NAPHTHA CATALYTIC REFORMER HYBRID MODELING

Isam A. B. Salem and Shams Khaled*

Abstract: Naphtha Catalytic reforming is a very important process because it is responsible for high percent of gasoline production in the petroleum refinery. Because of the complex nature of naphtha reforming process and its reaction chemistry, mathematical modeling of such a process with First Principle Method (FPM) will provide highly non linear relations. This nonlinearity of the developed model will reduce the prediction capability and the model results will deviate from the actual plant data.

A hybrid modeling (HYB) method adapted in this paper, which is the first principle model in parallel to neural network (ANN) model are used to simulate naphtha reformer. The aim of the HYB is to add the corrections from ANN to the deviated results obtained from FPM.

Two months of operational data of a Libyan refinery is used in this study to simulate the semi regenerative naphtha reforming reactor, each data point was properly prepared by HYSYS Software to be used as input to FPM model which is simulated by MATLAB Software.

The paper focused on one output variable (reactor outlet temperature Tout) from the FPM which showed high deviation between the predicted and actual data.

Also same data is also used as input to ANN model, the data is normalized, outliers removed and verified with variance and correlation coefficient to select the proper input variables. Correlation coefficients between input and output showed high dependency between the proposed variables. Different architectures of ANN are carried out using MATLAB where mean square error (mse) was used as performance parameter. The results showed that neural network with structure [4-5-1] provided best performance. This ANN provided best residual predictions to reduce the deviations in reactor outlet temperature.

Keywords: modeling, hybrid, naphtha reformer, neural and network.

INTRODUCTION

The mathematical modeling of the chemical processes is very important in many aspects such as the process optimization and control. The progress in understanding the complex kinetics and chemical mechanisms of naphtha reforming and the structure of the reactions network provided the basis to establish mechanistic models which contains the fundamentals of the process and can provide good predictions of the results, such modeling is called (white-box) or first principle modeling. The prediction capability of such models can be affected by several reasons such as the parameter estimations, deactivation of the catalyst.

Modeling with Artificial Neural network (NN) which depends on information regarding the input and output variables allowed complex chemical processes to be modeled easily. Modeling by neural network is very good in capturing the nonlinearity of the complex chemical process which some first principle model may fail, on the other hand neural networks provide good estimate in the range of the data which the model trained on but it is very weak in extrapolation. Combinations of both neural network and first principle configuration was used and tested and the main idea behind this is to take the advantages of both in modeling process.

Arrangement between first principle and neural network (hybrid modeling) can be either serial or parallel. Such combinations are well covered in the literature for different chemical process and with good results (Bhutani et al, 2006; Dimitris and Lyle, 1992).

*Department of Chemical Engineering, University of Benghazi, Benghazi, Libya.
Corresponding author: isam.salem@uob.edu.ly ; Tel: +218 913799271

Modeling napththa reforming with first principle approach is extensively studied and available in literature, but due to the complexity of process and its chemistry which resulted in deviation in the obtained results.

Many attempts like the better estimate of the kinetic parameters or detailed reaction network can be used to reduce the deviations in predictions. In this paper a hybrid model of naphtha catalytic reforming reactor was derived which contains neural network in parallel to first principle. This arrangement contains the principles governing the chemical process such as (reaction network, catalyst deactivation) and on the other it also contains the neural network which will capture the nonlinear behavior of the process.

PROCESS DESCRIPTION

The reforming process modeled in this paper starts with the feed which is straight run naphtha goes through hydrotreater. The major reforming reactions are endothermic, this will lead to temperature reduction of the feed stream and causes reaction rate to decrease, and because of this, the catalyst is distributed over two reactors. The straight run naphtha feed is mixed with recycled rich hydrogen stream and heated to desired temperature before goes to the first reactor which is called reformer. The product from the first reactor after heating enters the second reformer, the outlet from the second reactor enters a separator in which hydrogen rich gas is separated and recycled back and mixed with fresh feed to the first reactor. This type of catalytic reforming is called semi regenerative naphtha reforming (SRR).

MODEL DEVELOPMENT

First principles model

The steps to model naphtha catalytic reforming reactor which used extensively in the literature and illustrated very well in our previous paper and can be summarized as follows (Isam, 2017).

- Naphtha mixture which contains three hydrocarbon classes; naphthenes, paraffins and aromatics is lumped into psudocomponents. The proposed psudocomponents have average properties of that class.
- ASTM D86analysis of about 53 data points obtained from operation were used as input to HYSYS software to predict the average properties of each cut.
- Smith model which describe the chemical reactions network for the whole system was adapted.
- Heat and component mass balance were carried out by considering the reactor as plug flow reactor and the resulting ordinary differential equations of mass and heat balances were solved simultaneously by suitable solver.
- Data available after reactor model simulation are the temperature outlet and psudocompenents concentration in the reactor effluent.

Neural network model

Neural network is used extensively in engineering application because of its simplicity and its ability to capture the nonlinearity in the process.

The basic element of the neural network is the neuron. Layers consist of a number of neuron (nodes) which contain an 'activation function'. Data presented to the nueral network via the first layer which is called input layer, which connected to the hidden layers where the data processing take place. The hidden layers also connected to an output layer where the data output is obtained.

Hybrid model

Three types of configuration of hybrid modeling are available in literature. Here in this paper the parallel configuration was selected because it showed better performance than the other two types (Bhutani et al, 2006). The hybrid model will contain FPM and the neural network both will simulate the reformer. The neural network will be trained to provide the difference between the calculated and the real variables. This difference is called the residual and is used as correction factor to the FPM parameters.

Model data pretreatment: the data gathered in for this study was obtained from a Libyan refinery for two months of operation of about (60 points of data set) which were properly logged.

Data Outlier detection and removal: Data that do not fit within a certain pattern of the gathered data are called data outlier. incorrect and faulty measurements can be the main source of outliers in industrial data The inclusion of such outliers in neural network will reduce the precision of the results and according to this data outliers removed with several methods . Simple technique is to plot the frequency histogram of the data, the frequency distribution plot will provide continuous and normally distributed curve, by this outliers can be detected easily. The method used to remove outliers ensured that all data are normally distributed. This method is simple and proved high accuracy with results (Khawla, 1997). This method detected 7 points which can be considered as outliers.

Normalization: Neural networks require that their input and output data are normalized to have the same order of magnitude. Normalization is very critical; if the input and the output variables are not of the same order of magnitude, some variables may appear to have more significance than they actually do. There are several methods used for normalization such as Z-Score Normalization, Min-Max Normalization, Median Normalization, Sigmoid Normalization (Al Mahdi, 2013; Jayalakshmi, and Santhakumaran, 2011).

Here in this paper min/max normalization as in (1) this proved to provide satisfactory results with neural network.

$$y = \frac{(x - min_d) * (max_n - min_n)}{max_d - min_d} - min_n \qquad (1)$$

Where
maxd is the maximum value in the data
mind is the minimum value in the data
maxni is the maximum value in the new range
minn is the minimum value in the new range
x is the input data

Input and output variables selection: Four input and one output variables where selected as the parameters of the neural network. The suitability of this selected was tested by statistical tools. Covariance and correlation analysis which is shown in Table 1. was carried out to show the dependence of the different variables.

Covariance will provide measure of the relation but on the other hand correlation coefficient (r) given as in (2) is a statistical tool to measure the strength of the relationship between two variables. They are in the range of [-1 1]; positive value indicates that one variable increases with the other while negative value indicates the opposite , and 0 shows no observed relationship between the two variables.

$$r = \frac{б_{xy}}{б_x б_y} \qquad (2)$$

Where $б_{xy}$ is Covariance and $б_x$ $б_y$ Standard deviation.

Neural network architecture: The neural network developed in this model is the feedforeward network, comprising of input layer (IP) , hidden layers (H) output layer (OP) having N_{ip}, N_h, and N_{op} nodes . Because the selection of the nodes in the hidden layer are problem dependent , the nodes Nh are adjusted by trial and error taking the advantages of the recommendation available in the literature (Su et al, 2016).

The *newff* function is used for data training. The transfer function used in the hidden layer are (tan sigmoid) tansig function in Matlab is used and output layer with linear transfer function purelin.

Training of the neueral network carried out back propagation algorithm Levenberg-Marquardt method is used *trainlm* function in Matlab also training with Bayesian regularization trainbr function was used. The performance of the neural network is based on the mean squared error and the correlation of determination and time was not used as comparison parameter because the data was small size. In this model the nodes Nh are adjusted.

RESULTS

The FPM and the HYB models both developed using Matlab, one output parameter from the FPM which is the reactor outlet temperature T_{out} where compared to the real production data, and the difference obtained is corrected by the neural network model. Different neural network architectures were tested to select best one. The selection is based on the performance of neural network which the minimum mean square error mse. Tables 2 and 3 show the results of using two different methods of training on different neural network architectures. Table 2 shows the results of using *trainlm* Matlab function on neural network with one and two hidden layer and can be observed that no constant pattern in the MSE change.

Table 1. The correlation coefficient of the input and output variables.

Input variable	IBP	FBP	SG	H2
Temperature residuals	-0.41	-0.52	-0.13	-0.41

Table 3 shows the results of using trainbr matlab function on neural network with one and two hidden layer and can be observed that no constant pattern in the mse change. Neural network with structure [4-6-1] provided best performance (mse=0.01) and this neural was used to calculate the corrections. In Table 4 the error percent of (some data points) for predict outlet temperature by FPM compared to the one of the HYB and improvement in the prediction capability is very clear.

Table 2. Performance for training using "trainlm".

	Training with one hidden layer			Training with two hidden layer		
Architecture	4-4- 1	4-5- 1	4-6-1	4-4-4 1	4-4-5-1	4-6 6-1
mse	0.024	0.01	0.024	0.039	0.046	0.255

Table 3. Performance for training ann using "trainbr".

	Training with one hidden layer			Training with two hidden layer		
Architecture	4-4- 1	4-5- 1		4-4-4 1	4-4-5-1	4-6 6-1
mse	2.08	0.6		2	2.91	2.6

Table 4. Error (%) between the real outlet reactor temperature and predicted one by using the FPM and HYM.

Days of study	Error using HYB%	Error using FPM %
1	0.03	-4.85
8	0.0008	-5.3
14	-0.007	-5.1
20	0.03	-4.8
30	-0.01	-3.9
40	-0.5	-5.3
50	0.01	-5.3

CONCLUSION

HYB mode which is FPM in parallel to ANN model is constructed and tested. The neural network model was used to correct the deviations between the real data and the FPM predictions. The hybrid model prediction capability was tested over a two months of operation data collected from a Libyan refinery. The hybrid model showed good prediction capability with maximum percent error less than 0.9 for all studied data points.

REFERENCES

Al Mahdi A. (2013). Modeling of Libyan Crude Oil Using Artificial Neural Networks. *Unpublished Ph.D. Dissertation, Dept. chem. Eng. Loughborough University*: 135p.

Bhutani, N.; Rangaiah G. P. and Ray, A. K. (2006). "First Principles, Data-Based, and Hybrid Modeling and Optimization of an Industrial Hydrocracking Unit" *Ind. Eng. Chem. Res.*, **V. 45**: 7807-7816.

Dimitris C. P. and Lyle H. U. (1992). A Hybrid Neural Network-First Principles Approach to Process Modeling. *AIChE Journal*, **V. 38(10)** :1499-1511.

Isam, A. B. (2017). The Effect of Feed Characterization on Naphtha Reformer Modeling. *Saudi Journal of Engineering and Technology,* **V. 2(12)**: 499-508.

Jayalakshmi, T. and Santhakumaran, A. (2011) "Statistical Normalization and Back Propagation for Classification. *International Journal of Computer Theory and Engineering*, **V.3(1)**: 1793-8201.

Khawla, A. A. (1997). Modeling, Simulation, and Optimization of Large-Scale Commercial Desalination Plants. Unpublished Ph.D. Dissertation, Dept. Chem. Eng., *Virginia Polytechnic Institute and State University, Virginia*: 453p.

Su Xin, X.; Wu, Y.; Pei, H.; Gao, J. and Lan, X. (2016). Prediction of Coke Yield of FCC Unit Using Different Artificial Neural Network Models. *China Petroleum Processing and Petrochemical Technology*, **V. 18(3)**: 102-109.

CAUSE AND CONTROL OF SULFUR TRIOXIDE FORMATION IN WASTE GAS THERMAL INCINERATOR

W. Alzamzam*, W. Alfaghi** and S. Almabrouk***

Abstract: Sulfur recovery unit is an integral part in natural gas treatment process. In which Incineration process is used in almost sulphur recovery units in order to make the process effluents releasable into the atmosphere.

This paper studies the formation of sulfur trioxide at thermal incinerator, its cause and control depend on two main factors which are an excess air and incineration temperature. ProMax software is used in this work to simulate the different combustion air flow rate and temperature changes of incinerator. Sulfur recovery unit (SRU) at a gas processing complex is the case study, which field data has been collected from the distribution control system (DCS). The investigation of SO_3 formation will be tested for the (SRU) with and without tail gas treatment unit (TGTU). Results show that the main causes of SO_3 formation are an excess air of O_2 in flue gas, and low incinerator furnace temperature. So, that to assure an almost complete combustion of H_2S and to control SO_3 formation, furnace temperature has to be higher than 700°C and excess air between 2 & 3Vol %. Finally, it's not possible to operate SRU without TGTU due to high dangerous environmental impact even at short periods (Mawle, 2010).

Keywords: Sulfur trioxide, incinerator, combustion air, sulfur plant, reaction furnace temperature.

INTRODUCTION

Climate change & air pollution due to different pollutants in the air is one of the major concerns all around the world. The air pollution is also known to cause adverse effect on crops, trees, lakes, animals, natural environment, building, monuments and statues. It has been estimated that large amount of premature deaths and adverse health effects are linked to air pollution. Over 350 manmade contaminants such as dioxins, volatile organic compounds, persistent organic pollutants are responsible for decreased hand-eye coordination, memory, physical stamina etc (Mawle, 2010).

Oil and gas exploration and production is source of pollution which are associated with many environmental and socio-economic impacts (Baptiste and Nordenstam, 2009), despite this, many nations throughout the world would still cherish to discover oil and gas within their territories. This is due to the fact that the availability of such natural resources is seen as a point of economic transformation and development fortunes of such nations. The problem here is that most of these countries are inexperienced in the oil and gas industry and usually their decisions are mainly based on economic transformation with little consideration for environmental and social implications.

Natural gas is a source of energy, which is widely used as an industrial, commercial, and domestic fuel. To make natural gas suitable for using, it is important to purify it from all impurities such as acid gases. The acid gases of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are common impurties existing in the natural (Al-Lagtah *et al*, 2015).

Usually, the acid gases are separated from natural gas in the gas treating unit (GTU) and the separaed acid gas stream is sent into the sulfur recovery unit (SRU). Sulfur recovery unit is one of the basic units of gas refineries; this unit is very important in economic and environmental issues.

*&** Operation Department, Mellitah Complex, Mellitah Oil and Gas Company, Mellitah, Libya. Email: walzmzam@yahoo.com
Email: walid6848@yahoo.com
***Petroleum Department, Faculty of Engineering, Tripoli University, Libya.

This work is to study the formation of SO_3 via thermal incinerator at sulfur recovery unit SRU. It will be done for two different mode (TGTU on line and TGTU off line) to know how SO_3 effected by temperature of thermal incineration and excess air.

MATERIAL AND METHODS

In order to investigate the formation of sulfur trioxide via the incineration stack at SRU, a typical an exist industrial sulphur recovery unit is studied as shown in (Fig. 1). ProMax software is used in this study as a simulator of the different parameters which effect on the incinerator especially combustion air and fuel gas to investigate the SO_3 changes due to these parameters.

RESULTS AND DISCUSSION

Incineration of tail gas streams in sulphur recovery unit (SRU) is a mandatory treatment in order to meet the environmental requirements and regulations. Simulating the performance of incinerator using combustion air and fuel gas in different levels were carried out for several air levels and studied pollutants of sulphur trioxide compound in each case to be compared with air quality limits. Figure 2 represents the scheme of simulation case; in addition, all tests were carried out based on 1-3vol% of O_2 excess air. And incineration temperature gradient (400-800°C) for both cases of Tail gas treatment unit on and off SRU system.

Tail gas is Running

Figure 3 shows the furnace temperature of the incinerator at different fuel gas quantities and with different excess air volume, which is clear the temperature is directly proportional with fuel gas and inverse with excess air. Figures 4 and 5 show sulfuric compounds concentrations that are being emitted to the environment via the stack by different incinerator temperature and different excess air.

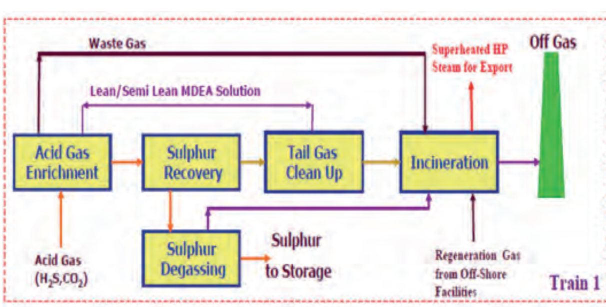

Fig.1. Scheme of sulphur recovery unit.

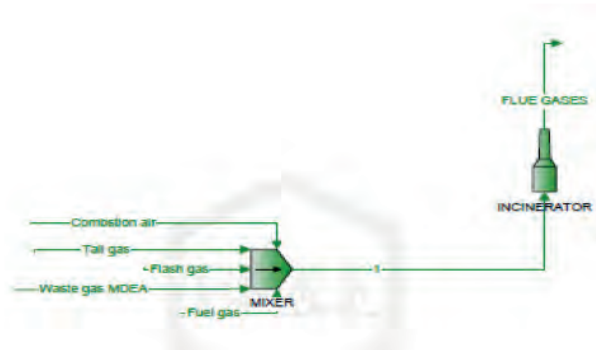

Fig. 2. Scheme simulation case (Incinerator).

Results depict that the increasing of incinerator temperature resists the formation of SO_3 especially when the temperature more than 700°C, and keeping at limit (less than 50ppm) even at excess air (1-3vol% O_2). SO_3 is more hazardous on health and environment than other sulphuric compounds, additionally, in order to obtain optimal working parameters for the case study and based on simulator results, the optimal temperature must be in range (700°C -800°C) for good environmental result and good operation conditions. On other hand the excess air is cause to increase the formation of SO_3 and reduce SO_2. This means that increasing the excess air increase the SO_3.

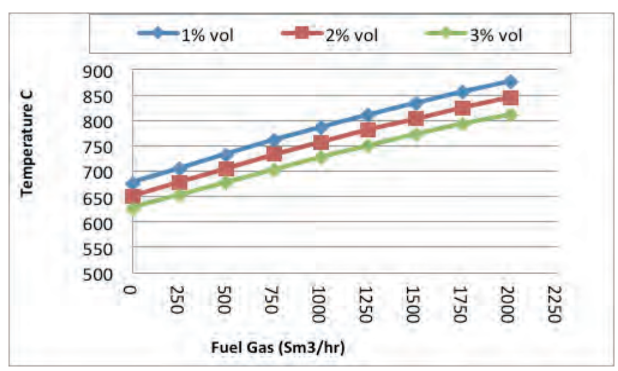

Fig. 3. Relation of furnace temperature to fuel gas and combustion air.

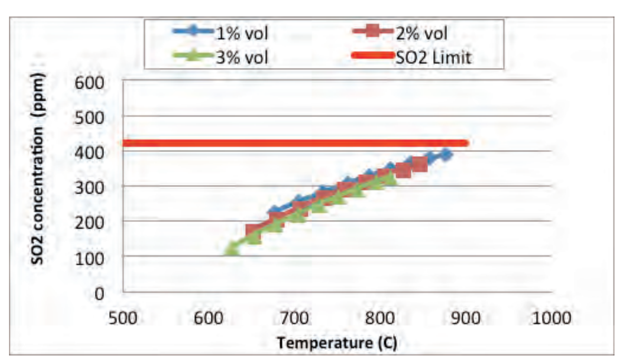

Fig. 4. SO_2 out of stack at different incineration temperature.

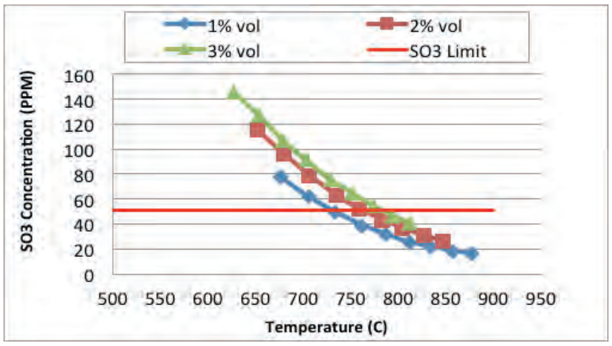

Fig. 5. SO_3 out of stack at different incineration temperature.

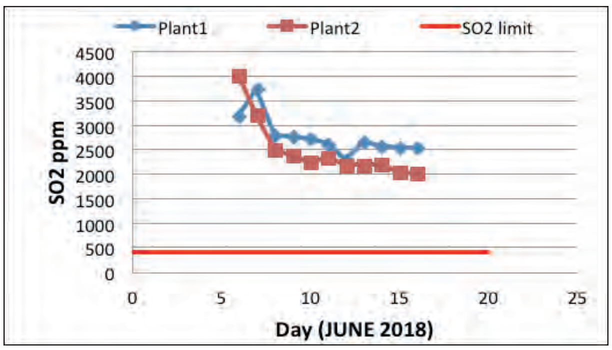

Fig. 6. SO_2 in tail gas to Incinerator (Exist SRU).

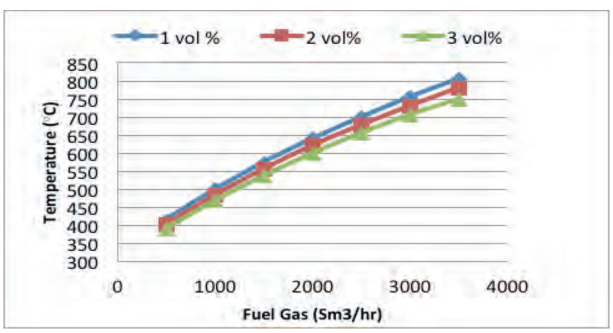

Fig. 7. H_2S in tail gas to Incinerator (exist SRU).

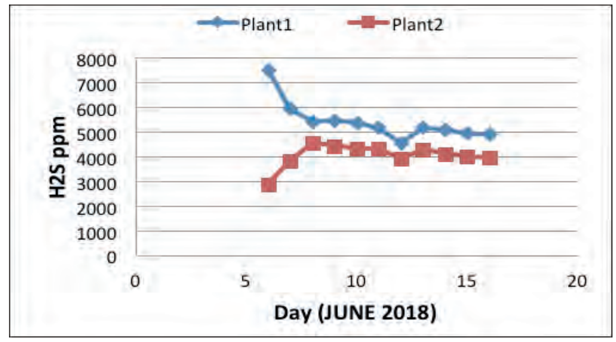

Fig. 8. Relation of furnace temperature to fuel gas and combustion air.

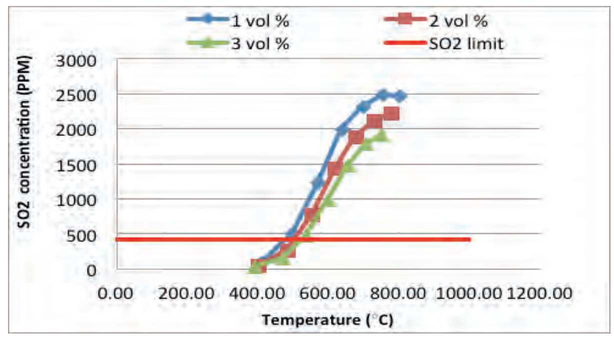

Fig. 9. SO_2 out of stack at different incineration temperature.

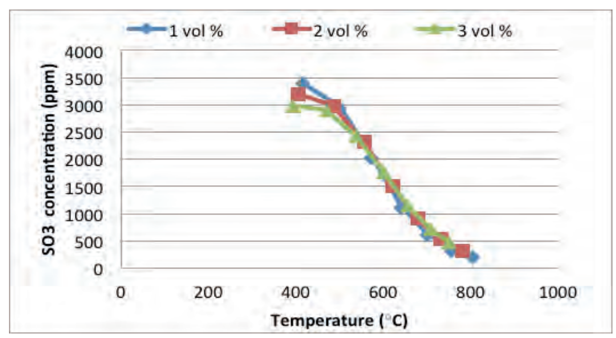

Fig. 10. SO_3 out of stack at different incineration temperature.

Tail gas out of SRU system

The tail gas stream from claus section for two exist sulphur plants contain toxic and hazardous compounds (mainly hydrogen sulphide, and sulphur dioxide) which cannot be released to atmosphere (Figs 6 and 7). So, in such emergency condition, the tail gases send to thermal incineration directly without further treatment in TGTU.

This work is done to study the pollutants vent via thermal incinerator to the atmosphere in case TGTU off, and investigate if this operation condition is possible to emitted pollutants to atmosphere.

Figure 8 shows the furnace temperature of the incinerator at different fuel gas quantities and with different excess air volume as thermal incinerator, in which it's clear that the temperature is directly proportional with fuel gas and inverse with excess air. Figures 9 and 10 show sulfuric compounds concentrations that are being emitted to the environment via the stack by different incinerator temperature.

Results show that the SO_2 is over range and does not meet the international standard which is 420ppm neither at high temperature nor at excess air. On the other hand SO_3 is over range and does not meet international standards which is 50ppm, neither at high temperature nor low excess air.

This disaster due to TGTU out of service and high SO_2, H_2S feed to incinerator from clause (Figs. 6 and 7). This work is good evidence for that Claus section must be follow by tail gas treatment unit to assure complete combustion of H_2S and to assure the other sulphur compounds (SO_2 and SO_3) on limit with the regulations standards. So, TGTU should be lined up with the SRU system and no possibility to be out of service.

Tail gas treatment unit is very important part for SRU and the environment, it is provide up to 99% the efficiency of sulfur recovery unit. The comparison is done for incineration unit emission gases to the atmosphere in case of TGTU on line and TGTU off line. (Figs. 11and 12) represent the SO_3 out of stack at different incineration temperature with and without TGTU at excess air 1vol% and 2vol%, the result show that all level of emission gas on specification in case of TGTU on line and off specification in case TGTU offline. This proves that it is not possible to run SRU without TGTU due to high risk of harmful gases emission to the atmosphere via incinerator stack.

CONCLSION AND RECOMMENDATIONS

Furnace temperature is a very important factor for the SO_3 formation at incineration unit; another factor is excess air in fact, oxygen excess favours the oxidation of sulphured compounds, besides increasing undesirable production of SO_3. In normal SRU system (TGTU on) results show that SO_3 inverse proportional with temperature. It means that the increase of temperature in incineration furnace reduces formation of SO_3 especially (more than 700°C) leads to meet the emission standards which is 50ppm at different excess air level 1-3% vol. On the other hand, SO_2 is on limit with regulation which is less than the concentration 420ppm. It's recommended that incinerator temperature is around 750°C so that to assure complete combustion of H_2S and to assure the other sulphur compounds (SO_2 and SO_3) on limit with regulations standards. Incinerator temperatures must not be lower than 700°C, excess air increases the formation of SO_3 due to oxidation SO_2 so it must be not high to avoid SO_3.

In another case (TGTU off line), the formation of SO_3 in incineration unit is flow the same behaviour as it in (TGTU on line) with both furnace temperature and excess air but the problem is the emissions are over range for both SO_3 and SO_2. So, it's not possible to work SRU without TGTU due to high toxic environmental impact even at short time.

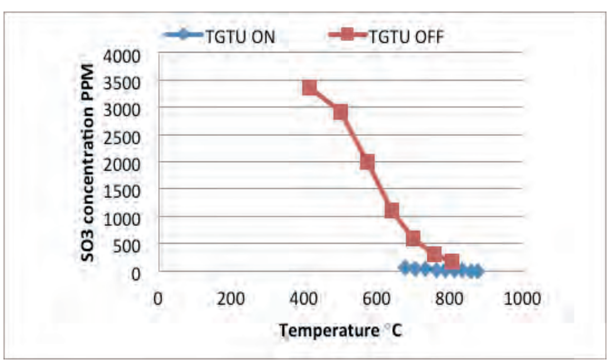

Fig. 11. SO_3 out of stack at different incineration temperature with and without TGTU at excess air (1 vol%).

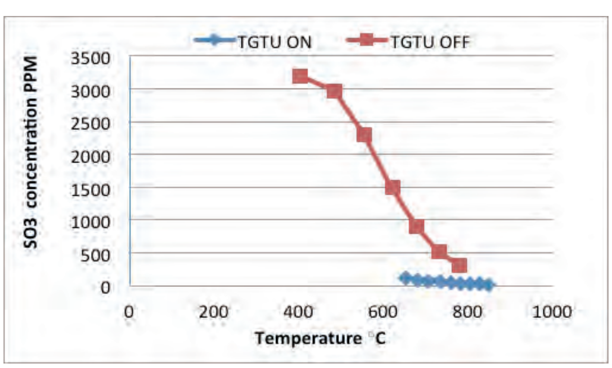

Fig. 12. SO_3 out of stack at different incineration temperature with and without TGTU at excess air (2 vol%).

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REFERENCES

Al-Lagtah, N. M. A.; Al-Habsi, S. and Onaizi, S. A. (2015). Optimization and Performance Improvement of Lekhwair Natural Gas Sweetening Plant using Aspen Hysys. Journal of Natural Gas Science and Engineering, ***V. 26***: 367-381.

Baptiste, A. K. and Nordenstam, B. J. (2009). Impact of Oil and Gas Drilling in Trinidad: Factors Influencing Environmental Attitudes and Behaviours Within Three Rural wetland communities. *Environmental Conservation*: 1-8. In Press.

Mawle, A. (2010). Climate Change, Human Health and Unsustainable Development. *Journal of Public Health Policy*: 272-277.