CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870334

Computer Aided Environmental Evaluation of a Refinery Unit for Sulfide Absorption and Mercaptans Oxidation

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Absorption with diethanol amine is a process used in the oil refinery to reduce the concentrations of hydrogen sulfide, due to this component is corrosive to the equipment which this is going to be used for, such as motors, reactors among others, also when this component is expulsed to the atmosphere could cause acid rain which is harmful for the vegetation, the environment, humanity, animals by the way this increase the aquifers toxicity. In this work, an environmental evaluation of the hydrogen sulfide (H_2S) absorption with dimethyl- ethyl amine was performed followed by mercaptans extraction and further conversion to disulfides and carbonile sulfur (COS) extraction by mono-ethanol-amine. The evaluation was carried out using computer-aided tools based on the waste reduction algorithm (WARGUI), quantifying the impacts of a process on its surroundings and classifying them into 8 categories. Four different case studies were considered, taking into account the products of the process and the COS removal unit. The results show that both atmospheric and toxicological impacts are generated by the process. The main wastes generated are hydrogen sulfide and disulfide oil.

1. Introduction

Currently, there has been an increase in interest in reducing emissions of toxic gases to the environment, one of the factors that has developed such interest is that air pollution over the years has become a great difficulty worldwide, organizations such as The WHO (world health organization) considers it a priority with regard to health. Health effects related to air pollution include impacts on pulmonary, cardiac, vascular, and neurological systems. Outdoor air pollution is estimated to lead to 3.3 M premature deaths per year worldwide, mainly in Asia (Nowak et al., 2018).

Therefore, many industries have sought alternatives to reduce emissions of certain gases and refineries are not the exception, they have chosen to implement in their processes ways to remove and convert the toxic waste present in their raw material to lower impact ones. Some of these toxic residues are the substances present in LPG that contain sulfur, such as hydrogen sulfide, carbonyl sulphide and mercaptans, which ones according to (Merlen et. al 2016) are the most common sulfur compounds in the environment, in addition to causing serious damage to the environment and human health, for example Kilburn and Warshaw (1995) mention that those who have been exposed to hydrogen sulfide (H_2S) as a result of working at or living downwind from crude oil processing facilities have persistent neurobehavioral dysfunction including depression and personality (Ramirez et al, 2017), they also have repercussions on the economy of a refinery, since they reduce the useful life of catalysts and corrode the equipment. All the above, has made refineries are in need of adding units that remove these substances in their production processes. Absorption by aqueous solutions of alkanolamines is the dominant industrial process for removing acid gases, (Varbanov et al., 2016).

At first sight the units of removal and / or conversion of these substances are a great help for the environment since they considerably reduce the pollution emitted by the industry, but even so, the emissions that are made continue causing air damage although with a less impact, which makes it useful and necessary to evaluate how feasible in the environmental sector these units are being implemented, that is, if they justify their implementation. To achieve this, it is essential to carry out an environmental assessment, since this allows us to know the environmental impact that this process can have, one of the tools to carry out this evaluation is the waste reduction algorithm (WAR), which calculates the potential environmental impact (PEI) of a process, based

Please cite this article as: Pajaro M.C., Ramos K.J., Gonzalez-Delgado A.D., 2018, Computer aided environmental evaluation of a refinery unit for sulfide absorption and mercaptans oxidation , Chemical Engineering Transactions, 70, 1999-2004 DOI:10.3303/CET1870334

on several different impact categories (Barrett et al., 2011). In this work, WARGUI software will be used to perform the environmental evaluation of a refinery unit for sulfide absorption and mercaptans oxidation.

2. Materials and methods

2.1 Process description

The Merox treatment unit aims to remove the sulfur compounds present in LPG, such as: hydrogen sulphide (H_2S), carbonyl sulphide (COS) and mercaptans (RSH) in order to comply with the current specifications in the country. The removal of hydrogen sulphide is carried out in the presence of diethanolamine (DEA) in an absorber tower, the LPG that comes out of this unit is subjected to a caustic soda wash (NaOH) to cause the H_2S that was not removed in the tower, react with the soda. Subsequently, this LPG enters an extractor tower in which the mercaptans present are extracted with the help of a NaOH solution, the mercaptan-rich soda of this unit is regenerated using merox catalyst and oxygen converting the mercaptans to disulfides.

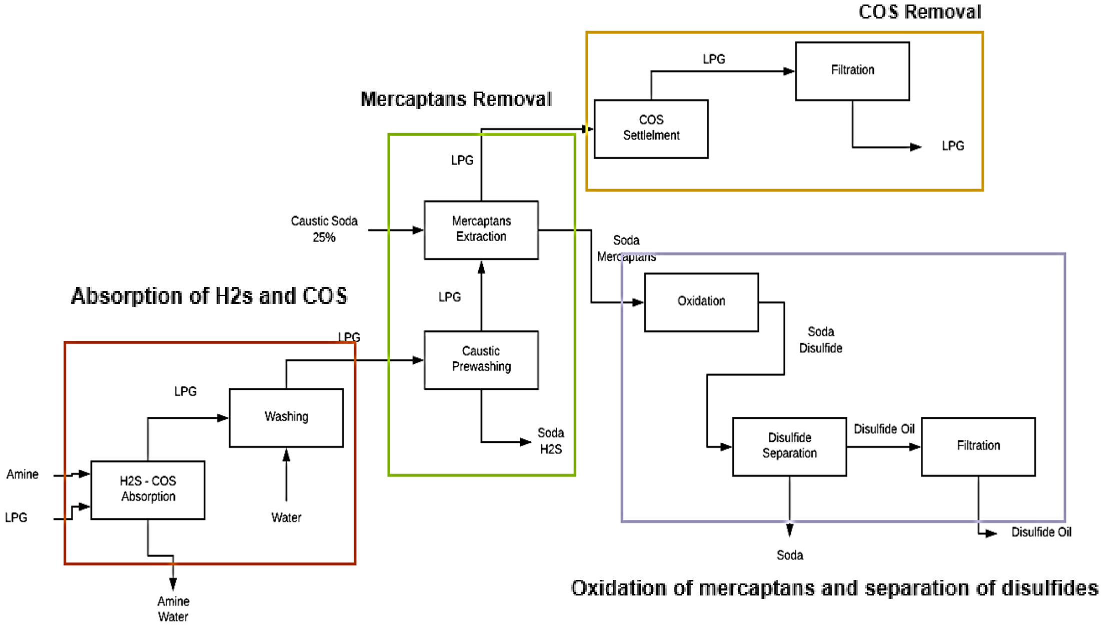

Figure 1: Sulfide absorption and mercaptans oxidation unit.

2.1.1 Absorption of H_2S and COS from LPG section

This unit removes H_2S present in the LPG by implementing a 25 vol.% Diethanolamine (DEA) solution as a solvent. To achieve this goal, it is necessary to use an absorption tower, which removes more than 99 % of the hydrogen sulfide, a condensate tank and a water washing drum. The process begins with the entry of LPG through the bottom of the absorption column at 38 °C and a pressure of 205 psig, where it comes into contact in countercurrent with the DEA solution, which enters at the top of the column to a temperature of 40.55 °C and a pressure of 340 psig. The products of this unit are: amine rich in H_2S and COS together with the LPG which leaves at the same inlet temperature and at a pressure lower than 182 psig and goes to the mercaptans removal unit.

2.1.2 COS removal section

This unit removes the carbonyl sulphide that is still present in the LPG after having passed through the absorber tower, for which it enters a temperature of 38 °C and 150 psig and goes towards a settlement drum with MEA (Methyldiethanolamine). Which is in solution at 20 % and NaOH at 10 % and finally goes to a sand filter in order to remove impurities.

2.1.3 Removal of mercaptans section

The objective of this unit is to remove the mercaptans present in the LPG. The LPG resulting from the H_2S removal unit enters this unit at a temperature of 38 °C and 179 psig, then enters a system of two extractor towers in series, where the LPG comes into contact in countercurrent with an aqueous solution of caustic soda at 25 %, in the first tower the remains of H_2S that are still present are extracted from the LPG and in the second tower a percentage greater than 99 % of mercaptans is extracted. The products of this unit are LPG, which is directed to the unit of removal of COS at a temperature of 38 °C and a pressure of 154 psig and caustic soda, which is directed to the unit of oxidation and separation of disulfides.

2.1.4 Oxidation of mercaptans and separation of disulfides section

For the conversion of mercaptans to disulfides, MEROX catalyst and oxygen (O_2) is used to regenerate mercaptan-rich soda, because mercaptans are very harmful, for example, ethylmercaptan is a malodorous sulfide, significantly toxic for human health, is a colorless liquid with a low threshold value of the odor and its maximum allowed concentration should not exceed 10.0 mg /l (Sedighi et al., 2016), for which it is preferred to convert them to disulfides since they are less harmful and are soluble in hydrocarbons. They are separated from the caustic solution because they are insoluble in it. The oxidation reaction occurs spontaneously but at a very low speed, for this reason it is necessary to implement the MEROX catalyst.

2.2 Environmental assessment using WAR algorithm

To carry out the environmental assessment, the WAR GUI software was used, where 4 different cases were taken into account. In the first case, the product stream was not taken into account and neither was the COS removal unit. The purpose of this is to see the results of the environmental evaluation if the LPG leaves the process even with small amounts of COS, in the second case the product stream was taken into account, even without adding the elimination unit of COS, in the third case unit was added but not had in account of the flow of products and the fourth case, the COS removal unit was maintained and the product flow was taken into account.
An environmental evaluation has the objective of showing the impacts that a process causes to the environment, this evaluation serves to identify the aspects that can be improved so that the process is better environmentally. The waste reduction algorithm or WAR is among one of the tools to perform the environmental evaluation of a process, this algorithm proposes the concept of potential environmental impact (PEI), which measures the effect of a quantity of matter or energy that has on average about the environment (Montoya et al., 2006). The potential environmental impacts are analyzed from two points of view, the first are the PEI output, which, measure the potential environmental impact emitted by the process to its surroundings, the second are the PEI generated in the process, which, determine the environmental efficiency of this.
In this algorithm 8 different categories of impacts are evaluated, which are grouped into two large groups, the first group being the toxicological categories, which includes potential for human toxicity by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP) and the second group is made up of the atmospheric categories, which are conformed by global warming potential (GWP), ozone depletion potential (ODP), potential acidification or acid rain (AP) and photochemical oxidation or potential for smog formation (PCOP).

3. Results and discussion

3.1 Total Potential Environmental Impact (PEI): generated and output

Figure 2 shows that the generation of environmental impacts is not significant in all cases, the second being the one with the highest PEI generated per hour (-40.4), while the third one has the lowest PEI generated per hour (-110,000), this value increases to (-41.8) in case 4, taking into account the flow of products, this is because the product of this process contributes considerably to the total impacts generated by this process. On the other hand, that the PEI generated per hour present a negative value, indicates that the process reduces total impacts, which means that this process is environmentally efficient.

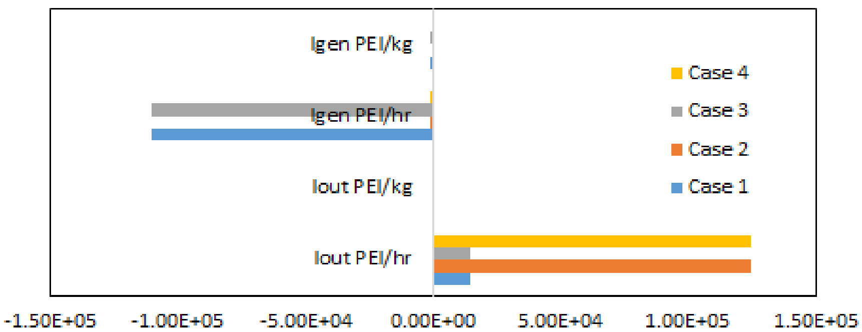

Figure 2: Total PEI generated and output of the sulfide absorption and mercaptans oxidation unit.

3.2 Local toxicological impacts of the process: output

Figure 3 shows output PEI values in the categories of toxicologists (HTPI, HTPE, TTP and ATP). It can be seen that the output PEI values per unit hour are the same for the HTPE categories (631 PEI) and ATP (3,430 PEI) in the 4 cases, the same happens with the output PEI values per unit of kilogram, that is, they are not affected by the inclusion or not of the product stream or the removal unit of COS. Unlike the HTPI and TTP categories, which change significantly with the inclusion of the product stream.

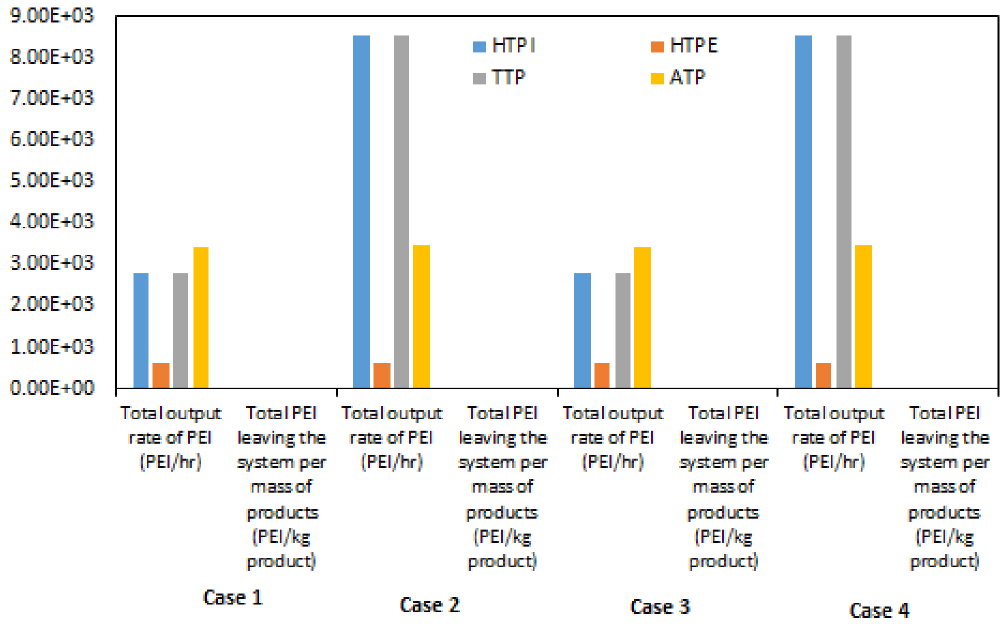

Figure 3: Local output toxicological impacts of a sulfide absorption and mercaptans oxidation unit

3.3 Local toxicological impacts of the process: generated

In Figure 4 shows the impacts generated from the toxicological categories. It can be seen that the inclusion of the product increases the generation of impacts in the categories HTPI and TTP in the different cases, while the other categories remain almost constant.

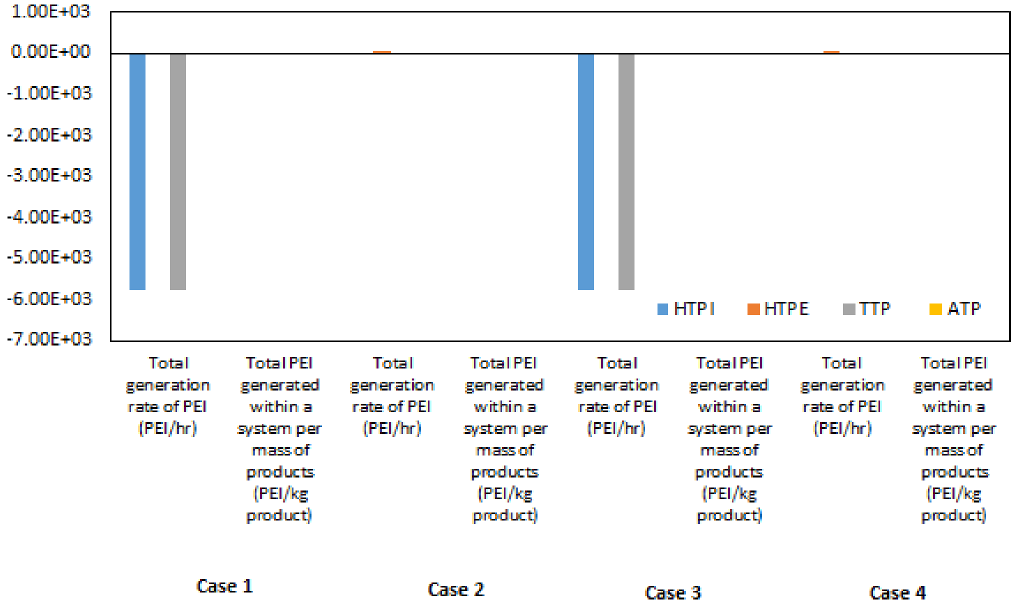

Figure 4: Local generated toxicological impacts of a sulfide absorption and mercaptans oxidation unit.

3.4 Atmospheric impacts of the process: output

Figure 5 shows the output impacts in the atmospheric categories (GWP, ODP, PCOP, AP), it can be seen that the PCOP category presents the highest IES generated per unit hour in cases 2 and 4, this is due to the inclusion of the product due to its nature, since according to (Manahan, 2007) the hydrocarbons react rapidly with a hydroxyl radical, which contributes to the formation of Smog.

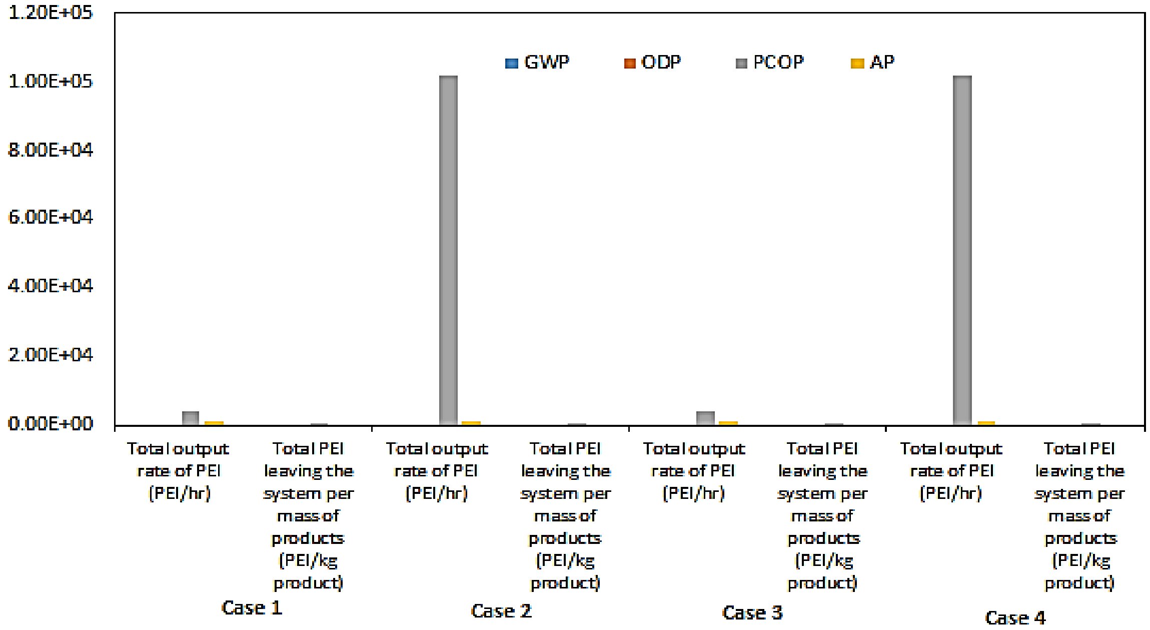

Figure 5: Output atmospheric impacts of a sulfide absorption and mercaptans oxidation unit.

3.5 Atmospheric impacts of the process: generated

Figure 6 shows the impacts generated from the atmospheric categories, it is observed that in cases 1 and 3, the PEI generated by the lowest hour of all the cases in the PCOP category is present, this is due to the exclusion of the product in the environmental assessment, while the other categories remain relatively constant.

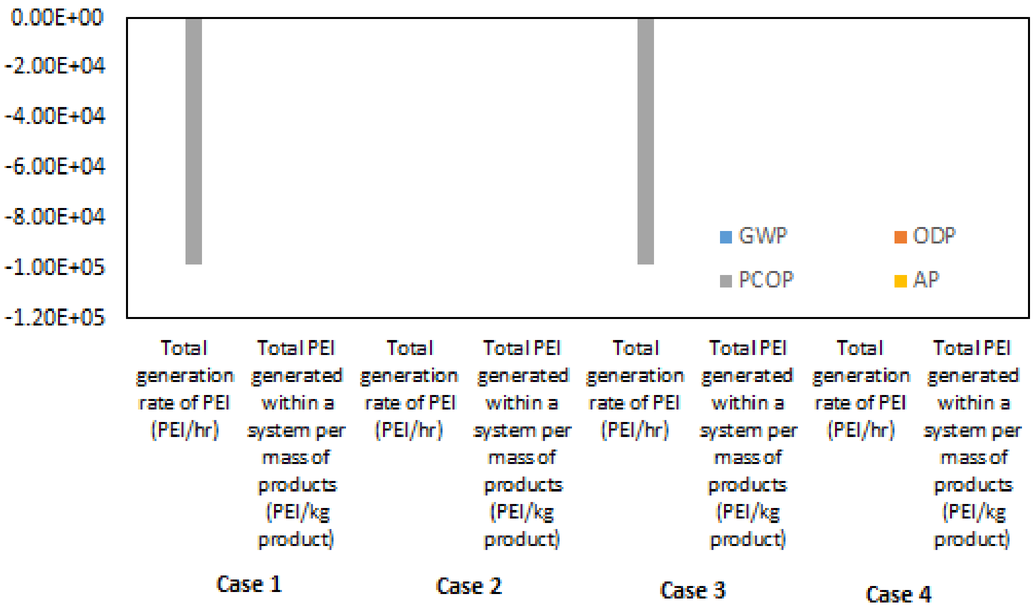

Figure 6: Generated atmospheric impacts of a sulfide absorption and mercaptans oxidation unit.

4. Conclusions

After using the WAR algorithm through the WAR GUI program, applied to refinery unit for sulfide absorption and mercaptans oxidation and previously analyzing the results, it can be concluded that the process is environmentally favorable, since in each of the cases the total impacts generated were negative. It can be deduced that the inclusion of the product, that is, of the LPG in some cases, resulted in an increase in the PEI generated due to its nature. In case 1 there was not much variation in the results compared to case 3, despite the inclusion of the COS removal unit, this is due to the small amounts of this component present in the LPG, which allows to deduce that these do not have great importance in the environmental evaluation carried out, in addition to the COS removal unit, although it has advantages in the technical aspect, because it helps to achieve the specifications of the product, environmentally, according to the results obtained by the WAR algorithm, it is not significant; presenting the same between cases 2 and 4.

Acknowledgements

The authors thank the University of Cartagena for providing all the tools used to successfully complete this work.

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