Aspen Plus simulation and optimization of industrial spent caustic wastewater treatment by wet oxidation method

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Abstract. Spent caustic is a waste generated by petrochemical refineries, which used to eliminate acid components such as hydrogen sulphide (H\textsubscript{2}S) and mercaptans from the refined product streams. A study was carried out on simulation and optimization of spent caustic wastewater treatment system by using Aspen Plus based on wet air oxidation (WAO) method. WAO method uses air under elevated temperature and pressure to carry out oxidation in the aqueous phase. Process flow diagram (PFD) of WAO method was drawn and relevant input data was keyed in Aspen Plus according to experimental results on WAO. Both results were validated and the results were match each another as the percentage of allowable error between both the results were less than 5 %. After that, optimization was carried out to determine the optimum ratio of spent caustic feed flow rate to air flow rate and operating temperature of the flash separator unit involved in the process. From the optimization results, it can come to a conclusion that 1: 9.2 is the minimum spent caustic feed flow rate to air flow rate ratio and optimum operating temperature of flash separator unit is 140\degree C in order for maximum flow rate of CH\textsubscript{3}SSCH\textsubscript{3} in offgas stream in this simulation model of spent caustic wastewater treatment system using WAO method.

1. Introduction

The availability of quality water has grown to be quintessential on a daily basis. In recent times, variety of activities that have affected the standard of water were inclining. Sewage from agricultural and industrial activities are viewed as one of the worst effluent to the water [1]. Water pollution is principally coming from industrial and domestic wastewater. Industrial wastewater incorporates high hazardous and toxic chemicals which will incredibly impact human health and aquatic lives. These additionally consist of heavy metal such as sulphide, copper, zinc, iron, cadmium and manganese [2]. Sodium hydroxide (caustic) which generally known with chemical formula NaOH are used in petrochemical and petroleum refineries for the elimination of acid components such as hydrogen sulphide (H\textsubscript{2}S), cresylic acids, mercaptans and naphthenic acids from the subtle product streams. When the sodium hydroxide is used in the plant to get rid of those components, the resultant waste is defined as spent caustic. According to Suarez [3], three types of spent caustic are typical from the petroleum industries, and they are from sulphidic, naphthenic and cresylic origins. Sulphidic spent caustic streams are generated when light petroleum fractions are treated with a dilute of 10% caustic solution to convert odorous or objectionable chemical constituents to their salt forms which are then soluble in aqueous solution. This caustic extraction is done to improve color, odor, and oxidation stability of the petroleum product [4]. Naphthenic spent caustic is produced from the caustic scrubbing of kerosene and diesel
products which contain high concentrations of polycyclic aliphatic organic compounds such as naphthenic acids. While the cresylic spent caustic is generated when gasoline scrubbing in the fluidized bed catalytic cracking processes with caustic containing high concentrations of organic compounds including phenols and cresols.

Once spent, the caustic solution can be a challenge to handle and dispose as it typically contains pH greater than 12, sulphide concentrations exceeding 2 to 3 wt%, and about 80% of residual alkalinity which comes from excess sodium hydroxide. Constituents in the spent caustic for example sodium bisulphide (NaHS) and mercaptans which can be represented by sulphide are extremely odorous as they have the tendency to cause diseases or even death to living organisms [5]. One of the most common methods used in industries for treating spent caustic is wet air oxidation (WAO) method. Other method included chemical oxidation[6–8]. WAO method can be categorized into three, which are low WAO, medium WAO and high WAO, depending on the reaction operating temperature and pressure. In detail, Clark [9] has compared properties and performances for both WAO and chemical oxidation methods, and has shown that medium and high WAO are better in terms of cost and handling. However, the elimination of pollutants in effluent may need one or combination of treatment techniques depending on the type of compounds and concentration in solution [10]. Like other processes, design and operational analyses of industrial wastewater are challenging without having a process model. In the case of WAO method, the specific challenges are to have an established mass balances for a typical flowsheet and finding the optimal operating conditions. Tian et al. [11] have simulated a scheme to treat organic wastewater produced from Eastman process. Weibin et al. [12] have developed Aspen Plus simulation and optimization of ammonia removal from azodicarbonamide foaming agent (ADC) wastewater for both absorber and stripper sections. Gamba et al. [13] have simulated scrubbing processes to obtain biomethane from municipal sewage sludge-derived biogas using Aspen Plus with emphasis to energy analysis. To the author’s knowledge, Aspen simulation of WAO method with optimization of process parameters has yet to be studied. Hence this paper would be detailing the simulation procedures using Aspen plus for the process, as well as to find the optimal ratio values of spent caustic and water flowrates, and flash separator temperature.

2. Methodology
The overall methodology for this work is shown in figure 1. Simulation model of WAO method was developed in Aspen Plus based on the process flow diagram (PFD) obtained from Siemens Water Technologies Corporation [14]. Validation of the simulation results was based on the experimental work by Jonathan [15]. Optimization was carried out for two purposes, firstly, to determine the optimum ratio of spent caustic feed flow rate to air flow rate in order to achieve constant sodium sulfate (Na$_2$SO$_4$) flow rate in the treated effluent stream. Na$_2$SO$_4$ was the product formed from conversion of NaHS by WAO method as shown in equation (1). Secondly, it was to determine the optimum operating temperature of the flash separator unit involved in the process, as to increase the flow rate of dimethyl disulfide (CH$_3$SSCH$_3$) in the off-gas stream. CH$_3$SSCH$_3$ was the product formed from conversion of mercaptans by WAO (see equation (2)). Increase flow rate of this compound was desired as it is less harmful compared to mercaptans.

\[
NaHS + NaOH + 2O_2 \rightarrow Na_2SO_4 + H_2O \quad (1)
\]
\[
4CH_3SH + O_2 \rightarrow 2CH_3SSCH_3 + 2H_2O \quad (2)
\]
2.1 WAO Process Description

Figure 2 shows the WAO flowsheet which was developed in Aspen Plus software. WAO is the oxidation of soluble or suspended components in an aqueous environment using 21 % O₂ in the air as the oxidizing agent. When air is used as the source of O₂, the process is denoted as WAO process. Oxidation reactions happen at the temperature range between 150 °C and 320 °C (423 K to 593 K), and at pressure range from 10 to 220 bar (1000 kPa to 22000 kPa). Requirement of the operating temperature is determined by the treatment objectives. Operation at higher temperature needs higher pressure to maintain a liquid phase in the system [14].

Rotating equipment such as pump is used to raise the pressure of spent caustic feed stream whereas compressor is used to raise the pressure of air feed stream to the required operating pressures. Once the pressure of spent caustic feed and air feed are raised, both of them are mixed in a mixer before entering heat exchanger for temperature increment with constant pressure. Heat exchangers are routinely employed to preheat the spent caustic feed and air feed mixture before entering the reactor and at the same time recover energy from the reactor effluent. Commonly in industries, the hot mixture outlet from heat exchanger is further heated using a heater to meet the operating condition of the reactor.

After that, the reactor operating temperature and pressure are set based on the compounds in the spent caustic feed stream that is desired to be converted into simpler form. Oxidation reaction occur inside the reactor whereby the reactants which are complex constituents in spent caustic and O₂ in the air react to produce simpler form of products that are soluble in water and is biodegradable. Hot effluent from
reactor re-enter into heat exchanger for cooling down and it is further cooled using a cooler before entering flash drum. Flash drum usually operates at low pressure. Thus, high pressure effluent from cooler is reduced to low pressure using a pressure control valve. Liquid effluent consist of several components is partially vaporized in a flash drum at a certain temperature and pressure. The vapour is taken off overhead in the off-gas stream meanwhile the liquid drains to the bottom of the drum in the treated effluent stream whereby it will further treat before the final discharge.

Figure 2. WAO Flowsheet in the Aspen Plus.

2.2 Selection of Blocks and Thermodynamic Property
Blocks used to build this simulation model were pressure changers (pump, compressor and valve), mixer, exchangers (heater, heat exchanger and cooler), reactor (R-stoic), and separators (flash). R-stoic reactor was chosen because stoichiometry of the reactions and fractional conversion of the reactants were known. Thus, by keying the stoichiometry of reactants and products involved in the reaction and entering the desired fractional conversion value of specific reactant in the R-stoic reactor, Aspen Plus would calculate and generate output result of reactants that being converted into products based on the input mass concentration or mass/mole fraction of reactants in the feed. Thermodynamic property applied in this simulation modelling was Soave-Redlich Kwong (SRK), as it was for non-polar and mildly polar mixture, as in the WAO process.

3. Results and Discussion
Aspen Plus simulation was carried out in the direction to validate the data by Jonathan [15], with emphasis on the H₂S and mercaptans concentrations after WAO treatment [15]. Initial concentration value of H₂S was entered into the spent caustic feed stream composition column with assumed flow rate 1000 of litres/hr. Table 3.1 showed the optimal operating conditions and simulation results. From these results have obtained the fractional conversions for NaHS (88.39%) and mercaptans (94.46%) were both less than 5% differences against the experimental data (NaHS, 88.39%; mercaptans, 94.26%). This was required and would be based for further process improvement through optimization.
Table 1. Optimal operating conditions & simulation results attained in Aspen Plus

| Optimal Operating Condition | FEED | OFFGAS |
|----------------------------|------|--------|
| Temperature °C             | 140  |        |
| Pressure bar               | 3    |        |
| Time minutes               | 40   |        |
| Mass Flow Rate L/hr        | 828.1340 | 46.2177 |
| O₂ L/hr                    | 0    | 0.0074 |
| N₂ L/hr                    | 0    | 8.4340 |
| H₂O L/hr                   | 823.4510 | 37.1916 |
| CH₃SH L/hr                 | 0.3682 | 0.0188 |
| CH₃SSCH₃ L/hr              | 0    | 0.3148 |
| NaOH L/hr                  | 2.1574 | 4.7021e-15 |
| Na₂SO₄ L/hr                | 0    | 0.0009 |
| NaHS L/hr                  | 2.1574 | 0.2503 |

3.1 Optimum ratio of spent caustic feed flow rate to air flow rate
Optimization was done to identify minimum ratio of spent caustic feed flow rate to air flow rate by fixing spent caustic feed flow rate and manipulating air flow rate. Flow rate of Na₂SO₄ which was product produced from the oxidation reaction acts as the responding variable. While spent caustic flow rate was set at 1000 litres/hr, seven simulated runs were done and results were plotted as shown in Figure 3. Based on Figure 3, the optimum spent caustic feed flow rate to air flow rate ratio is 1:9.2 which represented by the dotted lines as Na₂SO₄ flow rate in the treated effluent stream reached steady state beyond this ratio value. Besides that, in order for WAO process occur completely in the reactor and results available without warning, O₂ in air must be in excess. Usually there will be 5 to 21 % of O₂ and some volatile compounds in the off-gas stream from flash drum indicates WAO reaction took place [16].

![Figure 3](image-url)

**Figure 3.** Response of Na₂SO₄ flow rate in treated effluent stream with different spent caustic feed flow rate to air flow rate ratio.

3.2 Optimum operating temperature of the flash separator unit
Optimization was done to determine operating temperature of the flash separator unit involved in the process in order for maximizing the flow rate of CH₃SSCH₃ produced in the off-gas stream. Pressure
of the flash drum was fixed at 3 bar. Simulation results of response in CH$_3$SSCH$_3$ flow rate in the off-gas stream by varying the flash drum temperature was observed and plotted in figure 4.

![Figure 4. Response of CH$_3$SSCH$_3$ flowrate in off-gas stream by increasing flash drum operating temperature.](image)

The flash separator unit separates a component into top product (off-gas stream) and bottom product (treated effluent stream) according to pressure and/or manipulations. In off-gas stream, the components present in vapour phase meanwhile in treated effluent stream, were in liquid phase. Initially operating temperature of the flash drum is set at 100 °C as it is boiling point of water and the response in flow rate of CH$_3$SSCH$_3$ is observed. At this temperature, major portion of CH$_3$SSCH$_3$ flows in off-gas stream and there is some portion of this compound which about 0.08 L/hr in treated effluent which is not preferred. Therefore, maximum flowrate of this component in vapour phase is desired as it is not hazardous. As the temperature of flash drum was increased beyond 140 °C at 3 bar pressure, flow rate of the compound remains constant at 0.34 L/hr. Therefore, this was the maximum flowrate of CH$_3$SSCH$_3$ in the off-gas stream. Moreover, CH$_3$SSCH$_3$ presence in the treated effluent stream was almost at zero flowrate and similar happened to mercaptans.

4. Conclusion
This paper has focused on developing Aspen Plus model for both simulation and optimization purposes. Based on the published experimental data and the reported WAO process flow diagram, Aspen Plus simulation model was developed and validated for fractional conversion of NaHS and mercaptans. With the difference less than 5% between the simulation result and the published experimental data, the model was successfully considered to approximate the actual system and provided a base for further improvement. Optimization for the ratio of spent caustic flow rate (fixed) to the air flow rate (varied), and operating temperature of flash separator were then done by simulating for the ranges which the response started to show constant value. It can be concluded that 1: 9.2 was the optimum spent caustic feed flow rate to air flow rate ratio and optimum operating temperature of flash separator unit was 140 °C.

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