

Modern Spent-caustic Wastewater Treatment Simulation by Aspen Plus in Electrolytic Medium

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Abstract— A novel treatment process is presented to separate the salts from the spent caustic. In recent years, refinery and petrochemical producer is forced by more stringent environmental regulations to better monitor and control their wastewater. One of the key contributors to relatively high chemical oxygen demand (COD) and biological oxygen demand (BOD) is from the acid gas (both CO₂ and H₂S) and mercaptan removal system(s) typically using dilute caustic soda (NaOH) as the active reagent. It's difficult to clean up and dispose of due to its toxic properties. Today's various methods are used for treating spent caustic, such as wet air oxidation and direct acid neutralization. In this paper, the treatment process is simulated by Aspen Plus software in an electrolyte environment to obtain the cold and hot streams. The wastewater is preheated by heat-exchanger before treatment and separation process. Secondly, considering energy utilization to improve the process. Then the parameters of recovery process and utility system are adjusted. The amount of utility and energy consumption is significantly reduced and some optimizations are presented. In a case study, three optimization schemes are adopted. The results showed that the energy consumption of optimized processes decreases due to type of process and equipment.

Keywords— *treatment; wastewater; spent caustic; simulation; recovery; aspen plus*

I. INTRODUCTION

Sodium hydroxide (caustic) scrubbing solutions are commonly used in petrochemical and gas/petroleum refineries for the removal of acid components such as hydrogen sulfide, cresylic acids, mercaptan and naphthenic acids from the refined product streams [1]. Due to being hazardous, odorous, and/or corrosive components of spent caustic, handle and dispose of them, can be a challenge. Spent caustic streams may also have other characteristics that can create issues with conventional biological processes such as noxious odors, pH swings, foaming, or poor settling of biological solids [1]. Effluent requirements may be difficult to achieve because some spent caustic contaminants are not readily biodegradable. Typically, the material is disposed of by high dilution with biotreatment, acid neutralization,

deep well injection, incineration, wet air/catalytic/Humid Peroxide Oxidation or other specialty processes [2]. The two basic methods for treating spent caustic solutions are wet air oxidation (WAO) and direct acid neutralization (DAN), respectively. In this paper, first spent caustics and then treatment methods were discussed in detail.

A. Spent Caustic

For ease of discussion, spent caustics will be classified into three general categories: Sulfidic, cresylic, and naphthenic: Sulfidic spent caustics produced from the caustic scrubbing of ethylene or LPG (light petroleum gas) products contain high concentrations of sulfides and mercaptans. Cresylic spent caustic, generated when scrubbing gasoline produced by fluidized bed catalytic cracking processes with caustic containing high concentrations of organic compounds including phenols and cresols. This type of spent caustic may also contain sulfides and mercaptans. Naphthenic spent caustic produced from the caustic scrubbing of kerosene and diesel products contain high concentrations of polycyclic aliphatic organic compounds such as naphthenic acids. Depending upon the types and quantity of products being produced, a refinery may have varying amounts of each of these categories of spent caustics that require treatment. In some instances, the spent caustics are combined to produce a mixture [2,3]. There are different problems with the treatment of spent caustic streams. Sulfides and mercaptans have very bad odors. The smell thresholds for these types of stuff are generally in the order of values of parts per billion. Moreover, per OSHA, these matters are considered very toxic and can be potentially hazardous to plant staff. This is particularly true in processes where the spent caustic is acid neutralized, which causes hydrogen sulfide and mercaptan gases to be escaped. High concentrations of phenols in the spent caustic effluent can lead to problems in biological treatment processes. Phenol in concentrations as low as 400 mg/L has been shown to prevent the elimination of COD, ammonia and phosphorous as well as negatively affect the settling characteristics of

the sludge. It must be noted that in many refineries, the production of spent caustics including cresylic acids is performed as a batch process. This can lead to periodic disposal of phenols and cresols to the effluent treatment plant. It has been reported that sudden discharges of waste containing high concentration of phenols have caused perfect prevention of the biological clean up system. The spent caustic streams often include a variety of matters that are bio-refractory. Literature reviews show that naphthenic acids have been shown to have finite biodegradation in common biological treatment processes. Naphthenic acids have foaming specifications that can create problems when aerated or agitated during biological clean up. The untreated spent caustic streams are generally high in chemical oxygen demand (COD), in the range of 15 (g/L) to larger than 400 (g/L). Depending on the volume of spent caustic that is present; this can result in a huge COD load on downstream biological processes [1, 3].

B. Major sources of spent caustic

Isomerization spent caustic, is used in ethylene cracker unit in order to caustic scrubbing of cracked gas. This solution is created by a caustic scrubbing column. Output ethylene product is contaminated with $H_2S(g)$ and $CO_2(g)$, and those contaminants are eliminated by absorption in the caustic scrubbing column to produce $NaHS(aq)$ and $Na_2CO_3(aq)$. The $NaOH$ is used and the resulting effluent (spent caustic) is mixed with the sulfides and carbonates and a small component of organic compounds. Refinery spent caustic, is created by various sources, such as the Merox processing in some industrial plants like gasoline, kerosene, jet fuel; LPG, gas sweetening unit and caustic scrubbing, Sulfides and organic acids are eliminated from the product streams into the caustic phase. The $NaOH$ is used and the resulting effluents (cresylic for gasoline; naphthenic for kerosene/jet fuel; sulfidic for LPG -spent caustics) are often mixed and called refinery spent caustic that is contaminated with sulfides, carbonates, and in some conditions a high fraction of heavy organic acids [8, 9].

II. SPENT CAUSTIC

A. Composition of Spent Caustic

It is toxic and highly odorous. The list below shows typical analytical results:

1. Chemical Oxygen Demand (COD): 10,000 to 100,000 (mg/L).
2. Biochemical Oxygen Demand (BOD): 5,000 to 50,000 (mg/L).
3. Total Organic Carbon (TOC): 1,000 to 5,000 (mg/L).
4. Sulfides: 5,000 to 35,000 (mg/L).
5. High pH value.

TABLE I. PERMISSIBLE LIMIT OF ENVIRONMENTAL INDICATORS.

Environmental Indicators	Permissible Limit (mg/L)
BOD	80-1600
COD	200-4000
TOC	80-260
Sulphide as H_2S	3

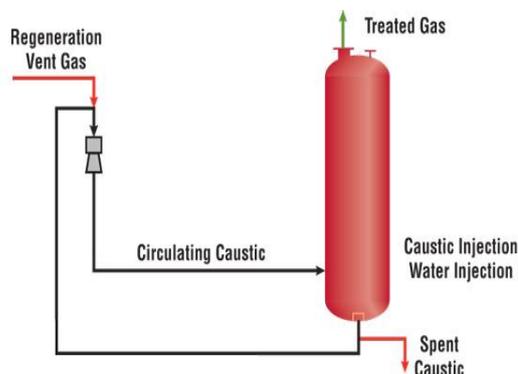


Fig. 1. Schematic design of spent caustic that is produced in various industries

B. Common treatment processes

There are various treatment processes which are divided as follows:

1. Chemical oxidation.
2. Neutralization.
3. Dilution Treatment.
4. Wet Air Oxidation (WAO).

III. Wet air oxidation technology process

The hydrothermal or WAO clean-up is a high-temperature process for the oxidation of matters which are solved or suspended in water with oxygen [4]. In other words, WAO is the process of oxidizing organic pieces of stuff in the presence of water. Theoretically, each substance that is able to burning can be wet oxidized in water. Spent caustic has high COD. This is not accepted in biological water purification plant. Wet air oxidation system oxidizes sulphides and mercaptans to reduce COD of spent caustic. After cleaning with WAO the wastewater has a lower COD and can then be treated in the biological refinement plant [5].

The oxidation reactions are performed at elevated temperatures requiring a pressurized system in order to control evaporation. The WAO technology when utilized for the treatment of spent caustic can be further divided into three categories based upon the temperature that is used to perform the oxidations [1,3].

- Low-temperature WAO – typically performed at 110-120 °C and (25 to 100 psig)

- Mid-Temperature WAO - typically performed at 200-220 °C and (300 to 600 psig)

- High-Temperature WAO - typically performed at 240-260 °C and (700 to 1100 psig)

Low- temperature WAO has been historically utilized for the treatment of reactive sulfides in spent caustic, while mid and high-temperature WAO has been utilized for the complete clean-up of sulfides and mercaptans also the treatment of organic components such as cresylic acids and naphthenic acids.

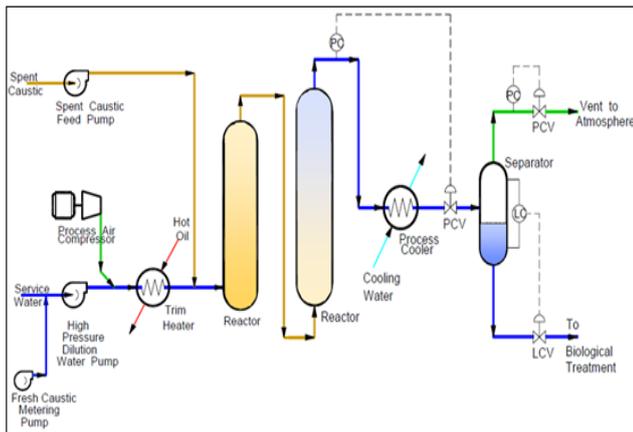
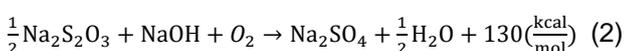
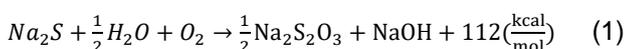


Fig. 2. WAO flow diagram [5]

In a conventional WAO system, the feed at a higher pressure is pumped to the system. The feed stream is pre-heated with outgoing wastewater from a reactor in a heat exchanger and mixed with compressed air. The feed stream can also be heated before it enters the reactor. The hot fluid flow is then kept in a reactor for one-hour residence time at 200°C without any catalyst. The reactions occurred in the liquid phase and the oxygen must be moved to the liquid phase from gas phase to do the reaction. Excess air is supplied to attain appropriate conversion. Sulphide compounds oxidize partially to form thiosulphate, moreover oxidation creates sodium sulphate. The organic materials present in the spent caustic are oxidized relatively. The total organic carbon is not affected much, but its nature is changed which results in lower COD and lower fouling rates. The process also improves bio-treatability of the organic compounds. A simplified process flow diagram of the WAO was shown in figure 2. WAO is generally used as a waste treatment technology when the waste is non-conductive to incineration or biological treatment. It is an idealistic process for pretreatment of wastes that are problematic to common biological equipment. The WAO process is uniquely adjusted to the oxidation of concentrated waste drinks, slurries, and sludge's where the oxygen requesting organic material is only a few percentages of the deliberate water flow.



IV. Direct acid neutralization method process

In the direct acid neutralization (DAN) treatment process, the spent caustic wastewater is acidified to release acidic components that were captured in the alkaline caustic solution. Sulphuric acid (98%) and hydrochloric acid are suitable. This results in sulfides and mercaptans being released as acid gases and naphthenic acids to be sprung as an oil layer or can be processed or incinerated in a sulfur improvement unit. One large differentiation between acid neutralization and WAO is that the acid components in the spent caustic are removed but not destroyed. In some cases, this results in additional treatment to be required. In others it allows for the capture and re-use of some of the components in the spent caustic. The neutralization reactions to reach a pH of 7 or above are sum up as follows [1].

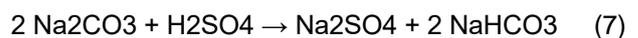
Caustic



Sodium sulphide



Sodium carbonate



Sodium mercaptide



Sodium phenolate



Each spent caustic including mercaptides or sulphides may be oxidized before neutralization to minimize COD of the final wastewater brine and sulfur amount of the neutralizer off-gas. The control of pH in the neutralization stage is critical because the metallurgy is not designed for low pH operation (below 6). It is also important to minimize the production of gases such as H₂S from any remaining Na₂S and CO₂ from the sodium carbonate. Any mercaptans released in the neutralizer will also result in a highly odorous brine solution [3, 6].

V. THE INNOVATION OF THE PLAN

1. Elimination of toxic materials from wastewater.
- 2- pH reduction and neutralization with lower cost.
- 3- Production of a new product from effluent.
- 4- Use of cheap feed (wastewater) and low-cost additives.
- 5- Benefit from energy optimization and exergy.
- 6- Utilization of new technology with high value-added.

7- Purification of hazardous wastewater without any environmental risk.

8- Protection from environmental effects with high alkalinity property.

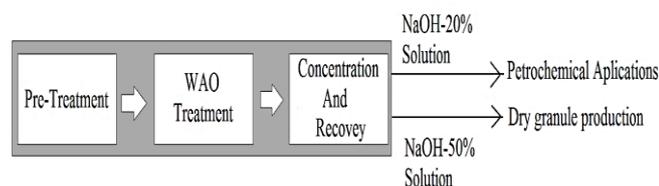


Fig. 3. The stages of the spent caustic treatment.

A. Advantages of the pre-treatment

Pretreat has two major advantages:

1. It converts the waste spent caustic to a saleable product.
2. If the spent caustic is not sold, it improves the oxidation of the spent caustic.

Downstream of the Pretreat unit, the WAO reactors oxidize the spent caustic to reduce its COD to the desired level before discharge. The efficiency of the oxidation step is a function of the amount of dissolved hydrocarbon present in the spent caustic.

B. Process overview

Different stages of technology implementation

1. Storage of wastewater in reservoirs and separation of fats or oils.
2. Oxidation of wastewater.
3. Separating of disulfide oil compounds.
4. Filtration process.
5. Concentration stage.

V. DESCRIPTION OF THE NEW METHOD

In this project because of the essential need of the industrial units to restore spent caustic following benefits are:

- 1- The ability to remove hazardous compounds from wastewater without producing hazardous wastewater and without any environmental risk.
2. hazardous sodium sulfide (Na_2S) removal in wastewater.
3. The production of a valuable substance such as NaOH and sodium carbonate rather than neutralizing it by acid or drop it in water due to high pH that is very harmful to the environment.

The use of new and modern technology compared to other technologies with more advantages.

1. Storage of wastewater in reservoirs and separation of fats or oils.
2. Advanced oxidation (AO) of wastewater.
3. Separating of disulfide oil compounds.
4. Filtration process.
5. Concentration stage.

Advanced oxidation (AO) of wastewater, is performed by wet air, ozone molecule, UV ray, and appropriate catalyst.

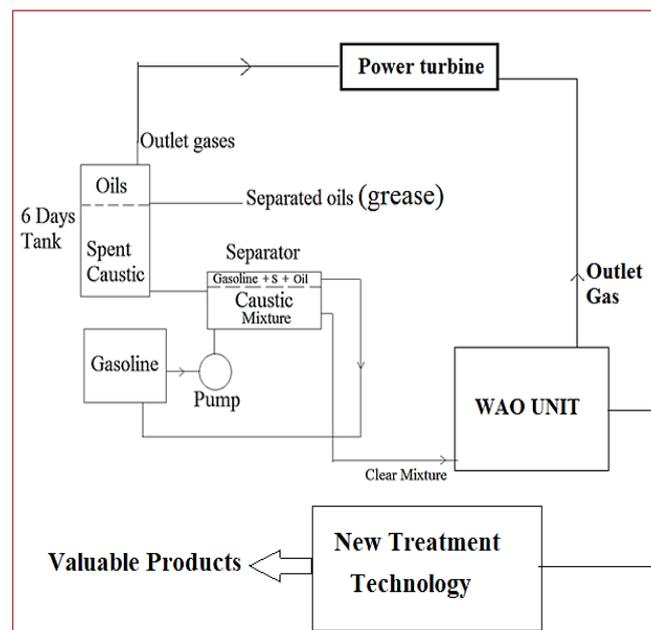


Fig. 4. Schematic image of spent caustic treatment technology.

A. Pre-treatment process

The pretreated spent caustic is filtered through 5 μm media upstream of the WAO reactor for removal of suspended polymers down to a hydrocarbon content of 10 ppm (wt). The oil and grease content of 146 ppm(wt) was largely a result of the polymer formation of the dienes left in the raffinate feed.

B. Storing and advanced oxidation (initial stage)

Upstream of the Pretreat unit, the spent caustic from the caustic tower is deoiled to remove the polymeric material formed in the spent caustic. It is then degassed by the flashing part of the dissolved hydrocarbon gases. The spent caustic is then stored in a spent-caustic tank where oil and polymers float and are skimmed off from the spent caustic [10,11].

Advanced oxidation (AO) will oxidize all decreased sulfur materials and phenols, remove the foaming tendency of the spent caustic, and decrease a majority of the COD producing biodegradable wastewater. AO is the best applied to refinery spent caustics used for treating heavy products and containing naphthenic

constituents. AO can also be used to treat mixed spent caustics that may contain naphthenic as well as cresylic and sulfidic constituents. The type of spent caustic can determine the best treatment technique. AO found to be the most common treatment method to treat all type of spent caustics. Safety factor plays a major role in spent caustic treatment.

The oxidation contactors exceeded its design values in two ways. Na₂S content in the oxidized product is less than 1 ppm (wt). The design guaranteed 5 ppm(wt). There was a 97% conversion of NA₂S to NA₂SO₄ in the oxidized product. The design guaranteed 90%.

VI. SIMULATION PROCESS

The simulation process of spent caustic wastewater for Na₂O₃ and NaOH recovery in Aspen Plus version 11, has been done. Since the main purpose of crystallization of sodium carbonate that is water-soluble, the simulation environment or tool should be defined as electrolyte to allow for the conversion reactions of sodium carbonate to crystalline salt. Therefore, the Crystallization process has been used in the software. Simulation and basic results based on the related PFD are as follows.

The spent caustic wastewater as a feed with a flowrate of 4500 (kg/hr) and 40 °C enters into the process line. The process simulation is shown in figure 5.

A. Simulation conditions

Using the Electrolyte Wizard module in software to define the ionic species and salts that can be

generated from the base components entered on the Components-Specifications tab, the Selection sheet, and to generate the reactions that occur among these components in the liquid phase [12,13].

The inlet feed (spend caustic) includes 80% water, 9% NaOH, 1% Na₂S and 10% Na₂CO₃, spent caustic mass flow rate is about 4500 (kg/hr), the pressure of 7.2 bar, initial temperature of 40 °C and pH of 13.8. Moreover, the pressure drop in each heat exchanger is about 0.1 bar and the low-pressure steam (LPS) with specification of 127 °C and 2.46 bar for heating was used. Forced-circulation evaporative crystallizer in atmospheric pressure was used for simulation and the residence time of the crystallizer was 3 hr. The crystallization temperature was about 108 °C as well as, the solubility data of the Na₂CO₃ in the water was used in simulation. The combined NRTL-RK thermodynamic model was used for electrolyte medium. The crystal size of Na₂CO₃ (sodium carbonate) particles is about 500 μm. The basket model of centrifugal equipment was selected in simulation with height of 1.4 m and diameter of 2 m, humidity of the 0.3%, retention size of 50 μm, rotation velocity of 3000 rpm, filter cake of 50% and efficiency of 0.9. Also, the cake resistance for sodium carbonate particles at 1 bar is between 70 × 10⁹ to 18.2 × 10⁹ (m/kg) from experimental data. For cake concentration by volume fraction is as follows:

$$C = C_0(1 - u)\Delta\alpha_0^n \quad (10)$$

Where α_0 , C_0 , n and u are empirically derived constants. Published values for constants used in the above equation.

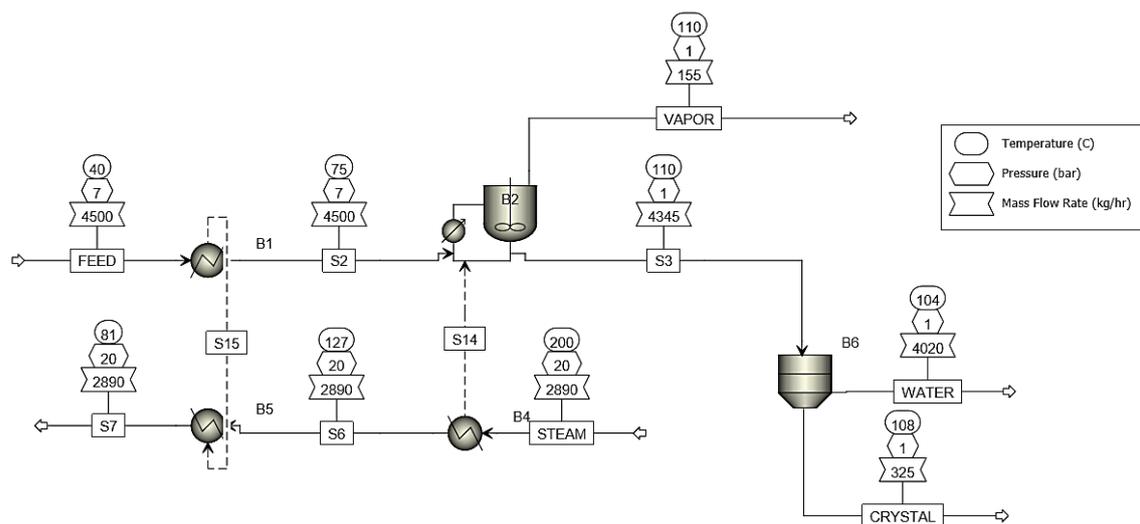


Fig. 5. Simulation environment in Aspen Plus. B1, B5: Heat exchanger (Cold feed waste caustic and hot condensate, B2: Crystallizer Evaporator – Steam condensation, B6: Centrifuge (Separation Na₂CO₃ crystal).

B. Simulation process optimization

According to the results, there are two cases of using limiting parameters and without them, it is clear that the amount of energy consumed by the saturated vapor is optimal. In this regard, it is necessary to note

that the change in the rate of steam consumption directly effects on crystallization temperature of equipment, amount of Na₂CO₃ crystalline and concentration of liquid caustic. Obviously, at the output, the decrease or increase in steam consumption does not result in the optimization of the unit.

Therefore, to study the integration points of energy, initial simulation is used with respect to limiting parameters. The optimum concentration is 25% wt, which is obtained by crystallization at 115 ° C. Therefore, the energy consumption of this equipment for evaporation has a direct effect on the consumption of saturated steam at 127 ° C. Hence, increasing the temperature flow to this equipment will have an optimal effect on reducing the energy consumption of the crystallizer.

C. Optimal combination of energy converters

According to current flows, the energy source that is used to increase the flow temperature of the input to the crystallizer is liquid spent caustic after centrifuge system. This stream for use in other processes or as a product (25% wt. of NaOH, about 30 ° Baume liquid caustic that is convertible to API), its temperature should be reduced. For this purpose, it can reduce the flow temperature to 45 ° C and use its energy in the first part of the unit. In this case, steam consumption at a temperature of 127 ° C reaches 2762 (kg/hr) by 5% reduction approximately.

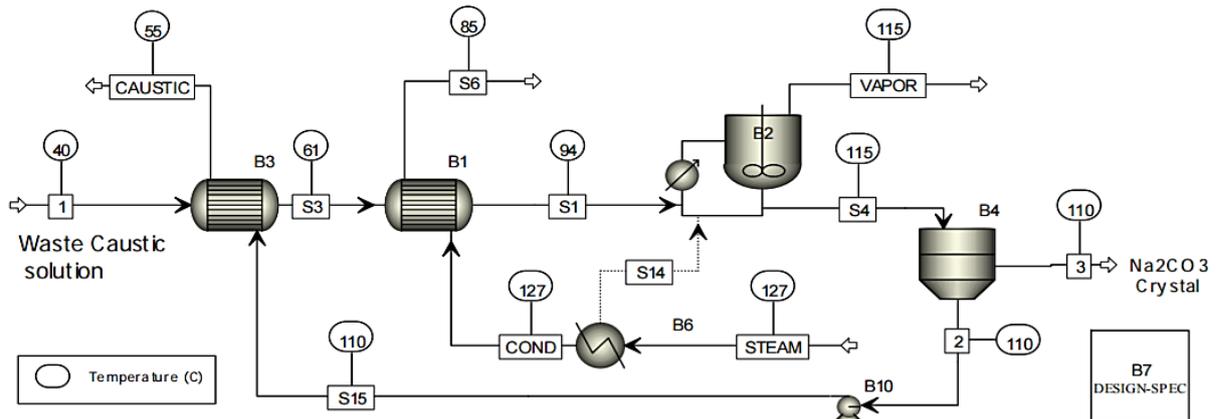


Fig. 6. The optimized process. B1, B3: Heat Exchanger (Feed spent caustic (cold), Lean Caustic stream (hot)), Condensate from the evaporator (hot)).

D. Optimum steam consumption conditions

Considering the new combination of heat exchangers, since steam consumption is reduced in this case, it is then appropriate to optimize the proper steam energy level. the temperature of the saturated vapor increases to obtain the appropriate energy level to reach the production rate at the basic stage. For this purpose, low-pressure steam (LPS) has been used in

the conditions (4barg and 175 ° C) as the input energy to the unit. Using a pressure control valve, its pressure is reduced to 3.5 barg and converted to saturated vapor by the condensate flow of evaporator. In this case, steam consumption decreases by about 8% relative to baseline and reaches to consumption rate of 2664 kg/ hr (figure 8).

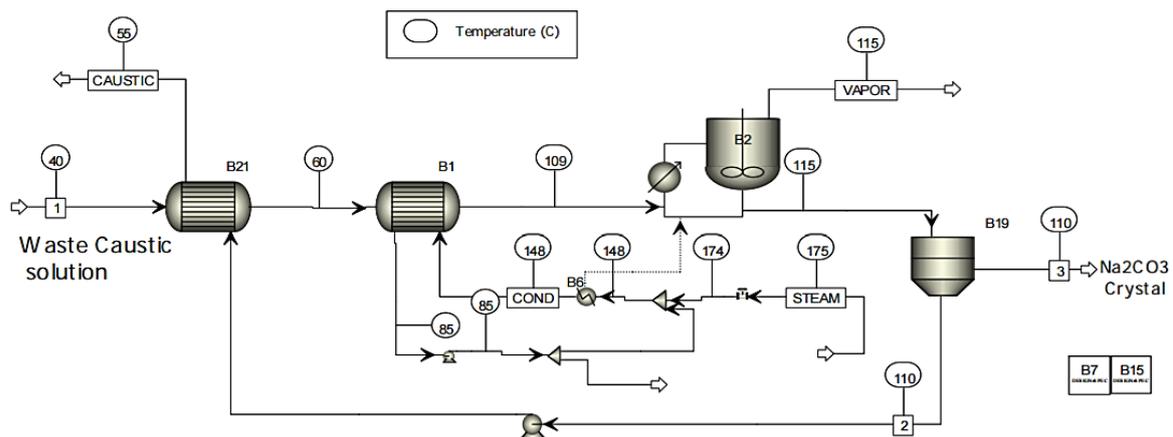


Fig. 7. Proposed optimized process.

In this case that is shown in figure 9, the medium pressure steam (MPS) was considered as the input current energy (19barg and 275C °). The pressure reducing valve reduces pressure to 5barg and finally,

the steam consumption decreases by 12% compared to baseline and reaches a consumption rate of 2535 (kg/hr).

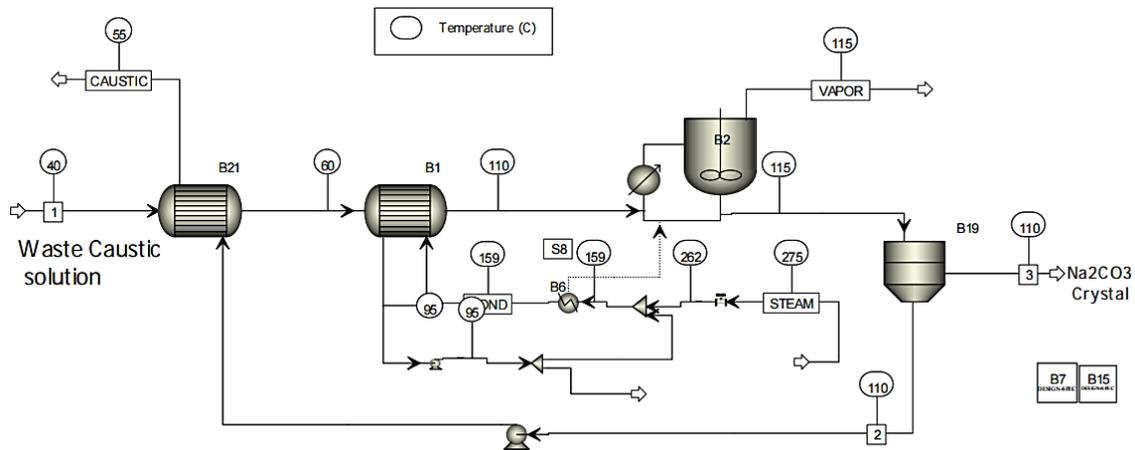


Fig. 8. Second, proposed optimized process.

VII. RESULTS AND DISCUSSION

The process simulation of Na₂CO₃ crystalline production from the flow of spent caustic that includes Na₂CO₃ soluble salts by means of heat transfer and evaporation. In this unit, the side flow of concentrated caustic is also received. The simulation of this section has been done by the Aspen PLUS software, which

has a special section for electrolysis and solid salts production in the fluid package and material selection. In the first step, the main structure of the PFD has been simulated. Therefore, the main source of concentrated energy of the flow is a saturated vapor of 127 degrees centigrade. The main results are taken in table.2.

TABLE II. THE SIMULATION RESULTS OF THE SPENT CAUSTIC TREATMENT PROCESS IN ASPEN PLUS.

Stream	1			2			3			Vapor	Steam
Description	Feed			Crystal			Caustic			Vapor	Steam
Temp (C)	40			110			110			115	127
Press. (bar)	7.213			1.013			1.013			1.013	2.465
Vapor Frac	0			0			0			1	1
Mole.Flow (kmol/hr)	214.8			4.4			73.9			136.6	160.4
Mass.Flow (kg/hr)	45000			434.2			1605.5			2460.3	2890
Vol.Flow (m3/hr)	3.7			0.2			1.3			4321.7	2113.7
Mass.Flow (kg/hr)	Kg/hr	wt%	Kmol/hr	Kg/hr	wt%	Kmol/hr	Kg/hr	wt%	Kmol/hr	Kg/hr	Kg/hr
H ₂ O	3600	80%	199.8	5.1	1	0.3	1134.6	71%	63	2460.3	2890
NaOH	405	9%	10.1	1.8	0	0	403.2	25%	10.1		
Na ₂ S	45	1%	0.6	0.2	0.0466	0	44.8	3%	0.6		
Na ₂ CO ₃	450	10%	4.2	0.1	0.0239	0	23	1%	0.2		
Na ₂ CO ₃ (S)				426.9	98%	4					
Density (kg/m ³)	1216.5			3434.2			1271			0.6	1.4
MW (kg/kmol)	21			99.5			21.7			18	18
pH	13.8						13.12				

A. The limiting parameters in the simulation are the following

With respect to the above explanation and the PFD structure, the solid sodium carbonate crystalline solids obtained at 427 kg per hour (crystal 434 kg / h with a maximum moisture content of 2%). Also, the concentrated liquid flow rate (max. 25% by weight) is 1605 kg per hour. According to the results obtained in the basic simulation, the temperature of the crystallizer section has a direct effect on the solidification of sodium carbonate. But, given the % wt, of NaOH in the liquid flow, no more energy can be transferred to the crystallization unit at a specific temperature (15 °C). Because the increase in temperature of this part increases the amount of water evaporation and increasing the concentration of NaOH. Also, by

ignoring this parameter, in order to increase the crystallization temperature, the amount of vapor consumption as only energy source in steam pipelines (in accordance with the original PFD, its temperature of 127 degrees and as a saturated vapor) should be increased. Two limitations are as follows.

1. Steam condensation @ 127 °C
2. NaOH concentration ≤ 25wt%

Regardless of two limiting parameters, the maximum output of crystalline Na₂CO₃ is shown in Table 2. In this case, Na₂CO₃ crystalline production is 447 (kg/hr) and steam consumption is 3450 (kg/hr) at the temperature of 140 °C and the caustic concentration in final flow is 35% wt.

TABLE III. THE SIMULATION RESULTS ACCORDING TO THE PROPOSED LIMITATIONS.

Stream	1			2			3			Vapor	Steam
Description	Feed			Crystal			Caustic			Vapor	Steam
Temperature (C)	40			110			110			125.4	140
Pressure (bar)	7.213			1.013			1.013			1.013	2.465
Vapor Frac	0			0			0			1	1
Mole.Flow (kmol/hr)	214.8			4.5			50.2			160	191.5
Mass.Flow (kg/hr)	45000			455			1162.4			2882.6	3450
Vol.Flow (m3/hr)	3.7			0.2			1.3			5201.5	1787
Mass.Flow (kg/hr)	Kg/hr	wt%	Kmol/hr	Kg/hr	wt%	Kmol/hr	Kg/hr	wt%	Kmol/hr	Kg/hr	Kg/hr
H ₂ O	3600	80%	199.8	5.1	1	0.3	1134.6	71%	63	2460.3	2890
NaOH	405	9%	10.1	1.8	0	0	403.2	25%	10.1		
Na ₂ S	45	1%	0.6	0.2	0.0466	0	44.8	3%	0.6		
Na ₂ CO ₃	450	10%	4.2	0.1	0.0239	0	23	1%	0.2		
Na ₂ CO ₃ (S)				447.4	98%	4.2					
Density (kg/m ³)	1216.5			3464			1375.6			0.6	1.9
MW (kg/kmol)	21			100			23.1			18	18
pH	13.8						13.64				

B. Advantages of the new method

1. Existence of dangerous sulphurous compounds in the wastewater of olefin unit and gas sweetening plant.
2. H₂S and CO₂ are included almost 10% off-gases.
3. A large amount of caustic soda is used for neutralizing of sulphurous compounds and is washed by water.
4. The high concentration of pH output wastewater.
5. High COD levels decrease the amount of dissolved oxygen available for aquatic organisms.
6. Production of a new product by means of cheap materials.
7. High interest in plan economically.

VIII. CONCLUSION

In this study, the new method for spent caustic recovery was simulated and a chemical treatment process was proposed for the recovery of spent caustic. The ratio BOD/COD is sometimes used as a guide to evaluating the treatment plant's ability to handle a specific waste material. A rule of thumb ratio when BOD/COD <0.5 shows that the stream is not biodegradable. Therefore, the conventional treatment methods are not feasible and the chemical treatment method is proper than biological methods. In general, after chemical treatment, biological treatment is used.

According to the simulation results of energy-consuming levels, the important point is that for higher energy levels, it should be more pressure, which would increase the pumping energy consumption and the mechanical and material costs of the equipment, including the main converter unit. Therefore, it is suggested that in the next study, material examination

and energy consumption costs should be selected on the basis of appropriate vapor levels for better decisions. Moreover, the obtained results show that the Aspen Plus is a powerful software for simulation of electrolyte environment and mass flow rates, temperatures, pressures, and pH value was completely calculated by Aspen Plus software.

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