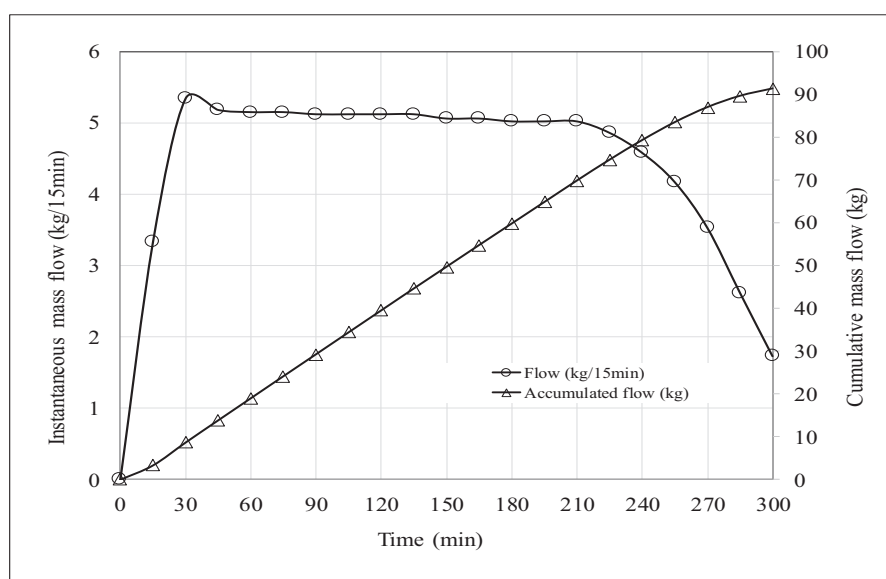


Fig. (4). H₂S flow pattern during a typical ADTF production operation.

2.2. Specification of H₂S Flow

The ADTF production plant has a flowmeter at the outlet of the condensers where the gas output is monitored at room temperature (22° C) throughout the reaction process. Figs. (4 and 5) show, the H₂S flow pattern and temperature profile in the industrial reactor during ADTF production. The mass flow is calculated with the following equation:

$$F \text{ (kgH}_2\text{S/min)} = Kf * \sqrt{\Delta P * \rho_{\text{H}_2\text{S}}} \quad (22)$$

The operating parameters of the flowmeter are specified taking into account the following: Kf: flowmeter constant 0.045 m² (22 ° C, 101.325 kPa). ΔP: mmH₂O ρ(H₂S): (1.42 kg.m⁻³, 21.1 ° C and 101.325 kPa) or (1.220 kg.m⁻³, 21.1 ° C

and 101.325 kPa).

2.3. Characteristics of the Stirred Tank Reactor: Batch Mode Experimental

The configuration of the stirred tank pilot reactor used for this study is shown in Fig. (6). The main parts that make up the pilot reactor are: (1) a reactor with variable agitation; (2) a pH meter; (3) A temperature meter; (4) an H₂S analyzer; (5) heating and cooling medium. Very close to our system is the industrial semicontinuous reactor for the production of ADTF, where H₂S is produced, which was conveniently used for experimental development. The reactor planned for this study operates at temperatures lower than the temperatures of recovery technologies by absorption towers (less than 70 °C) in order to facilitate the H₂S absorption in the reaction medium.

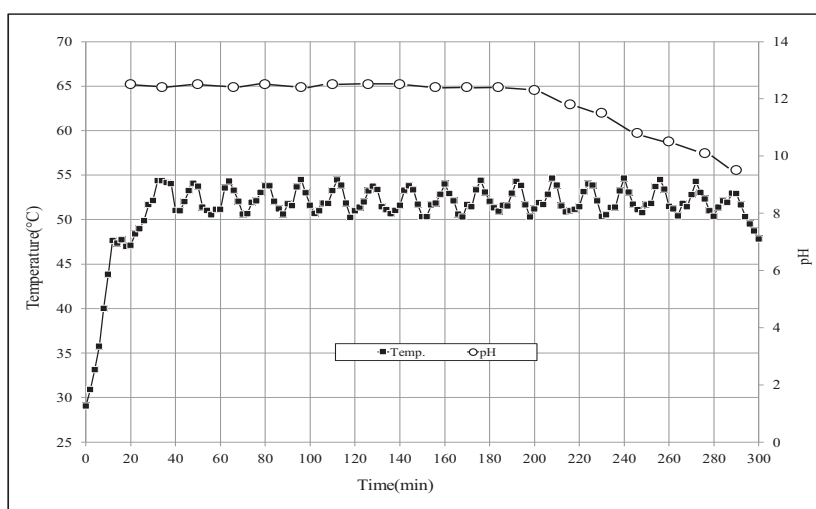
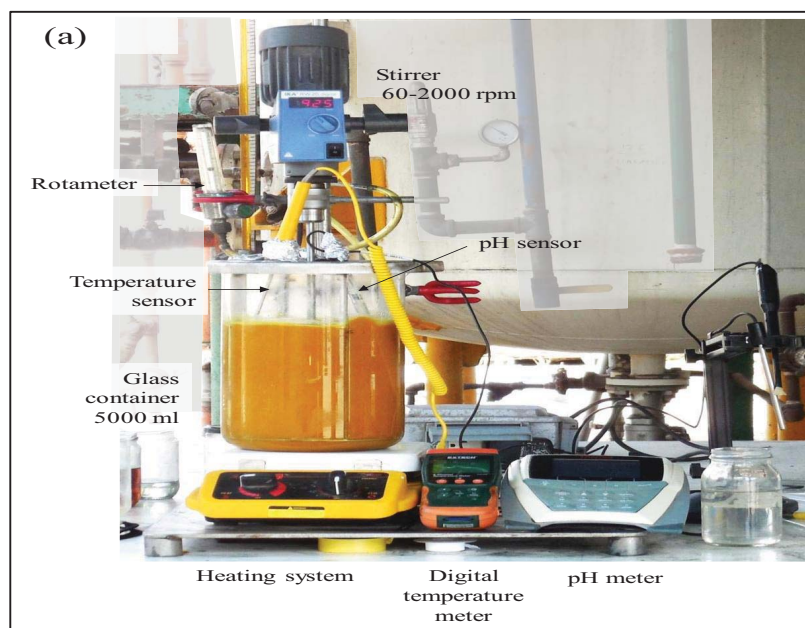


Fig. (5). Temperature profile in the industrial reactor during ADTF production.



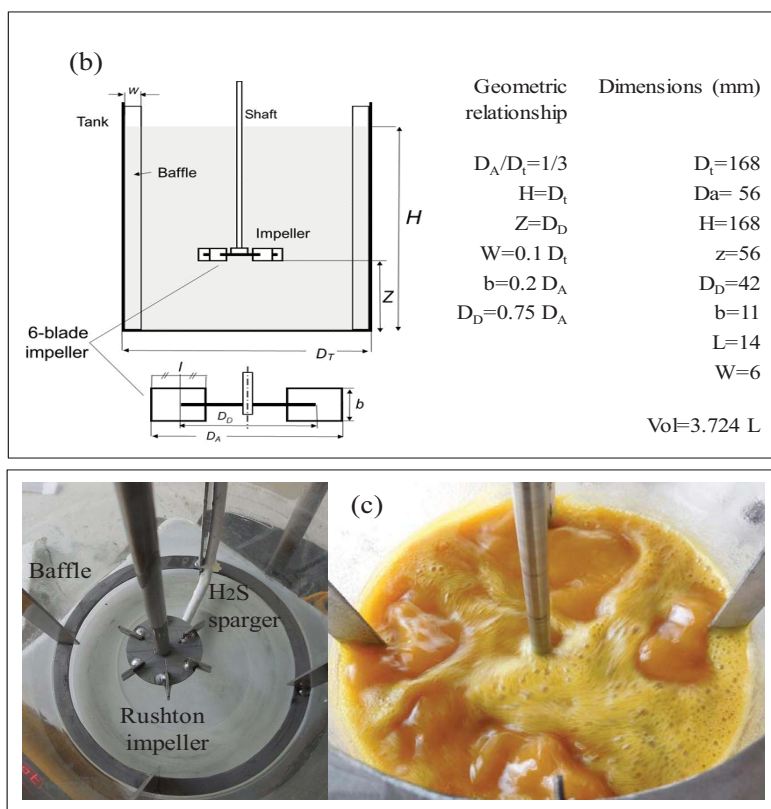


Fig. (6). (a) Configuration of the stirred tank pilot reactor (b) Geometric configuration of the pilot reactor [42, 46], (c) Impeller installed in the pilot reactor, the deflectors and the H₂S bubbler are observed. Where: D_T is tank diameter, D_D is impeller diameter, W is baffle width, I is impeller blade length.

For the experimental development, a cylindrical glass vessel of 168 mm internal diameter and 210 mm in height was used, with a liquid level equal to the tank diameter, with a total volume of 5 L. The agitation system described by [46], was applied to design the components of the stirred tank, such as the impeller and deflectors (Fig. 6). Similar geometric relationships (Fig. 6b) are also shown in [47, 48]; [49, 50, 51]. With this configuration there is available a reaction volume of 3.72 liters sufficient for the end pursued. The composition of the reaction mixture is Na₂S (13%), NaHS (27%) and H₂O (60%) with an average density of 1.26 g / l at 50 °C. The reactor can treat 4650 g of reaction mixture with a final volume of 3.910 liters, which is equivalent to approximately 5000 g of NaHS when the final product is formed. Fig. (6) shows the detailed dimensions of the reactor used for the experiments. The rotameter was calibrated for a water column of 218 mm H₂O with flow rates ranging from 0.1 vvm (at 25 °C) to 0.8 vvm (at 25 °C). Take into account that vvm represents the volume of gas per volume of the reaction medium per minute. Taking into account that the volume of the medium is 3.8 liters of biphasic mixture (composed of crystals of sodium sulfide and aqueous solution of NaHS) we have: (0.8 liters H₂S/min = 0.21 vvm, 1.6 liters H₂S/min = 0.42 vvm, liters H₂S/min = 0.85 vvm). To measure the presence of H₂S that could escape from the reactor, a gas detector has been used (Brand: Aeroqual, Model: Series - 200, Sensor: EHT / EHT2 range: 0 - 100ppm, peaks up to 300ppm). The device is a precise meter for the measurement of H₂S concentrations in the air or in gas streams. The gas detector has a built-in pump in the head that

sucks gases from the reactor to be analyzed. When there is a high presence of H₂S in the pilot reactor, a large amount of foams will be observed on the reaction medium. So in these circumstances the gas sensor should be disconnected to avoid saturation of the catalytic sensor.

3. RESULTS AND DISCUSSION

3.1. Determination of the Bubble Diameter of H₂S

The bubble size cannot be determined by mathematical models for this type of reactors, because the system is a complex mixture, that is why we have proceeded to measure directly by photographic captures using the microscope (UNIMAKE, USB Digital Microscope 1000X) to determine the size of the bubbles closest to the surface of the reactor.

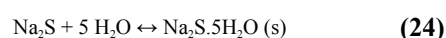
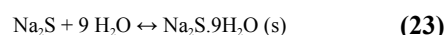
The photographic capture (Digital Camera, Nikon Coolpix S6500) was made stopping untimely agitation and gas entering the reactor. The measurement must be fast because the bubbles reduce their size since they are absorbed in the aqueous solution or they abandon the reaction medium. A uniform distribution of the bubbles in the liquid is observed and it can be inferred that the bubbles have diameters of less than 300 μm measured at a reaction temperature of 53°C, stirring speed of 700 rpm and a flow of H₂S 0.4 vvm. The bubbles were (Fig. 7a) (A= 300μm, B= 80μm, C= 60μm). The bubbles are of H₂S and it occurs quite frequently when the reaction solution is almost saturated with H₂S and when NaHS is already formed in its entirety (the pH of the reaction mixture is around 8). On the

other hand, when air enters the system, O₂ becomes thiosulphate and collapses, and if there are bubbles, it is due to Nitrogen (N₂). The vacuum pressure prevents the entry of air, the gas flow meter does not show the passage of any gas, and if CO₂ has passed must be negligible because the content of thiosulphate is minimal and almost always maintained at values of 100 mg /L, and has no impact on the specification of the final product. Fig. (7b) shows the multiphase reactor in operation, the foam that is formed when the flow rate of H₂S (g) is much greater than 0.8 vvm is observed. This foam mattress arrives until the empty space of the reactor is reached. In other research work [52], the photographic method was used for this purpose, where the bubble diameters were evaluated for selected bubbles in different locations at different times. The foam formed from sodium sulfide crystals Na₂S.5H₂O, when cooled, crystallizes and adheres to the walls of the reactor generating various problems such as the impediment of the flow of H₂S. The hydration temperature of Na₂S is 73°C [28], and the dehydration temperature is 80 °C (Eq. 11) [24, 53], which represents a process of hysteresis. Mechanically, stirred tank reactors in which the gas phase is dispersed by means of a dispenser and/or a stirrer are used in many chemical processes (gas absorption etc) [54]. Stirred vessels are very commonly used for gas-liquid reactions on account of their flexibility and good performance for mass and heat transfer [55]. When a single phase is present, the fluid flow induced by the impellers is relatively easy to predict. The addition of a second phase to the reactor increases the hydrodynamic system complexity [54, 56]. Gas flow pattern is important. It controls the degree of recirculation and backmixing of the gas phase, which in turn determines the mean concentration driving force for mass transfer. In the homogeneous regime in an agitated vessel, the superficial gas velocity, $v_s < 0.02$ to 0.03 m/s, and the bubbles have a monomodal size distribution with a small mean size, generally between 0.5 and 4 mm. Here, the impeller controls the flow pattern and bubble size [55]. Good mass transfer performance requires large interface area between gas and

liquid (resulting directly from small bubble size and high gas fraction, given the fixed gas rate), and a high mass transfer coefficient (associated with local levels of turbulence) [55].

3.2. Formation of Na₂S.5H₂O Crystals at 50-55 ° C

It is important to bear in mind that the formation of Na₂S.9H₂O crystals occurs in a temperature range of 30 to 35 ° C, with a low content of Na₂S.5H₂O. The reaction parameters for the transformation of sodium sulfide crystals in the pilot reactor were the following: Stirring speed: 700 rpm; initial temperature: 26°C, maximum reaction temperature: 30°C, stirring time 30 minutes. This can be explained taking into account (Eq. 2), in addition to:



When the temperature of material is lower than its melting point, crystalline hydrate will wholly or partially strip its water of crystallization. When the temperature decreases, Na₂S(s) adsorbs water and transforms into Na₂S.nH₂O(s). Under many circumstances, such hydration heat could be much higher than dissolution heat [57]. A curve showing the solubility of hydrates of Na₂S can be consulted in [58]. If crystallization with agitation takes place much longer (48 hours) and with temperatures of 25°C, most of the Na₂S.5H₂O will have been transformed into Na₂S.9H₂O crystals with particle size that will be around 4mm. Working at low temperatures with a high concentration of crystals (Fig. 8) causes suspension problems in the reaction mixture, blockage of the bubbler holes and makes it difficult to react the reaction mixture with H₂S for the conversion of Na₂S to NaHS. With formulation of Table 2 and reaction conditions (stirring speed: 700 rpm; initial temperature: 26 °C; maximum reaction temperature: 50 °C; and stirring time: 30 minutes), mainly Na₂S.5H₂O crystals are formed according to Eqs 2 and 3.

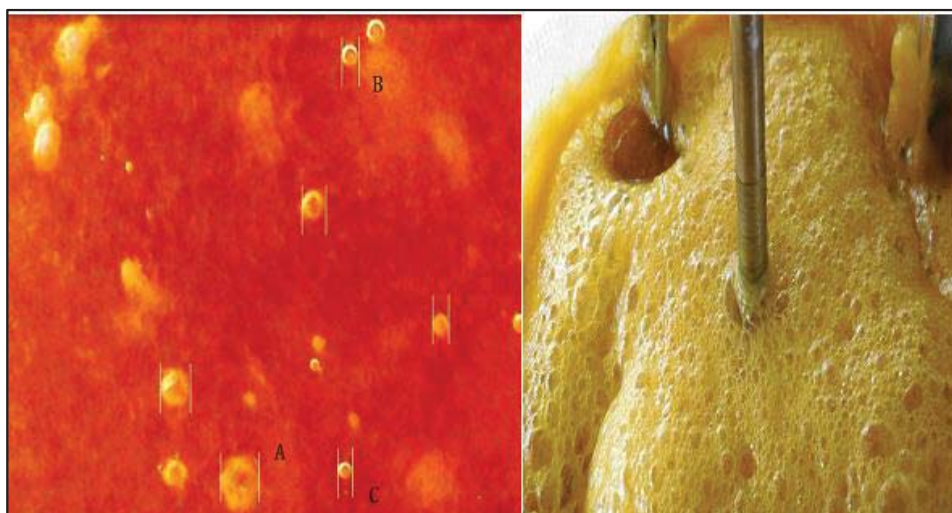
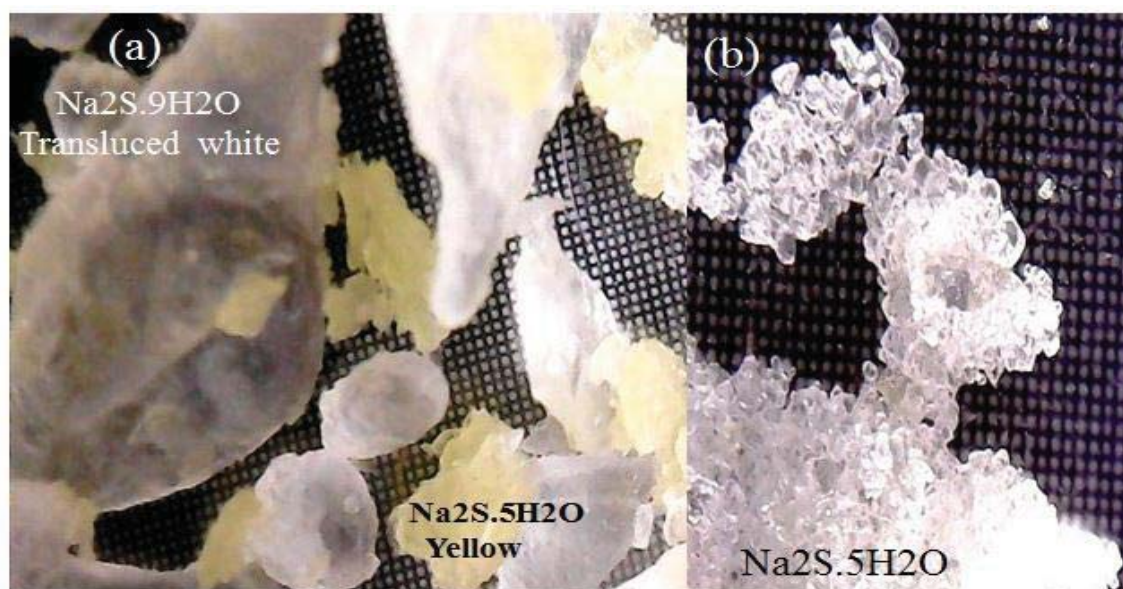


Fig. (7). (a) Distribution of H₂S bubbles in the multiphase reactor, (b) Foam crystals of Na₂S and water with H₂S bubbles.

Table 2. The formulation for the crystallization test.

| Components | Quantify |
|---------------------|----------|
| NaHS (43%) | 3964 g |
| [NaHS] | 43.20% |
| [Na ₂ S] | 0.20% |
| H ₂ O | 110 g |
| NaOH (50%) | 638 g |

**Fig. (8).** Sodium sulfide crystals formed at 35 °C.**Fig. (9).** Effect of temperature on the formation of Na₂S5H₂O crystals: (a) 30 -35 ° C, (b) 50 -55 ° C.

With formulation of Table 2 and reaction conditions (stirring speed: 700 rpm; initial temperature: 26°C; maximum reaction temperature: 50°C; and stirring time: 30 minutes), mainly crystals of Na₂S.5H₂O are formed which explains by Eqs 2 and 3. When the aqueous sodium hydroxide is contacted

with the sodium sulfhydrylate solution, the conversion to sodium sulfide crystals immediately occurs. The reaction is exothermic and instantaneous, and in less than 1 minute the NaHS is transformed into Na₂S, the reaction mixture raises its temperature to 48 °C. The amount of crystals obtained is 1047 g,

which represents 22% according to the weight of the mixture. The crystals show particle diameters less than 1500 μm . The shape and distribution of the crystals is more homogeneous when the temperature is maintained in a range of 50 °C to 55 °C. Dehydration of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ changes to a yellow color [25], indicating the presence of $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$, this effect is shown in Fig. (9).

3.3. Influence of the Solid Content of the Reactioning Mixture in the Progression of the Reaction

To confirm that the reaction mixture with a solids concentration of 22% ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$) has good reaction properties as opposed to solids concentrations of less than or greater than 22%, three tests were organized where each reaction mixture (NaOH and NaHS) form crystals of sodium sulphide ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$) (see Table 3) and finally react with hydrogen sulphide to give 43% NaHS. The amounts of NaHS used include stoichiometric amounts which will react with the sodium hydroxide and those which keep the crystals formed in suspension. The amounts of water used in the formulations allow to correct the final concentration of the product. The formulations used make it possible to initiate the reaction with the H_2S with a volume of reaction mixture of 3578 mL corresponding to the volume of reactor established to maintain the configuration of the reactor which is also object of analysis. The conditions of these tests were: reaction temperature (50-55°C); agitation (impeller: 700 rpm); reaction time (2.25 hrs); and H_2S flow (0.41 vvm). When the reaction mixtures were prepared with NaOH and NaHS, the stirring was stopped for 30 minutes so that the $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ crystals formed sedimented while maintaining the reaction temperature at

50°C. Fig. (10) shows the presence of solids ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$) in each case.

The presence of solid particles causes different results in gas-liquid and gas-liquid-solid systems. In gas-liquid systems, a higher agitation speed can effectively break bubbles into smaller ones and hinder the bubble coalescence. But this capacity is weakened when solid particles are introduced into the system because the particles reduce the velocity of fluid flow and may collide with bubbles [59]. For very fine particles (< 10 μm) at low solids concentration (< 0.6% v/v) and very large particles (> 2000 μm) at high solids concentration (> 10% v/v), the trend is an increase in the gas holdup [60, 61]. Gas-liquid-solid three-phase mechanically stirred tank reactors are widely applied in many industrial processes [59], where particles suspension are influenced in a complex manner by gassing [55]. When solid particles are added in gas-liquid systems, the better understanding of solid suspension and mass transfer is important to the design and scale-up of gas-liquid-solid stirred tank reactors [59, 62, 63].

Reaction mixtures Test 1, 2 and 3 are located within the biphasic region and the concentrations of the species will be displaced until 43% sodium sulphhydrate solutions are obtained. Fig. (11) shows the location of these points (N° 1, 2, and 3). The shaded region shows the different ternary mixtures with good agitation properties. The reaction mixtures are reacted with the hydrogen sulfide with a gas flow rate of 0.41 vvm and the progress profile of the reaction is shown in Fig. (11). The reaction mixtures with 11, 22 and 33% solids are reacted with the hydrogen sulfide with a gas flow rate of 0.41 vvm and the progress profile of the reaction is shown in Fig. (12).

Table 3. Formulation to determine the ratio NaHS 43% / NaOH 50%.

| Reagents | Test 1 | Test 2 | Test 3 |
|---------------------------------|---------------|-----------------|----------------|
| NaHS, 43% | 4341 g | 3964 g | 3585 g |
| [NaHS] | 43.40% | 43.40% | 43.40% |
| [Na_2S] | 0.33% | 0.33% | 0.33% |
| [Na_2CO_3] | <0.1% | <0.1% | <0.1% |
| H_2O | 60 g | 121 g | 181 g |
| Reagents | | | |
| NaOH 50% | 319 g | 538 g | 957 g |
| H_2S (0.4 vvm) | 137 g | 275 g | 412 g |
| NaHS, 43%/ NaOH, 50% | 13.6 | 6.21 | 3.74 |
| Mass balance | | | |
| [Na_2S], % | 6.89 | 13.46 | 20.02 |
| [NaHS], % | 35.14 | 26.95 | 18.74 |
| [H_2O], % | 57.9 | 59.59 | 53.84 |
| Crystals weight | 512 g (10.8%) | 1047 g (22.16%) | 1586 g (33.5%) |
| Liquid weight | 4208 g | 3676 g | 3137 g |
| Total weight | 4720g | 4723 g | 4723 g |
| Solid phase volume | 1052 mL (29%) | 1473 mL (41%) | 2526 mL (70%) |
| Liquid phase volume | 2525 mL | 2105 mL | 1053 mL |
| Total volume | 3577 mL | 3578 mL | 3579 mL |

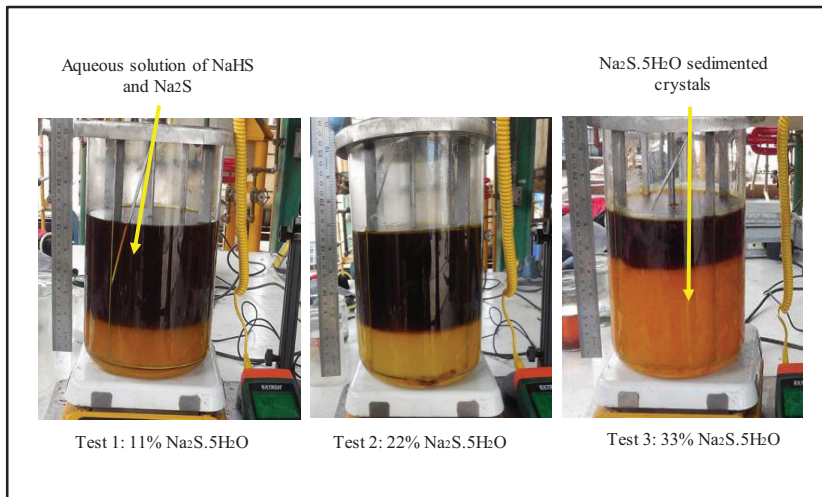


Fig. (10). Presence of solids (Na₂S.5H₂O) in the reaction mixture.

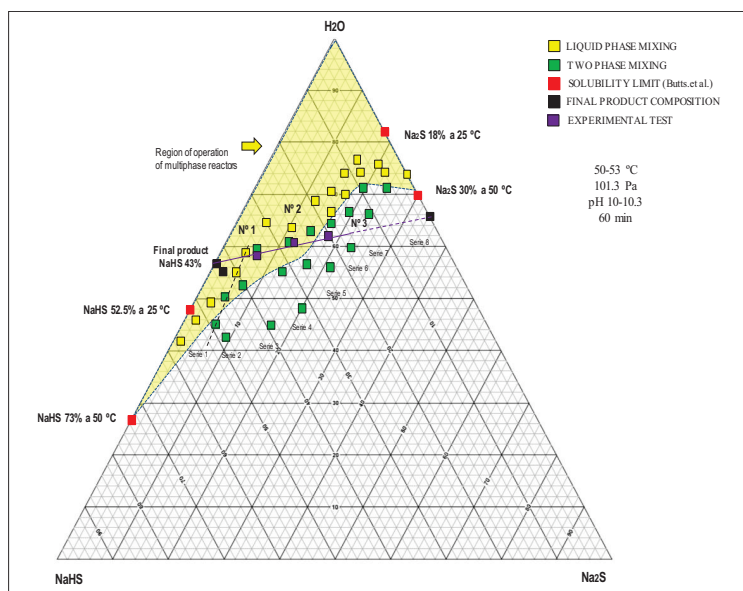


Fig. (11). Locating the test points in a ternary diagram NaHS - Na₂S - H₂O.

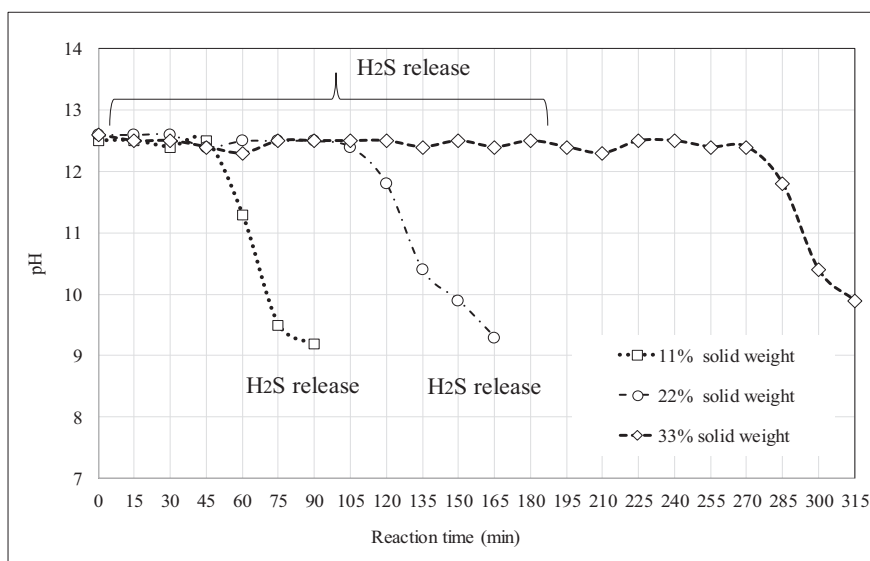


Fig. (12). Advance reaction with different solids contents in the reaction mixture: Effect on the pH.

3.4. Influence of Temperature on the Absorption of H₂S

One of the most discussed topics in the treatment of H₂S is the low solubility of it in concentrated solutions of sodium sulfhydryte and sodium sulfide. To this end, four tests were organized at 50, 60, 70, and 80°C in reaction solutions with an approximate of 40.5% NaHS and 2.8% Na₂S. The volume of the solution was 3 725 ml; the flow of H₂S was 0.12 vvm (0.44 L.min⁻¹) at 25 °C; and the impeller speed 700 rpm. The reaction solution under study at 50 °C does not have sodium crystals that disturb the absorption results. Once the sodium hydroxide is added, it is necessary to cool the solution, then heat the solution to the test temperature; then proceed to bubble the H₂S. Table 4 shows the results of these tests. At 50 °C an acceptable absorption time is obtained and there is almost no presence of Na₂S.9H₂O crystals that affect the suspension and dispersion of gases in the reactor. The solid phase of the reactor is composed almost entirely of Na₂S.5H₂O and a good absorption of H₂S is obtained in the reaction mixture. The choice of 50 °C is more due to the absorption capacity of H₂S with adequate agitation.

The reactant solutions started from the same concentration value of sodium sulfide and sodium sulfhydryte around 2.85% Na₂S; 40.58% NaHS and 56.57% H₂O. After 60 minutes of H₂S bubbling, Na₂S reactants whose temperatures are 50°C and 60°C which are very close to the value of 1%, while solutions

of 70°C and 80°C are very far from this value (see Fig. 13) were observed.

At 90 minutes, the reactants that are at temperatures of 50°C and 60°C have reached equilibrium with concentrations close to 0.15% and remain at this value until 120 minutes, while solutions that are at 70°C and 80°C continue to fluctuate around 0.4%. These solutions reach equilibrium at 120 minutes with approximately 0.15% Na₂S. It is clearly observed that hot solutions greater than 70°C have a delay in the progress of the reaction, as a result of the decrease in the solubility of H₂S in hot solutions, other works also indicate the decrease in solubility with the increase in temperature in absorption towers [64]. The solubility minimum occurs at higher temperatures. The reasons for these related phenomena are not fully understood, but derive to a large extent from the changes in water structure (breakdown of hydrogen bonding) that take place at increasing temperatures [65]. Up to 30 minutes, the samples of the four tests have almost the same content of Na₂S approximately 1.8%. This means that the sodium sulphide in the reactant solution allows the absorption of H₂S and when the Na₂S content decays, the solubility of the H₂S also decays. It is observed that the reactants have absorbed on average 51.8 grams of H₂S and according to the content of Na₂S it was expected to capture an approximate amount of 57.4 grams of H₂S. Therefore, almost 90% of the H₂S that has been bubbled was absorbed.

Table 4. Influence of the temperature on the absorption of H₂S in the batch reactor.

| Reactants | Temperature | | | |
|---|-------------|---------|---------|---------|
| | 50 °C | 60 °C | 70 °C | 80 °C |
| Preparation of the Reactioning Mixture | | | | |
| NaHS 43.6% | 4 536 g | 4 536 g | 4 536 g | 4 536 g |
| [NaHS] | 43.6% | 43.6% | 43.6% | 43.6% |
| [Na ₂ S] | 0.32% | 0.32% | 0.32% | 0.32% |
| Reactants | | | | |
| NaOH 50% | 120 g | 120g | 120g | 120g |
| Balance of materials | | | | |
| [Na ₂ S] | 2.85% | 2.83% | 2.85% | 2.83% |
| [NaHS] | 40.58% | 40.43% | 40.58% | 40.53% |
| [H ₂ O] | 56.57% | 56.74% | 56.57% | 56.74% |
| Weight of the reactant solution. | 4 654 g | 4 653 g | 4 658 g | 4 657 g |
| H ₂ S | 57.4 g | 57.4 g | 57.4 g | 57.4 g |
| Results | | | | |
| Final weight reaction.solution | 4 706 g | 4 707 g | 4 713 g | 4 710 g |
| Amount H ₂ S absorbed | 51 g | 53 g | 52 g | 51 g |
| Balance de materiales-calculado | | | | |
| [Na ₂ S] | 0.14% | 0.13% | 0.16% | 0.18% |
| [NaHS] | 43.95% | 43.79% | 43.66% | 43.41% |
| [H ₂ O] | 55.91% | 56.05% | 55.56% | 56.07% |

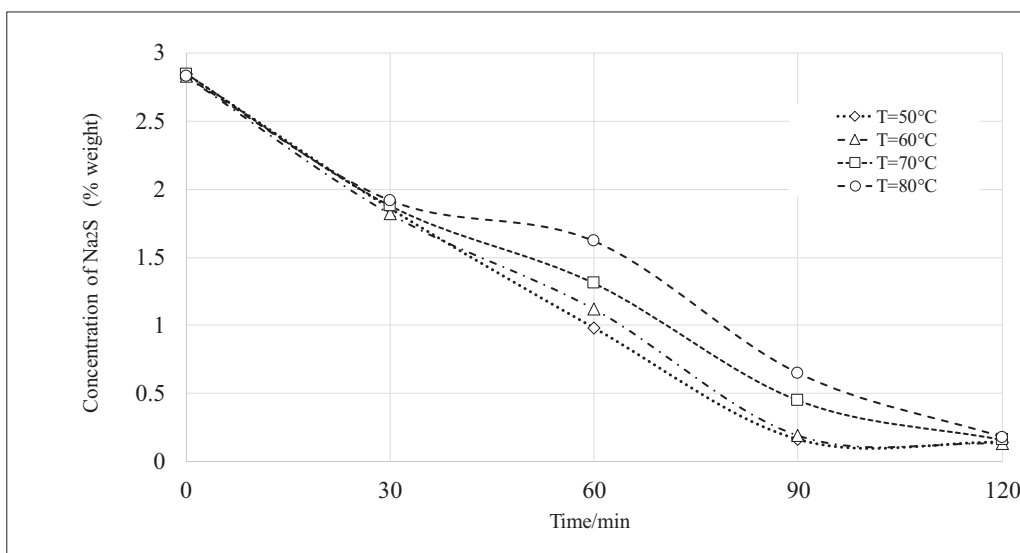


Fig. (13). Na_2S concentration profile, influence of temperature in the absorption of H_2S : H_2S flow (0.44 L / min)

Table 5. Results of the test of influence of the temperature in the reaction.

| | Test N° 1 | Test N° 2 | Test N° 3 |
|----------------------------------|--------------------------------|-------------------------------|-------------------------------|
| Mean temperature | 30 °C | 50 °C | 70 °C |
| Presence of H_2S | Yes (Until 45 minute- 125 ppm) | Yes (from minute 150, 85 ppm) | Yes (from minute 135, 95 ppm) |
| Total, NaHS 43% | 4 952 g | 4 977 g | 4 967 g |
| [NaHS] | 43,75% | 43,27% | 41,83% |
| [Na_2S] | 0,21% | 0,15% | 1,76% |
| [H_2S] | 56,34% | 56,58% | 56,41% |

3.5. Influence of Temperature in the Advance of the Reaction

The influence of temperature on the reaction for the proposed formulation (13.3% Na_2S , 26.9% NaHS and 59.8% H_2O) was studied (Table 5). This reaction medium allows the sodium sulfide crystals to remain in suspension when appropriate agitation is applied. In addition to sodium sulfide, ions react with the absorbed H_2S in the middle. After 180 minutes of reaction, the reaction solution shows crystals of sodium sulphide, and in a higher proportion when the reaction mixture is at 30°C. After 10 minutes of settling, a reactant solution is observed whereby practically 50% of the reactor volume consists of sodium sulfide crystals. This level of solids in the reactor is unfavorable and affects the agitation as well as in the conversion process.

The reactions at 30°C and 50°C end before the reactions at 70°C end because at lower temperatures the reaction solution absorbs more H_2S . This effect was expected since at temperatures close to 70°C H_2S solubility is lower than at the previous ones. According to the chemical analysis of the product obtained at the temperature of 70°C, it is observed that it had not exceeded the required concentration (greater than 43%), and the analyzer of H_2S from minute 150 registered high values of H_2S that left the reactor (95 ppm H_2S). A generation of NaHS of 1 023 g (i.e. 4 990 g NaHS in the reactor) was

expected. However, 4967 g of NaHS was obtained in the reactor. That is, a difference in weight of 23 g which means that about 8% of the initially planned H_2S (275 g) had not been absorbed. On the other hand, the reaction at 30°C releases H_2S from the reactor from the start of bubbling and the release continues until 60 minutes later, after which the load becomes lighter and the H_2S level escaping from the reactor slowly decreases. From the agitation point of view, the high presence of solids in the reaction mixture that is at 30°C causes the crystals to deposit in the deflectors of the reactor and vary the final concentration of the obtained product.

Working at temperatures of 30°C according to the proposed formulation, problems at the beginning of the reaction due to the adherence of the sodium sulfide crystals on the surface of the reactor that affect the correct agitation of the medium because at this temperature there is a high load of sodium sulfide crystals that represent about 52% according to the volume of the reactor that affects H_2S absorption. The most favorable test is at 50°C because no significant amounts of H_2S are detected at the beginning of the reaction, but until minute 150 which is where practically all the Na_2S has reacted and no more H_2S is absorbed. At a temperature of 50°C, the amount obtained differs from what is expected by 11 g. In Fig. (14) the pH profile is observed with respect to each reactor temperature and the delay in the completion of the reaction when tested at 70°C is clearly seen.

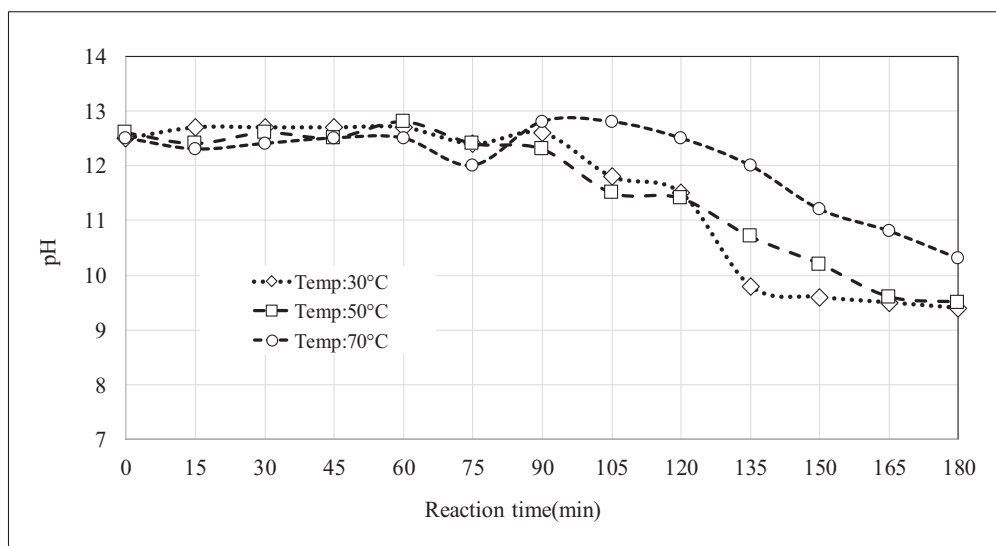


Fig. (14). pH profile in the advance of the reaction: Influence of temperature.

This work was carried out in the Reactivos Nacionales S.A, in order to solve a serious environmental problem related to hydrogen sulfide produced as a byproduct in the production process of dithiophosphoric acids. The problem was solved by producing NaHS, which the company can commercialize. Next we show the dimensioning of the industrial reactor.

3.6. Chemical-industrial Reactor Design

The stirred tank reactor is the most frequently used in process industries [66] to bring about an excellent solid-liquid, gas-liquid or gas-solid-liquid contact. The adequate degree of suspension of solid particles mean homogenization of slurry so formed or a near homogenization such that the suspension ensures uniform process conditions leading to predictable results. And the adequate degree of mixing is the required degree of turbulence which minimizes the mass transfer resistances [67]. For the industrial manufacture of sodium sulfhydate in aqueous solution, the three-phase reactor has the following functions:

- To ensure the adequate contact of the reactants to obtain NaHS: H_2S (gas) - sodium sulfide crystals(solid) - reaction solution (liquid).
- To provide sufficient contact time between substances.
- To allow temperature conditions and composition of the reactants so that the chemical reaction develops at the desired speed.

The hydrodynamics of the fluids and the geometrical configuration of the reactors are key to understanding the mixing phenomena. The geometric configuration is so important that the processes can be considered of specific geometry. The turbine of discs with six flat blades for the systems of agitation with radial flow was developed from the studies of Rushton and is considered like a geometric configuration of reference [68]. For that reason, this

configuration has been used for the present study. The 6-blade Rushton disc turbine was shown to be the best impeller over a wide range of gas flow rates for dispersing both solids and gases simultaneously [69].

3.6.1. Dimensioning the Sparger

The **sparger** is an important element of the reactor. Its design should allow easy cleaning of the device. Inside the **sparger**, sodium sulfide crystals are deposited from the reaction mixture when the H_2S gas does not enter the reactor. Fig. (15) shows the cross section of the lower part of the reactor, where the agitator is installed, and (Fig. 16) shows the dimensions and capacity of the industrial reactor, based on the correlations shown in Fig. (6c) [42, 46], as well as the Rushton turbine of stainless steel. If it becomes clogged, it must be cleaned on the outside with a stream of hot water to dissolve the crystals inside. The sparger provided for this application consists of a straight tube of 1 1/2 "diameter Schedule 40, the material is made of AISI 316 stainless steel. The sparger is provided with three holes of 0.75 inches of diameter, through **sparger** the H_2S bubbles are discharged near the impeller. The location of the sparger is important and is related to the interfacial area (bubble size). In the design of the reactor, the sparger has been placed in favor of flow current for both pilot and industrial tests. The main problem that arises in the design of gas-liquid reactors is the correct evaluation of the interfacial area, a magnitude for which there are no general methods of estimation and which suppose the greatest difficulty in scale changes. Most researchers have found that the specific interfacial area in a bubbling tank is related to gas surface velocity and the power supplied to the dispersion (per unit volume). Molina and collaborators analyze the influence of the variables of operation in the region of low intensities of agitation, on the interfacial area in cylindrical tanks where the disposition of the sparger is modified so that the gas bubbles in favor and against the flow currents [70].

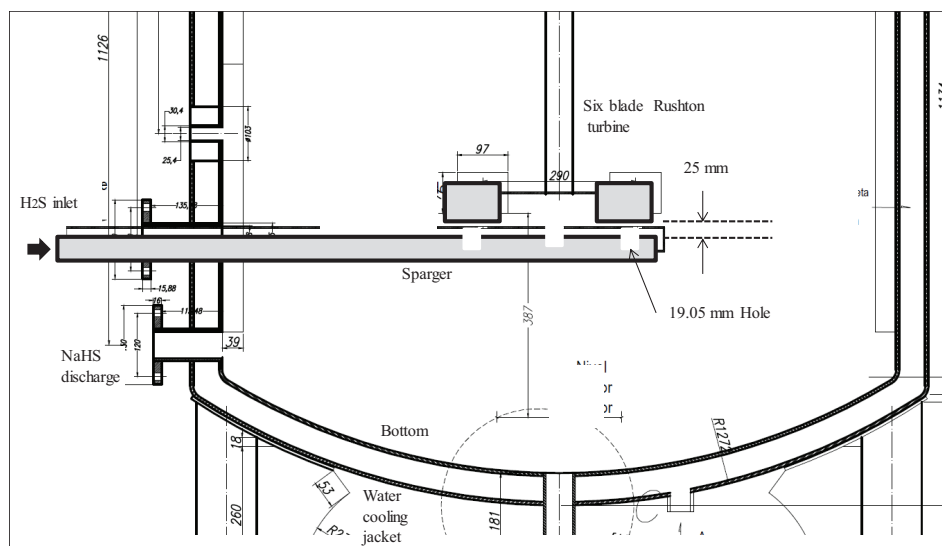


Fig. (15). Position of the bubbler in the industrial reactor.

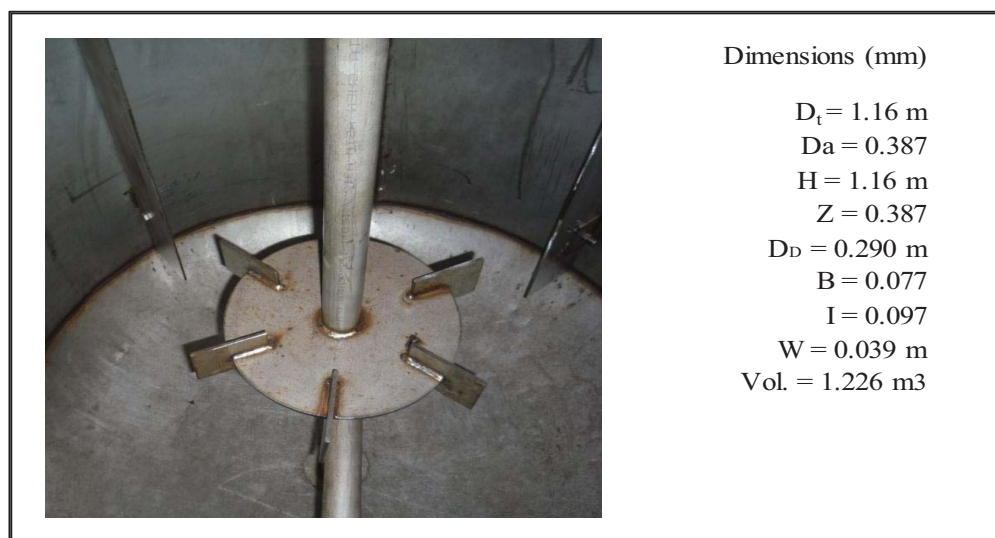


Fig. (16). Photographic view of the interior of the industrial reactor: Rushton turbine.

3.6.2. Reactor Temperature Control System

The objective of controlling the temperature in the reactor is to achieve an adequate conversion in the formation of the product and to keep the system operating around the specified conditions. Two stages take place in the reactor:

- Product training
- Heat removal from the reactor through the cooling jacket

The reagent (H_2S) entering the reaction with sodium sulfide generates heat and heats the system. Temperature is the variable to control, although the most important for the production of NaHS is to control the concentration of the species that are formed in the reactor.

A strict control of the minimum temperature ($50^\circ C$) of the

NaHS reactor is essential to avoid the formation of $Na_2S \cdot 9H_2O$ crystals that can cause problems. Controlling the temperature below $55^\circ C$ will allow maintaining a good solubility of the H_2S in the reaction solution and thus avoid losses of H_2S outside the reactor.

3.6.2.1. Thermostat

The temperature controller is an electronic device that receives the signal from the sensor, and transforms it into temperature values according to the algorithms established for each type of sensor. The controller sends an electrical signal to the final control element (water valve) when comparing the value of the process with the control value using the control mode set. The driver used is of the brand Autonics, Model TZ4M. The type of control that can be done with this device are ON-OFF, P, PI, PD, PIDF and PIDS. For our case, the ON-OFF basic mode was used (Fig. 17).

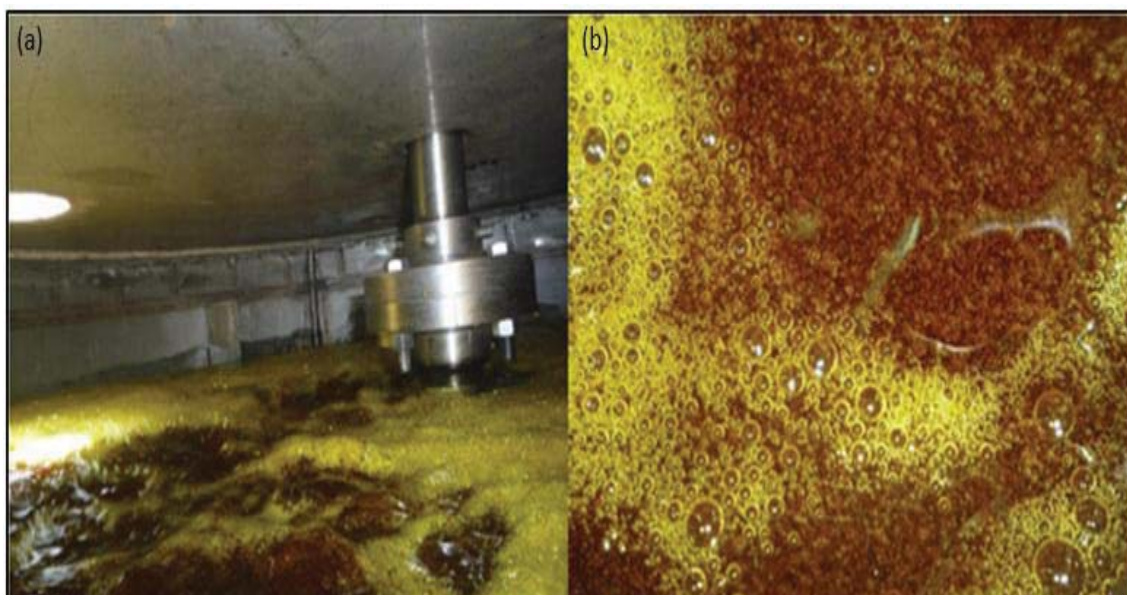


Fig. (17). Photographic view of the bubbling process inside the industrial reactor: (a) Agitator, (b) Foam formation: Reactivos Nacionales S.A Plant, Lima Peru.

3.6.2.2. Temperature Sensor

The temperature sensor installed in the reactor is a three-wire Pt100 sensor, whose measuring range ranges from $-100\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$, 6" bulb length, $\frac{1}{4}$ " bulb diameter, aluminum head.

3.6.2.3. Control Valve

The control valve used is a full-pass valve with a diameter of 1", sufficient for the passage of cooling water with a maximum flow of $6.02\text{ m}^3/\text{h}$.

3.6.2.4. Control Mode

The ON-OFF mode is the one used for the temperature control of the reactor, this control is the most basic and efficient enough for our purpose. The equipment of the TZ4M controller of the AUTONICS brand is configured in such a way that:

- It turns on when PV (process value) is less than SV (control value) ($53\text{ }^{\circ}\text{C}$)
- It turn off when PV is greater than SV ($53\text{ }^{\circ}\text{C}$).

3.6.3. Balance and Stoichiometry of the Reaction: Industrial Essay

As in the pilot tests, for the industrial tests, it has been determined that the reaction medium will be formed initially of 43% sodium sulphydrate concentrated solutions (liquid solution at temperatures higher than $20\text{ }^{\circ}\text{C}$). In this medium, the sodium sulfide ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$) crystals will form when stoichiometric amounts of NaHS and NaOH react. According to preliminary work at the pilot level it has been confirmed that one of the best proportions (of sodium sulfide, sodium sulphydrate, and water) in the reaction mixture should start from a weight ratio of 43% NaHS / 50% NaOH = 6.24 and a reaction mixture of overall percentage composition as follows: 13.3% Na_2S , 26.9%

NaHS and 59.8% H_2O . All the industrial tests will be carried out starting with a 50% sodium hydroxide industrial grade and sodium sulphydrate greater than 43% (with contents less than 0.4% Na_2S) in the commercial grade that is available at the plant.

For the purposes of this calculation, the NaHS available for the first test has a concentration of 43.2% (with contents less than 0.1% of Na_2S). Formation of Na_2S , taking into account (Eq. 7), starting with 212 kg of 50% NaOH. This equation allows to determine the requirements of reactants and reaction media for the formation of sodium sulfide. NaHS requirement at 43% for the formation of Na_2S :

$$M_{\text{NaHS}} = \frac{0.5 \cdot 212\text{ kg NaOH}}{39.9 \left(\frac{\text{g NaOH}}{\text{mol NaOH}} \right)} \cdot 56.063 \left(\frac{\text{g NaHS}}{\text{mol NaHS}} \right) \left(\frac{1\text{ mol NaHS}}{1\text{ mol NaOH}} \right)$$

$M_{\text{NaHS}} = 148.6\text{ kg}$, $M_{\text{H}_2\text{O}} = 195.0\text{ kg}$ (water that accompanies sodium sulphydrate), $M_{\text{Na}_2\text{S}} = 0.3\text{ kg}$ (Sodium sulphide that accompanies sodium sulphydrate): $M_{\text{NaHS}, 43.2\%} = 343.9\text{ kg}$

Na₂S generation:

$$M_{\text{NaHS}} = \frac{0.5 \cdot 212\text{ kg NaOH}}{39.9 \left(\frac{\text{g NaOH}}{\text{mol NaOH}} \right)} \cdot 78.045 \left(\frac{\text{g Na}_2\text{S}}{\text{mol Na}_2\text{S}} \right) \left(\frac{1\text{ mol Na}_2\text{S}}{1\text{ mol NaOH}} \right)$$

$$M_{\text{Na}_2\text{S}} = 206.8\text{ kg}$$

H₂O generation:

$$M_{\text{H}_2\text{O}} = \frac{0.5 \cdot 212\text{ kg NaOH}}{39.9 \left(\frac{\text{g NaOH}}{\text{mol NaOH}} \right)} \cdot 18.015 \left(\frac{\text{g H}_2\text{O}}{\text{mol H}_2\text{O}} \right) \left(\frac{1\text{ mol H}_2\text{O}}{1\text{ mol NaOH}} \right)$$

$$M_{\text{H}_2\text{O}} = 47.7\text{ kg.}$$

Water from 50% sodium hydroxide (considering that the content of carbonates and other substances are less than 0.1%) is: $M_{H_2O} = 106$ kg (of sodium hydroxide).

NaHS Requirement 43.2% as Reactant and Reactant Medium

The requirement of NaHS at 43.2% as reactant and reactant means is 1 322 kg of NaHS 43.2% of which 978.9 kg, will serve as a reaction medium that will promote the suspension of the sodium sulfide crystals formed. In 978.9 kg of NaHS 43.2% it has as: NaHS = 422.9 kg, $Na_2S = 1$ kg and $H_2O = 555$ kg.

Adjustment of the Reaction Mixture

Soft water is added for the NaHS dilution in order to correct the NaHS concentration to 43.5%. The water for the compensation and readjustment of the concentration of the reaction mixture is: $M_{H_2O} = 34$ kg

The sum of all the contributions and the chemical species present in the reaction mixture corresponding to the sodium sulfide formation step makes a total of 1568.9 kg for a reactant solution with the following weight percentage composition: $M_{Na_2S} = 208.2$ kg (13.27%), $M_{NaHS} = 422.9$ kg (26.95%), $M_{H_2O} = 937.8$ kg (59.78%), $M_{total} = 1 569$ kg (100%). It has experimentally been verified that under this formulation and at 50 °C, about 40% by volume of solids formed by sodium sulfide crystals and 60% of a liquid phase are obtained. The mixture possesses good properties for agitation. The content of solids (sodium sulfide crystals) at 50 °C is 22.16% by weight. Weight of the solid phase: 347 kg, Weight liquid phase: 1 220 kg.

Initial composition of the chemical species in aqueous phase (reactant solution) at 50 °C is: 3.6% Na_2S , 35.0% NaHS, 61.0% H_2O .

Generation of NaHS: According to (Eq.8)

For the conversion of all the sodium sulfide content of the reaction mixture the amount of H_2S required is:

$$MH_2S = \frac{208,2 \text{ kg } Na_2S}{78,045 \left(\frac{g Na_2S}{mol Na_2S} \right)} \cdot 56,063 \left(\frac{g NaHS}{mol NaHS} \right) \left(\frac{2 \text{ mol NaHS}}{1 \text{ mol } Na_2S} \right)$$

$M_{NaHS} = 299.1$ kg of which 149.5 kg is generated as final product and the rest is reincorporated into the reaction medium (NaHS 43%): $M_{NaHS} = 149.5$ kg. From the total balance of the reaction mixture and finishing the reaction there is a total mass of: $M_{total} = 1 659.8$ kg

3.7. Determination of Critical Speed (N_{js}) for the Suspension of Na_2S Crystals in a NaHS Solution for the Pilot Reactor and Industrial Reactor

Solids suspension applications require accurate specification of the impeller speed because these operations are power intensive. These stirred tanks are usually operated at the just suspended speed, N_{js} , which is the impeller speed at which no particles remain stationary at the bottom of the tank for more than 1 or 2 s [71 - 76], and five states of suspension were

observed that occur in solid liquid agitation with respect to the speed of the agitator (N). When the agitator speed reaches the N_{js} it can be said that a complete suspension is found [77]. The critical impeller speed for solids suspension (N_{js}), also has been studied in gas inducing mechanically agitated contactors fitted with two impellers by Saravanan et al., the study shows various stages of the solid phase during the process of solid suspension [78]. A critical analysis of this correlation (Eq. 25) can be consulted in [72]. The geometric parameters that affect N_{js} are impeller diameter, tank diameter, off-bottom clearance of the impeller, type of impeller, off-bottom clearance of baffles and shape of the tank bottom [72, 79]. S is a function of impeller type, impeller diameter and off-bottom clearance [72]. S is very sensitive to geometry [72], but also depends on the type of the particle [72, 80]. The amount of suspended solids as a function of impeller speed depends on the presence of fine particles in the suspended material. The more fines are present, the higher the amount of suspended solids are result [81]. For the design of the critical speed of suspension of the industrial reactor it is necessary to know the correlation constant of Zwietering (S), which is visually characterized [73]. For this, the characteristics of the suspension in the pilot reactor were observed considering (Eq. 25).

$$N_{js} = S \cdot v^{0.1} \cdot \left[\frac{g \cdot (\rho_s - \rho_l)}{\rho_l} \right]^{0.45} \cdot X^{0.13} \cdot dp^{0.2} \cdot D^{-0.85} \quad (25)$$

For the reaction mixture (see 3.5): $v = 0.00488$ m²/s (NaHS kinematic viscosity 43% at 50 °C), $g = 9.806$ m/s² (Gravity), $\rho_l = 1.28$ kg/m³ (NaHS density 43% at 50 °C), $\rho_s = 1.58$ kg/m³ (Density of solid $Na_2S \cdot 5H_2O$), $X = 0.22$ concentration of solids (weight ratio), $dp = 1500$ μm (particle diameter), $D = 0.056$ m (agitator diameter). With the pilot reactor, different speeds have been tested and it has been concluded that for a speed of 600 rpm (10 rev / s) an adequate suspension of the crystals is achieved.

The vortex on the agitation surface and the distribution of particles is not appreciated in the solution. It is homogeneous, even from 550 rpm. While 600 rpm (10 rev / s) is the critical suspension rate (N_{js}) in the multiphase reactor, the correlation constant "S" has a value of 4.516. The critical velocity for the solids suspension (N_{jsg}) in the Gas-Liquid-Solid reactor is calculated according to (Eq. 26) [82].

$$\Delta N_{js} = N_{jsg} - N_{js} = k \cdot Q_g \quad (26)$$

Constant k was determined by [83] whose value is 0.94. Where: $N_{js} = 10$ rev / s (Critical speed for the dispersion of gases in an S-L reactor) and $Q_g = 0.41$ vvm (gas flow). Applying (Eq. 26), the minimum value for N_{jsg} is 623.12 rpm (10.39 rev / s). For the industrial reactor, the critical speed (N_{js}) for the suspension of Na_2S crystals in a NaHS solution is evaluated taking into account: $S = 4.516$, $D = 0.387$ m (diameter of the agitator), and the other parameters of the (Eq. 25) are the same as mentioned above: it is 58.06 rpm (0.967 rev / sec). For an aeration rate of 0.2 vvm and with Eq. 26, the minimum critical velocity (N_{jsg}) for the suspension of solids in

the industrial reactor results in 69.34 rpm (1.16 rev / sec). Finally, the conditions for NaHS production at the industrial

level are established as follows: Composition mentioned above, temperature of 50°C, agitation speed of 80 rpm, and a luxury of

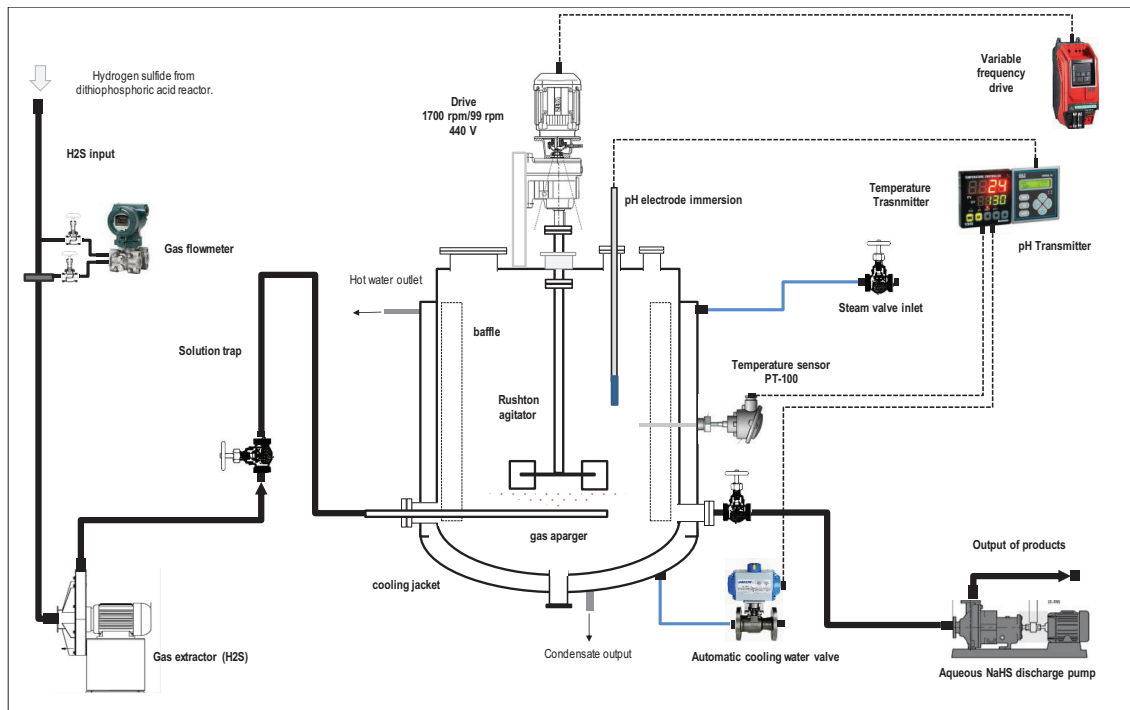


Fig. (18). Instrumentation diagram of the industrial reactor (Reactivos Nacionales S.A).

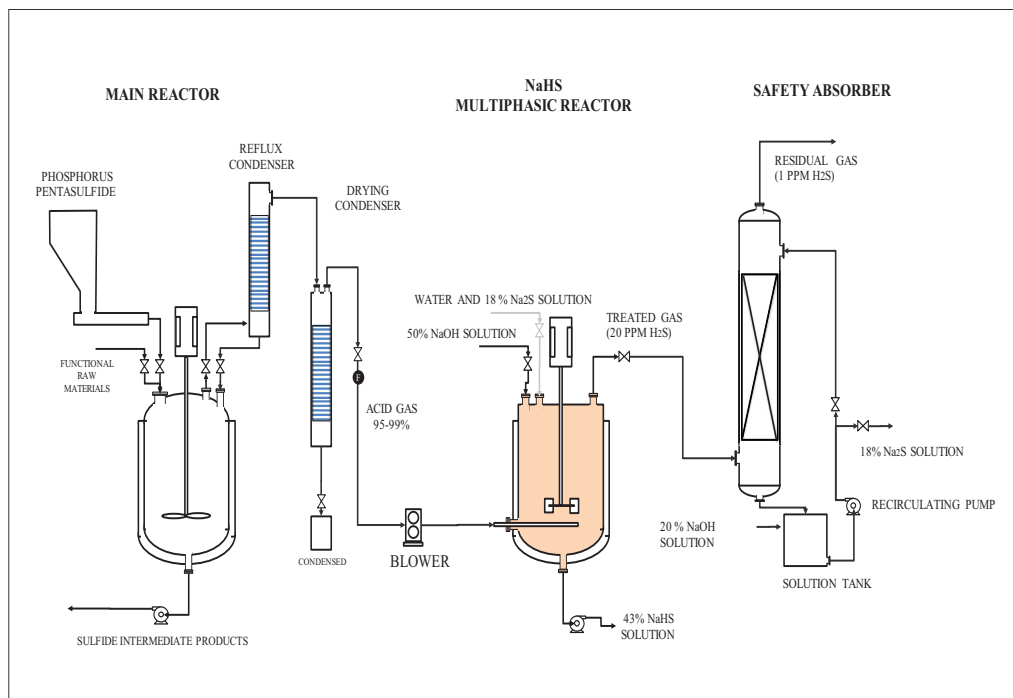


Fig. (19). NaHS production reactor integrated to the main process (Reactivos Nacionales S.A).

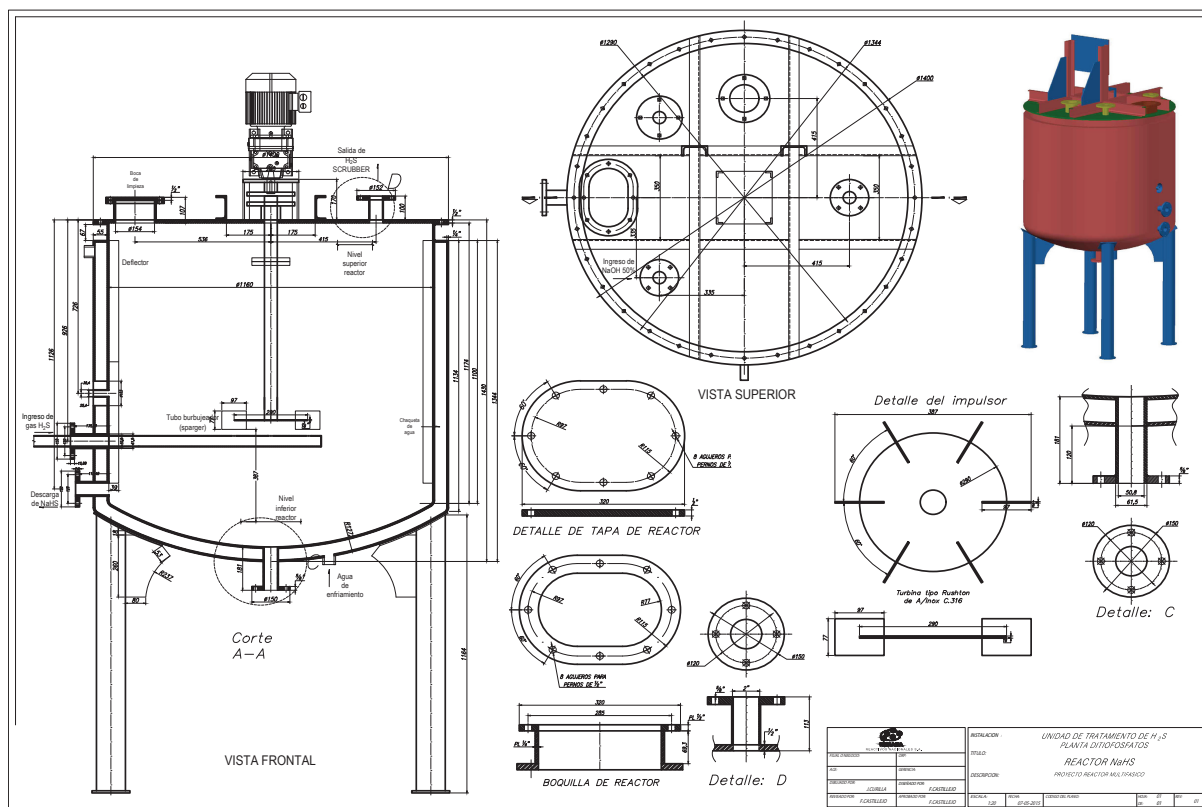


Fig. (20). Detailed plan of the NaHS reactor, for the dithiophosphate acid plant of the company Reactivos Nacionales. S.A.

H₂S gas of 0.2 vvm (for 4-hour reaction) which is on average that a stable production of H₂S is recorded, although the H₂S is generated in the ADTF reactor for 6 hours until it is completely extinguished, and the cooling water flow of the system is 1930 L (8.04 L / min). The calculations of this part are not presented. Figs. (17-20) show the internal part of the reactor in full operation, the instrumentation diagram of the industrial reactor, the integration of the reactor within the process of production of dithiophosphoric acids, and the complete design of the reactor respectively.

The gas hold-up (Eg) corresponding to a gas flow of 0.2 vvm, at a temperature of the NaHS solution 43% of 50 °C, pH of 8.5, where the absorption of H₂S has decayed, therefore the gas It retains in the reaction mixture and it is observed that bubbles and foams are produced on the surface. The maximum volume displaced is 1397 L (without considering the foam mattress). The volume of the aqueous solution of NaHS with agitation and without gas flow is 1285 liters. Therefore the Eg [84] is: Eg (hold-up) = (1397-1285) / 1397 = 0.0801.

When the pH is greater than 11, there are few H₂S bubbles and the foam mattress is not observed. The maximum displaced volume is 1397 L, at this point the H₂S bubbles collapse and are absorbed in the reaction mixture, and no gas retention is observed. When the industrial reactor with an impeller diameter of 0.387 m and agitator speed of 1.33 rev / s, works with the 43% NaHS solution at 50 ° C, the viscosity and density of the solution are 0.00624 Pa.s and 1280 kg / m³

respectively. The value of the Reynolds Number ($NRe = ND^2\rho / \mu$) [85, 86] is 40860. For a Rushton type impeller with $W / D = 1/5$, graphically [85, 86] the value of the power number of 5.

The power number (Np) has not been directly measured, however the power consumption of the agitator motor is 1230 Watts, which allows to maintain an adequate agitation, suspension of the crystals and dispersion of the H₂S bubbles, for a reaction mixture of 1644 kg. In all forms of the reaction mixture (single phase, two phase and three phase) there is no significant change in power consumption. However, there is a major change in the adjustment of the axial seals of the (packed gland) agitator.

CONCLUSION

In this study, the synthesis of sodium sulfhydrate was carried out from hydrogen sulphide, which is a highly toxic gas and a by-product of the dithiophosphoric acids production process in the Reactivos Nacionales S.A. Company.

- A recovery method has been established and implemented that allowed obtaining sodium sulfhydrate with concentrations higher than 43%, in a semicontinuous form and at temperatures ranging from 50 °C to 55 °C, with an average temperature of 52.5 °C. The temperatures reached are much lower than the temperatures of recovery technologies currently available in the market.

- It is possible to produce aqueous solutions of sodium sulphydrate from Gas-Liquid-Solid reactions. The conversion of hydrogen sulphide into sodium sulphydrate was carried out in a stirred multi-phase reactor at 700 rpm, which allows the solids to be kept in suspension, which are mainly made up of sodium sulfide crystals ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$).
- According to the tests carried out, the conversions of H_2S in NaHS obtained in the multiphase reactor are greater than 90%.
- From sodium hydroxide at 50% of commercial grade, 43% sodium sulphydrates have been obtained, chemical Eqs. (2-4, 8 and 13) explain the process. The reaction medium that promotes the conversion is formed by an aqueous solution of NaHS and Na_2S that allows the suspension of the sodium sulfide crystals and the contact with the H_2S gas in a multiphase reactor.
- Temperature is a critical parameter in the process. At temperatures below 30°C , the presence of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ crystals affects gas dispersion, reactor hydrodynamics, crystal distribution, heat transfer and absorption of H_2S in the multiphase reactor. At temperatures above 60°C , a low absorption of hydrogen sulphide in the reaction medium is registered and consequently a slow conversion of Na_2S into NaHS.
- It has been found in this investigation that the main drawback for the manufacture of aqueous solutions of sodium sulphydrate at concentrations higher than 40% by weight, starting directly from sodium hydroxide, is the formation of sodium sulfide crystals ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) due to its low solubility of these crystals, it is not possible to obtain sodium sulphydrate safely and efficiently in stirred chemical reactors.
- To obtain 43% NaHS, sodium sulphide and water with percentages of 34% and 56% respectively are necessary. At temperatures higher than 50°C , two phases could be obtained, comprising an aqueous Na_2S solution and $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ (C2) crystals. At lower temperatures, the combination of $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ (C2) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (C1) crystals will appear, starting the solidification of the system, which is a serious problem.
- The agitation speed in the multiphase reactors (pilot and industrial level) studied allows to adequately disperse the gases and maintain the suspension of the sodium sulfide crystals in the reaction mixture to favor the chemical conversion. The best agitation speeds for the reactants established in this study are: 700 rpm for the pilot reactor and 80 rpm for the industrial reactor.
- The results obtained experimentally in the pilot reactor of 5 liters, provided sufficient information to size the reactor of the industrial type of 1 300 liters of capacity, which is appropriate for the requirements of treatment of the residual current of H_2S produced in the manufacturing process of dithiophosphoric acids.
- The proposed process has been integrated into the dithiophosphoric acids manufacturing plant, where it has been possible to recover more than 95% of the

hydrogen sulfide in the form of NaHS 43% (around 90% of H_2S in the multiphase reactor and plus 5% in the safety absorber).

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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