



Simulation Of Acidic Water Purification Process In Refinery Based On Determining Appropriate Operating Conditions

Mufida Mohamed Bey

Industrial Engineering Department, Faculty of Engineering, Sabratha University, Reqdalin, Libya

Keywords:

Acidic Water
Aspen Hysys
Refinery
Pollution
Simulation

ABSTRACT

Acidic process water produced by refineries contains some hazardous pollutants such as (H_2S and NH_3). Acid water extraction units remove both compounds from the water. The removed contaminants are sent to a sulphur recovery unit to produce sulphur and avoid any acid emissions contrary to environmental regulations. Water pollution is a problem that concerns all people in the world. In view of the importance of preserving the environment and water resources, in this research, the simulation of the acid water treatment unit in the refinery was studied using the Aspen Hysys software based on determining the appropriate operating conditions. The NRTL electrolyte activity coefficient model was used to predict the system's thermodynamic behaviour. The simulation results showed that the suitable temperature for the feed entering the tower is about $38^\circ C$ and the convenient distance for the trays in the disposal tower is 0.54 mm. Under these conditions, the concentration of hydrogen sulphide 0.1694 and 0.2418 of ammonia in the acid gas exiting the tower reaches its maximum at a molar flow rate of the mixture of about 39.86 kgmol/h, according to the economic considerations of the operating tower.

محاكاة عملية تنقية المياه الحامضية في المصفاة بناءً على تحديد ظروف التشغيل المناسبة

مفيدة محمد إبراهيم بى

قسم الهندسة الصناعية ، جامعة صبراتة ، رقدالين ، ليبيا

الكلمات المفتاحية:

أسبن هايسس
الماء الحامضى
المصفاة
التلوث
المحاكاة

الملخص

تحتوي مياه العمليات الحامضية التي تنتجها المصافي على بعض الملوثات الخطرة مثل (NH_3 و H_2S). تقوم وحدات استخراج الماء الحامضي بإزالة كلا المركبين من الماء. يتم إرسال الملوثات المزالة إلى وحدة استرداد الكبريت لإنتاج الكبريت وتجنب أي انبعاثات حمضية مخالفة للوائح البيئية. تلوث المياه مشكلة تهم جميع الناس في العالم. نظراً لأهمية الحفاظ على البيئة والموارد المائية، تم في هذا البحث دراسة محاكاة وحدة معالجة المياه الحامضية في المصفاة باستخدام برنامج Aspen Hysys القائم على تحديد ظروف التشغيل المناسبة. تم استخدام نموذج معامل نشاط الإلكتروليت NRTL للتنبؤ بالسلوك الديناميكي الحراري للنظام. أظهرت نتائج المحاكاة أن درجة الحرارة المناسبة للتغذية الداخلة إلى البرج تبلغ حوالي 38 درجة مئوية والمسافة الملائمة للصواني في برج الصرف 0.54 مم. في ظل هذه الظروف، يصل تركيز كبريتيد الهيدروجين 0.1694 و 0.2418 من الأمونيا في الغاز الحامضي الخارج من البرج إلى أقصى حد له عند معدل تدفق مولاري للخليط يبلغ حوالي 39.86 كجم مول / ساعة، وفقاً للاعتبارات الاقتصادية لبرج التشغيل.

Introduction

Oil refineries use large amounts of water for various purposes and generate significant amounts of ruin. The properties of the wastewater produced are strongly dependent on the process configuration. Refinery effluents contain contaminants such as cyanide, petroleum, phenols, benzene, sulfide, ammonia, and heavy

metals. In addition, chemicals dosed to control corrosion and biofouling are also set up [1, 2]. These effluents typically consist of many types of organic and inorganic compounds that can be hazardous to the environment. Several methods have been developed for biology

*Corresponding author:

E-mail addresses: mofedab@gmail.com

Article History : Received 25 June 2023 - Received in revised form 10 September 2023 - Accepted 02 October 2023

treatment of wastewater containing complex organic compounds [3-10]. The acid water extraction process has become an important pollution abatement technique due to its focus on regulating wastewater quality and saving energy [11]. Therefore, the removal of chemical contaminants such as hydrogen sulfide, carbon dioxide, and ammonia from wastewater using the steam stripping method is the focus of research [12, 13].

Numerous developments have been proposed by researchers aim to improve acid water extraction technology.

Darton [14] and Melin [15] used the single stripper system for the acid water filter and manipulated the method by modifying its working parameters. The result of their work showed the CO₂ reduction efficiency on a low plate.

In refineries whose operations deal with sulfur-containing raw materials, the sulfur is released in various units in the form of hydrogen sulfide. Water containing sulfides is called acidic water, and the process used to separate sulfide compounds from water is called dewatering or abstraction. In this process, compounds such as hydrogen sulfide and ammonium dissolved in water are separated by steam and heat, and the water is purified. This operation can also be done by airflow. Acid water is disposed of in refineries and other industries to purify water containing hydrogen sulfide and ammonia. In most cases, in addition to the compounds mentioned, this water also contains carbon dioxide and other impurities [16].

The main objective of the sour water disposal process is to reduce the ammonia concentration to less than 50 ppm (part per million) and the hydrogen sulfide concentration to less than 10 ppm. In fact, the concentration of said impurities in the water must reach such a level that this water can be reused in the refinery or returned to the environment as a safe flux [16-18]. In general, the amount of hydrogen sulfide in water is more than ammonium and this high potential can make the water very acidic and toxic. If this pollution is not removed from the water, the amount of water pollution may become uncontrollable. The water purification process is a simple process that is done with heat. In the purification tower, heat is exchanged between the steam and the acid water in the re-boiling boiler causing its temperature to increase. As a result of chemical reactions in the tower, compounds such as CO₂, H₂S, and NH₃ are separated from the water. In short, it can be said that the desalination process takes place through the following steps:

1-Raising the temperature of the acid water until it reaches the boiling point.

2- Occurrence of reciprocating chemical reactions.

3-Reducing the partial pressure of the gases emitted from the vapor flow and their exit from the aqueous phase.

Acid water can be supplied from different sources depending on the complexity and variety of operations in the refinery. One of the main sources of sour water production in refineries is water obtained from the top of the atmospheric distillation tower, which is formed by the condensation of dewatered steam in the distillation tower [3]. H₂S is acidic and is considered one of the types of water pollutants. The acid water after purification is used in other units of the refinery, such as the crude oil desalination unit. This purified water, which is no longer dangerous to the environment, can also be used to wash the area or appliances in the refinery.

In this paper, the acid water treatment unit in the refinery was simulated in acid water purification units. Another new process for ammonia removal and acid gas purification was simulated by reducing the pH from 9 to 7 and removing phenol with an extraction solvent under acidic conditions using Aspen Hysys software. The results indicated that the removal of phenol was more compared to the old processes [4]. The removal of phenol was studied using surface adsorption methods [5], [electrolysis [6], and liquid membrane separation [22]. Considering that the workability is high and the percentage composition and properties of acidic water are complex [4], the mentioned methods are not suitable for removing phenol in water. The proposed methods for purifying sour water are distillation and extraction [16, 17, 19].

Given the importance of preserving water resources and the

environment, acid water treatment and water reuse are a necessity. Also, due to the compounds present in acidic water, which mainly include ammonia, carbon dioxide, hydrogen sulfide, phenols, fatty acids, etc. [16–17], acidic water in nature cannot be left unpurified. Therefore, in this paper, the acid water purification process of the refinery was investigated. The refinery is fed heavy crude oil, acid, and gas condensate, which are transported to the refinery by conveyors and pipelines. Refinery products can include high-octane number gasoline, various solvents, aviation fuel, various petroleum raw materials, gas oil, fuel oil, liquefied gas, bitumen, and sulfur.

Description of the process

The acid water is treated in two units which are completely identical in design. The capacity of each is 33 m³/h. The task of these units is to separate hydrogen sulfide and ammonia gases of high concentration from the acidic water solution produced in other units. The output of these units is pure water, which is used in the salting devices of the distillation units. The separated acid gases are also used as a feed line to the sulfur production unit. The acid water with a temperature of 38°C first enters the heat exchanger and after the heat exchange with water enters the drain tower. After separating in the tower, the sour gas, which contains H₂S and NH₃ and reaches a temperature of 105°C, enters the receiving tank after passing through air fans and reducing the temperature and reaching a temperature of 98°C. In this tank, the acid gas enters the sulfur recycling unit from the top of the tank, and the liquid in it as a stream may also produce acid water. The acid water produced in different processes is sent to the storage tank of the unit by the pump. The task of this tank is to stabilize the feed in terms of percentage composition and separate possible hydrocarbons with water. In this tank, natural gas and nitrogen are used in order to create positive pressure and prevent the release of unpleasant odors into the atmosphere, and prevent ignition. The return is injected from the bottom of the tank to the top of the tower. At the bottom of the tower, the water free of H₂S and NH₃ enters the heated exchangers, and after the heat exchange, it is sent to the required units.

Process simulation

In this paper, the sour water unit in the refinery was simulated with the help of Aspen Hysys software. In the sour water purification process, the main and important processes of the process include the feed preheated unit and the separator unit (removal tower). Figure 1 depicts the flow diagram of the process [23].

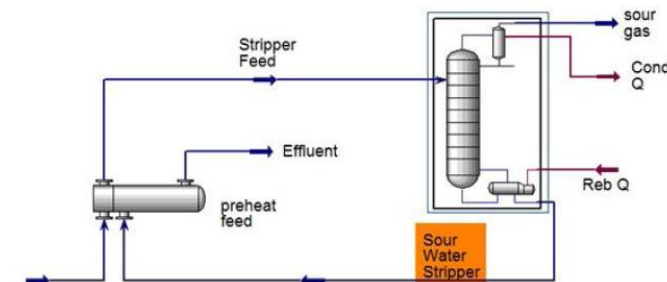


Fig.1: Process flow diagram of an acid water unit for an oil refinery. The molar ratio composition of the components in the feed stream is presented in Table 1. The information regarding the feed flow and tower specifications are provided in the process flow chart in Table 2.

Table 1: Composition of the sour water feed [23].

Component	Composition
Hydrogen sulfide	0.0070
Ammonia	0.0050
Water	0.9880

Table 2: Stream Condition of the Sour Water Stripper.

Name	Stripper Feed	Sour gas	
		1	0
Vapor	0	1	0
Temperature [°C]	93.33333	105.3523	124.0309
Pressure [kPa]	206.8428	197.8796	225.4586
Molar Flow [kgmole/h]	18203.36	3.99E+02	17804.74
Mass Flow [kg/h]	328925.4	8.17E+03	320754.1
Std Ideal Liq Vol Flow [m3/h]	331.2241	9.820795	321.4033
Molar Enthalpy [kJ/kgmole]	-277990	-153675	-277621
Molar Entropy [kJ/kgmole-C]	70.58481	185.8197	76.22074
Heat Flow [kJ/h]	-5.1E+09	-6.1E+07	-4.9E+09

The process was carried out under real conditions (information in Tables 1 and 2) in the program taking into account that the purpose is to purify acidic water, the purity of the purified water is the validation criterion for the results of the program.

Results and discussion

According to the operating conditions in the acid water purification unit, it is during the implementation of the simulation on the program, we reached some important results that will be clarified in the tables and figures that will be presented later:

Table 3: Composition Streams of the Sour Water Stripper.

Stream	Stripper Feed	Sour gas	Striped water
Hydrogen sulfide	0.0037	0.1695	0.0000
Ammonia	0.0053	0.2418	0.0000
Water	0.9910	0.5887	1.0000

Table 3 shows the results of the molar fraction on the stream lines of the purification tower, as well as Figure 2, the amount of energy required to operate the purification tower and the heat exchanger versus flow of sour water.

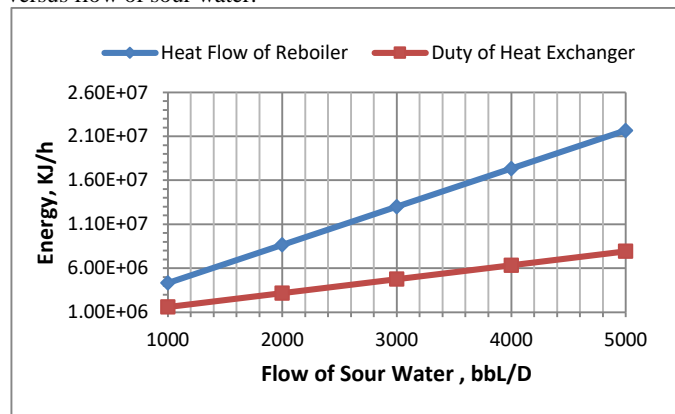


Fig. 2: Energy required for the unit

Figure 3,4 shows the decrease in the concentration of hydrogen sulphide and ammonia with the rise in the temperature of the tower from the top to the bottom, as well as with the increase in the number of separation stages, which reach ten stages. This decrease is due to the high temperatures, as well as the increase in the number of stages.

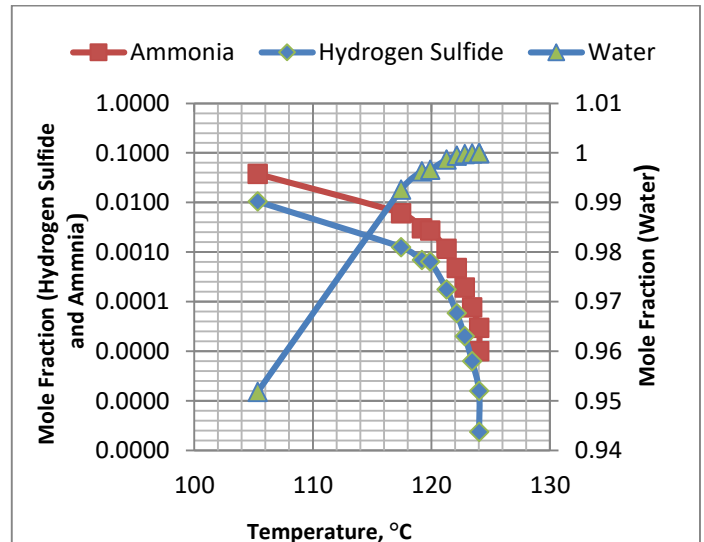


Fig. 3: The effect of temperature on pollutant concentration

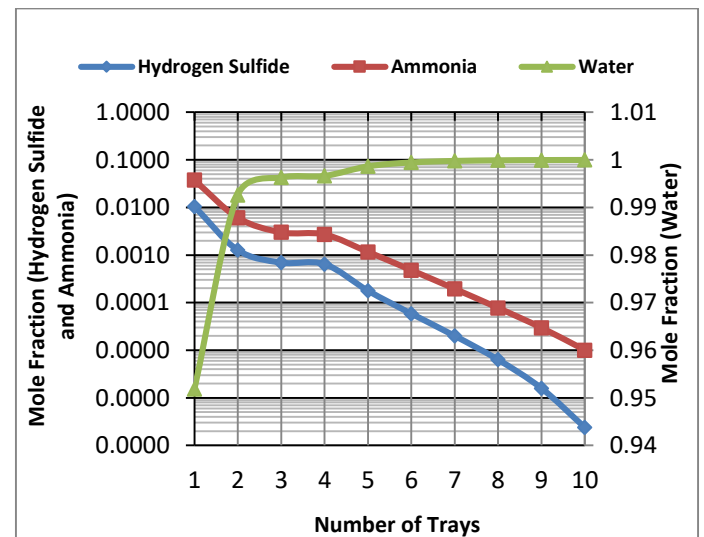


Fig. 4: The molar fraction changed along the separation tower
Figure 5 shows the change in the molar flow of gas and liquid through the tower.

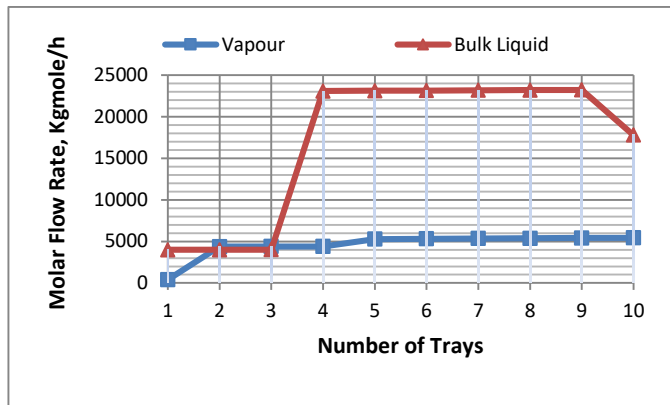


Fig. 5: The molar flow rate changed along the separation tower

From the previous figure, it is clear that the rate of flow increases with increasing separation stages through the purification tower.

Conclusion

Considering the importance of preserving water resources and the environment, in this research, the acid water treatment unit in the refinery was simulated using Hysys Aspen software, and appropriate operating conditions were determined. In order to predict the thermodynamic behavior of the system, the electrolyte activity coefficient - NRTL model, which is shown as ELECTROLYTE-NRTL in the software, was used to simulate an acidic water treatment unit. The simulation results indicated that the range of feed discharge ranged between 58 and 38 m³/h. Also, there is no significant change in the purification performance of the tower by increasing the inlet flow rate of the purification tower, while the increase in the flow rate will lead to an increase in costs per unit cubic meter. Therefore, the feed flow is recommended to be 38m³/h. Also, to increase the performance of the acid water filtration unit, the distance between the trays should be 0.54 mm and the temperature of the feed inlet should be around 40°C. In this case, the composition of the ingredients coming out of the top of the tower includes 24% ammonia, 17% hydrogen sulfide, and 59% water vapor.

References

- [1]- Patel H, Madamwar D. Effects of temperatures and organicloading rates on biometanation of acidic petrochemical wastewater using an anaerobic upflow fixed-film reactor. *Bioresour Technol* 2002;82:65–71.
- [2]- Rasheed, Q.J., Pandian, K. and Muthukumar, K. (2011) ‘Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles’, *Ultrasonics Sonochemistry*, 18(5), pp. 1138–1142. doi:10.1016/j.ulsonch.2011.03.015.
- [3]- Karkare, M.V. and Murthy, Z. (2010) ‘Kinetic study and modeling of aerobic biological oxidation of organic wastewater’, *Chemical Product and Process Modeling*, 5(1). doi:10.2202/1934-2659.1467.
- [4]- Mathur, A.K. and Majumder, C.B. (2008) ‘Biofiltration and kinetic aspects of a biotrickling filter for the removal of paint solvent mixture laden air stream’, *Journal of Hazardous Materials*, 152(3), pp. 1027–1036. doi:10.1016/j.jhazmat.2007.07.112.
- [5]- Chao, Y.-M., Tseng, I.-C. and Chang, J.-S. (2006) ‘Mechanism for sludge acidification in aerobic treatment of coking wastewater’, *Journal of Hazardous Materials*, 137(3), pp. 1781–1787. doi:10.1016/j.jhazmat.2006.05.024.
- [6]- Alva-Argáez, A., Kokossis, A.C. and Smith, R. (2007) ‘The design of water-using systems in petroleum refining using a water-pinch decomposition’, *Chemical Engineering Journal*, 128(1), pp. 33–46. doi:10.1016/j.cej.2006.10.001.
- [7]- Yavuz, Y., Kopal, A.S. and Ögütveren, Ü.B. (2010) ‘Treatment of petroleum refinery wastewater by electrochemical methods’, *Desalination*, 258(1–3), pp. 201–205. doi:10.1016/j.desal.2010.03.013.
- [8]- Yan, L. et al. (2011) ‘Electrochemical treatment of petroleum refinery wastewater with three-dimensional multi-phase electrode’, *Desalination*, 276(1–3), pp. 397–402. doi:10.1016/j.desal.2011.03.083.
- [9]- Hasan, D.B., Abdul Aziz, A.R. and Daud, W.M. (2012) ‘Oxidative mineralisation of petroleum refinery effluent using Fenton-like process’, *Chemical Engineering Research and Design*, 90(2), pp. 298–307. doi:10.1016/j.cherd.2011.06.010.
- [10]- Davarnejad, R. et al. (2015) ‘Numerical Analysis of petroleum refinery wastewater treatment using electro-fenton process’, *Chemical Product and Process Modeling*, 10(1), pp. 11–16. doi:10.1515/cppm-2014-0020.
- [11]- Lee, D. et al. (2002) ‘Dynamic simulation of the sour water stripping process and modified structure for effective pressure control’, *Chemical Engineering Research and Design*, 80(2), pp. 167–177. doi:10.1205/026387602753501889.
- [12]- Hassan, S.Q. and Timberlake, D.L. (1992) ‘Steam stripping and batch distillation for the removal and/or recovery of volatile organic compounds from industrial wastes’, *Journal of the Air & Waste Management Association*, 42(7), pp. 936–943. doi:10.1080/10473289.1992.10467044.
- [13]- Hwang, Y.L., Keller, G.E. and Olson, J.D. (1992) ‘Steam stripping for removal of organic pollutants from water. 1. stripping effectiveness and stripper design’, *Industrial & Engineering Chemistry Research*, 31(7), pp. 1753–1759. doi:10.1021/ie00007a021.
- [14]- Darton, R.C., Van Grinsven, P.F.A. and Simon, M.M. (1978) *Development in steam stripping of Sour water*, Chem. Eng. (London); (United Kingdom). Available at: <https://www.osti.gov/etdeweb/biblio/6826036> (Accessed: 25 June 2023).
- [15]- Melin, G.A., Niedzwiecki, J.L. and Goldstein, A.M. (1975) Optimum design of sour water strippers. [injection of base into lower section for NH/sub 3/ and H/Sub 2/s removal], *Chem. Eng. Prog.*; (United States). Available at: <https://www.osti.gov/biblio/5104209> (Accessed: 25 June 2023).
- [16]- Kohl, A.L. and Nielsen, R.B. (1997) *Gas purification*. Houston: Gulf Pub.
- [17]- Higman, C. and Van der Burgt, M. (2003) *Gasification*. Gulf Professional Publishing, Elsevier, New York.
- [18]- Lee, D. et al. (2002) ‘Dynamic simulation of the sour water stripping process and modified structure for effective pressure control’, *Chemical Engineering Research and Design*, 80(2), pp. 167–177. doi:10.1205/026387602753501889.
- [19]- Yu, Z. et al. (2010) ‘Process development, simulation, and industrial implementation of a new coal-gasification wastewater treatment installation for phenol and ammonia removal’, *Industrial & Engineering Chemistry Research*, 49(6), pp. 2874–2881. doi:10.1021/ie901958j.
- [20]- Lin, S. H., & Wang, C. S. (2002). Treatment of high-strength phenolic wastewater by a new two-step method. *Journal of Hazardous Materials*, 90(2), 205-216.
- [21]- Körbahti, B. K., & Tanyolac, A. (2003). Continuous electrochemical treatment of phenolic wastewater in a tubular reactor. *Water Research*, 37(7), 1505-1514.
- [22]- Venkateswaran, P., & Palanivelu, K. (2006). Recovery of phenol from aqueous solution by supported liquid membrane using vegetable oils as liquid membrane. *Journal of Hazardous materials*, 131(1-3), 146-152.
- [23]- Aspen Technology. *Aspen plus Electrolytes Manual*; Aspen Technology Inc.: Cambridge, MA, 1998.