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Technical and Economical Evaluation of Oleum Elimination from Sulphuric Acid Unit of Petrochemical Industries

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In present study, one of the sulphuric acid production units in Iran was investigated. By utilizing HYSYS v3.1 software the condition of this unit was simulated. On the basis of the simulation results analysis, a patent was considered to study the new method on it to reach a minimum amount of oleum generation. Therefore, generated oleum was reduced from 0.917 to 0.498 m^3/h which was measured from the stack of investigated unit. To gain the extra amount of oleum produced before the absorption tower, another method was considered. Therefore, liquid oleum was achieved *ca.* 8.376 m^3/h which converted to initial raw materials, *ca.* 7.129 m^3/h SO_3 gas and 0.386 m^3/h liquid H_2SO_4. To ensure that the patent is economically cost-effective, economical indices and sensitivity analysis was considered by utilizing COMFAR III software. The economical results shows internal rate of return 19.49 %, payback period 5.5 years and net present value 31,985,781 Euro. Considering external costs, the mentioned values would be 74 %, 2.3 year and 149,016 Euro. Consequently, emission of oleum from this sulphuric acid production unit would be cost-effective with or without considering external costs.

Key Words: Oleum, Fuming sulphuric acid, Sulphuric acid unit, HYSYS v3.1, COMFAR III.

INTRODUCTION

Sulphuric acid is by far the largest-volume chemical produced more than 130 million tons worldwide. It is used in the production of all kinds of chemicals, of which fertilizers are the most important. Other major uses are in alkylation in petroleum refining, copper leaching and the pulp and paper industries[1-3].

Sulphuric acid production involves the catalytic oxidation of sulphur dioxide into sulphur trioxide. The process has developed *via* the lead chamber process to the modern contact process. The contact process originally used a supported platinum catalyst, but since 1920s, it has been gradually replaced by a supported liquid-phase vanadium catalyst[3].

Many researches define that some pollutants such as CO, H_2S, SO_2, NO_x and fuming sulphuric acid or oleum are produced undesirably during sulphuric acid production. Fuming sulphuric acid or oleum is an aggressive and corrosive material whose major hazard potential comes from the clouds of H_2SO_4 mist produced when reaction between moisture and sulphur oxides is occurred. Mist particles are an inevitable product of sulphuric acid production process. Within the process, these particles can cause problems such as corrosion of equipment, contamination of product, fouling of heat exchangers and catalysts and damage to instruments[4,5]. Occupational exposures to fumes or mists containing sulphuric acid are specifically associated with laryngeal and lung cancer in workers. Furthermore, when released to the atmosphere, they can cause violations of air pollution emission standards or opacity of regulations significantly. It has a main role in generation of acid rain. Therefore, control of oleum emission is vital[6,7].

In present study, one of the sulphuric acid production units of a petrochemical plant in Iran was investigated. The main purpose of the study is identifying an optimal and economical technique for removal of oleum from sulphuric acid units of petrochemical plants.

EXPERIMENTAL

Existing condition of investigated sulphuric acid unit: The process of acid production in the investigated sulphuric acid unit involves the catalytic oxidation of sulphur dioxide into sulphur trioxide *via* the contact process. In the contact process a supported liquid-phase vanadium catalyst is used in 4 catalyst beds with intermediate cooling[8], as shown in Fig. 1.

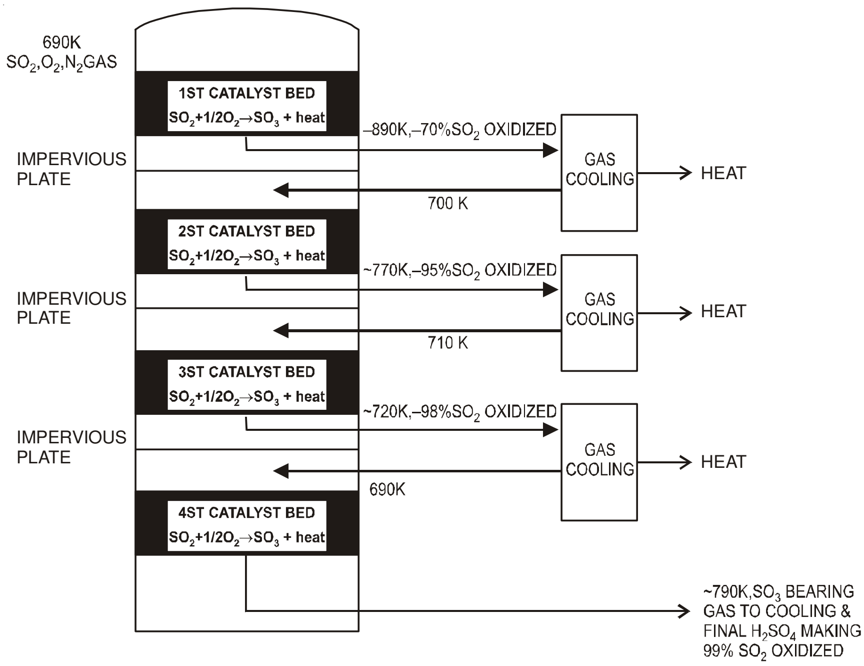

Fig. 1. Schematic presentation of four catalyst beds and its cooling between catalyst beds for oxidation of SO_2 to SO_3 in investigated sulphuric acid unit [Ref. 8]

Three main sections in this unit could be distinguished as follow: (1) Combustion of sulphur to produce SO_2 in sulphur burner furnace (2) Catalytic oxidation of SO_2 to form SO_3 (3) Absorption of SO_3 in concentrated sulphuric acid in absorption tower.

In this sulphuric acid unit, daily capacity of sulphuric acid production is about 3220 tones. The main portion of this product is used for producing of phosphoric acid and the residual is used for producing of industrial water[8].

Simulating of the investigated sulphuric acid unit: At the present study, by utilizing HYSYS v3.1 software, the existing condition of the investigated unit was simulated which is shown in Fig. 2. In this unit, the amount of H_2O (g) in-combustion air entering sulphur furnace burner is *ca.* 0.658 m^3/h. Gas output temperature from sulphur furnace burner is about 949.9 ºC which is marked as line 3 in Fig. 2. The temperature of output gas from sulphur furnace burner is reduced to the desired inlet temperature of the first catalyst bed about 436.1 ºC. The heat of reaction of SO_2 oxidation raises the temperature in first bed significantly about 600 ºC. The hot exit gases are cooled before entering the second bed about 387 ºC, where further conversion takes place. The gas leaving this bed with the temperature of 520 ºC is cooled by heat exchanger 1203C near to 453 ºC. It subsequently undergoes further conversion in the third and forth beds. The gas leaving the last bed is cooled through heat-exchanger 120 ºC by *ca.* 216 ºC and fed to the absorption tower. The amount of oleum emission[8] from the gas stack outlet of this unit is *ca.* 0.917 m^3/h.

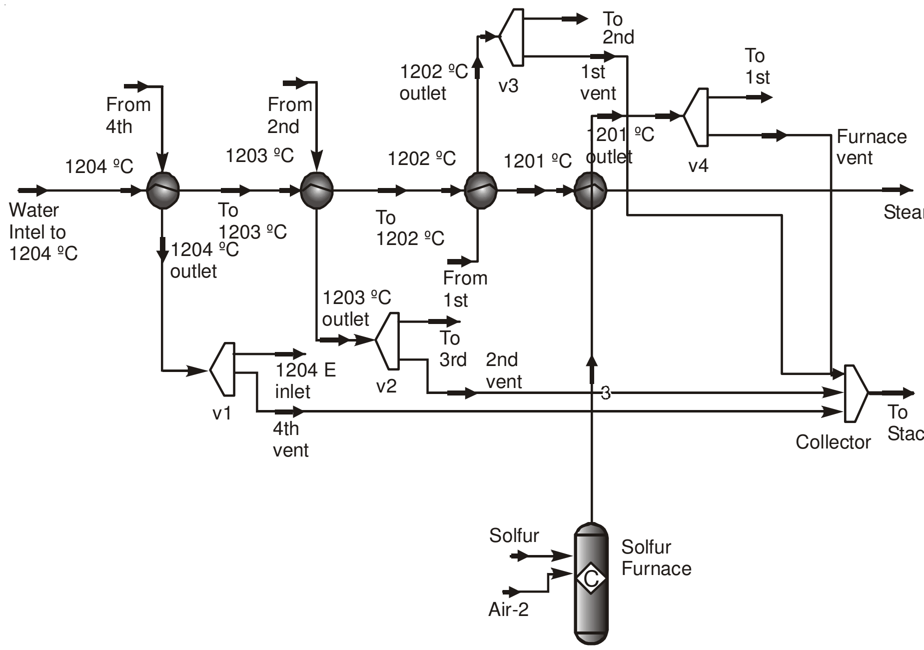

Fig. 2. Existing condition of investigated sulphuric acid unit through using HYSYS v3.1 software

Selection of a suitable technique for dehydrating of sulphur combustion air: Since the main reason to produce oleum is moisture in sulphur combustion air and concerning to simulating results of investigated unit which is indicated the lack of a feasible system for removing of moisture from sulphur combustion air, therefore providing a feasible system for reduction of moisture is indispensable[3,9-11].

There are at least three industrial methods for removing water vapour from gases: Absorption with hygroscopic liquids, condensation by means of cooling and adsorption with dehydrating solids. In condensation by means of cooling, a simple refrigeration cycle could be used. Two main parts of a simple refrigerant are a compressor for compressing the gas to be dehydrated and a cooling device for cooling the compressed gas, whereby the water vapour condenses[3]. In present study, dehydration through a simple refrigerant is suggested for this investigated sulphuric acid unit. The most important reasons to other techniques are as below[1,5,10]: (a) Short time to reach for utilization (b) Convenient dimensions for developing patterns (c) Minimum necessity to repairing (d) Less initial investment cost (e) Abundance and reasonable costs of refrigerants.

RESULTS AND DISCUSSION

Simulation of investigated unit by using a refrigeration cycle for dehydrating of sulphur furnace combustion air: Fig. 3 shows the simulation of investigated unit by utilizing HYSYS v3.1 software. H_2O (g) -in- air entering sulphur furnace burner is *ca.* 0.658 m^3/h in existing condition. In the simulated patent, a refrigerant was used to dehydrate the humidity of sulphur combustion air. By using the refrigerant, the temperature of sulphur combustion air was decreased from 25 to 7 ºC. Consequently, some water vapour in sulphur combustion air was condensed to water. Then, a liquid-gas separator was attached to the refrigerant, in which all the condensed water vapour is separated from the sulphur combustion air. The amount of moisture was reduced from 0.658 m^3/h in existing condition to *ca.* 0.391 m^3/h in simulated sulphuric acid unit. As a result, the amount of oleum after reduction of moisture was reduced from 0.917 m^3/h - of the stack outlet of existing condition - to 0.498 m^3/h from the stack outlet of simulated sulphuric acid unit.

Table-1 presents a comparison of the amount of existing moisture in sulphur combustion air before and after using the refrigeration cycle and its effect on oleum generation by utilizing HYSYS v3.1 software.

TABLE-1
COMPARISON OF THE MEASURE OF MOISTURE IN SULPHUR COMBUSTION AIR BEFORE AND AFTER USING THE REFRIGERATION CYCLE AND ITS EFFECT ON OLEUM GENERATION BY UTILIZING HYSYS V3.1 SOFTWARE

(m^3/h)	Before using refrigeration cycle	After using refrigeration cycle
Moisture in sulphur combustion air	0.658	0.391
Oleum outlet from the stack	0.917	0.498

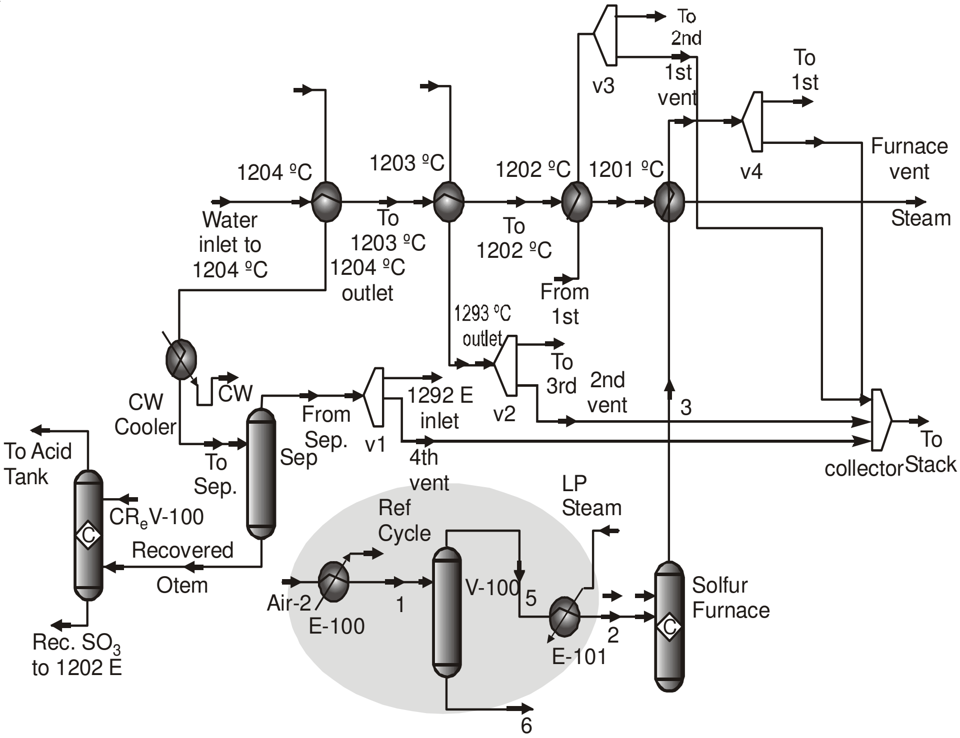

Fig. 3. Simulation of investigated unit by utilizing a simple refrigeration cycle through utilizing HYSYS v3.1 software

Separating and recovering of oleum before absorption tower: A refrigeration cycle, however, was used to reduce the amount of moisture of sulphur combustion air, residual and produced moisture during the process could be reacted with sulphur oxides -especially produced SO_3 from catalytic beds-before sulphuric acid absorption tower to produce more oleum. To gain the extra amount of oleum which is produced before the absorption tower, a cooler was installed after all of the catalyst beds. Therefore, the temperature was decreased from 216 to 120 °C which led oleum into liquid. Then, a liquid-vapour separator was utilized to separate the liquid oleum and free SO_3 gas. The free SO_3 gas was transmitted to absorption tower to produce sulphuric acid. The achieved liquid oleum which is *ca.* 8.376 m^3/h was transmitted to an endothermic reactor to heat oleum up to 200 °C. After heating oleum, SO_3 was produced up to 7.130 m^3/h and liquid H_2SO_4 up to 0.387 m^3/h. Produced SO_3 gas was fed to sulphuric acid absorption tower and produced liquid H_2SO_4 was transmitted to sulphuric acid storage tank. Accordingly, nearly all achieved liquid oleum before absorption tower was recovered to initial valuable material which can be used in the investigated sulphuric acid unit. Fig. 4 shows the simulation of investigated unit for separating and converting of oleum before sulphuric acid absorption tower by utilizing HYSYS v3.1 software.

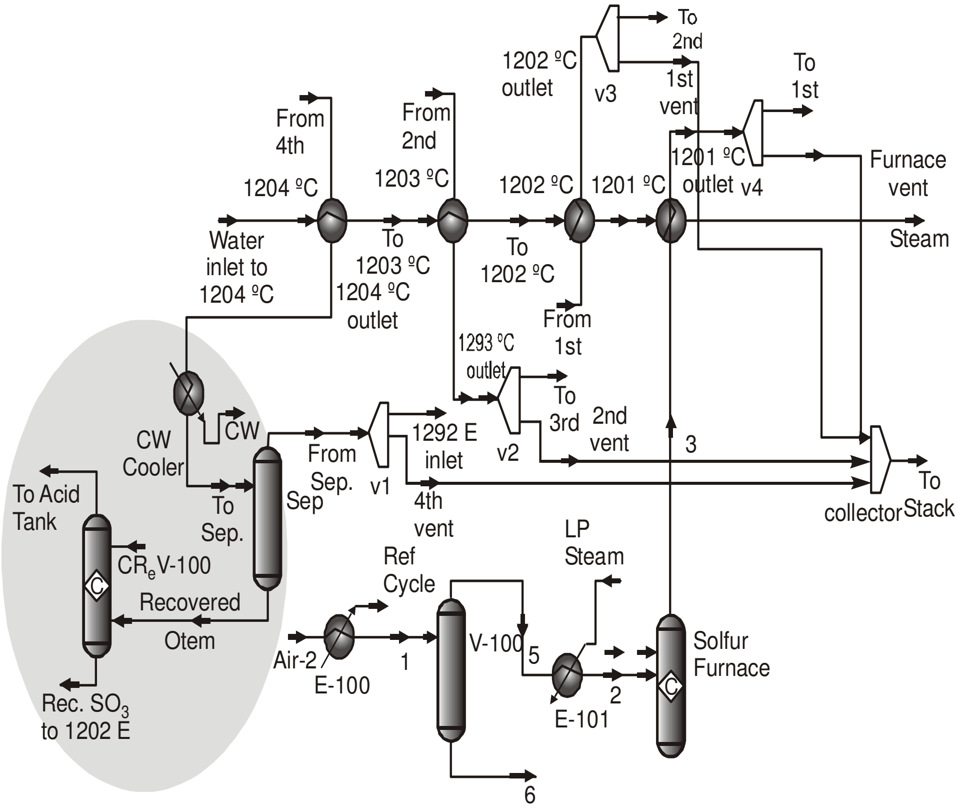

Fig. 4. Simulation of investigated unit for separating and recovering oleum before sulphuric acid absorption tower by utilizing HYSYS v3.1 software

Economical evaluation of simulated sulphuric acid unit: To ensure that the simulated patent is economically cost-effective, all extra parts in simulated sulphuric acid unit including the refrigerant, separator, heater, cooler and reactor were considered as a cost center[12]. To calculate the tables and economical indices of investigated unit Microsoft Excel and COMFAR III software were utilized. To use COMFAR III the basics and assumptions of investigated unit including the investment costs, financial resources, production costs, revenues, *etc.* were computed by Microsoft Excel. The expected duration to accomplish the simulated patent is the year of 2008-2010 during which all the activities relating to negotiation with foreign manufactures, registration of orders, opening letter of credit, transportation, installment and so forth will be completed. The time span for the plan is predicted to be 15 years from 2010 to 2024.The investment costs of investigated unit are trivial, therefore the financial resources of the unit can be provided from the stockholder and the annual profit of investigated unit[8]. The constant costs of investments (1,284,524 Euro) in the investigated unit based on 2008 prices by utilizing Excel software[12].

The production costs are mainly included energy supplying costs, repair and maintenance costs and depreciation cost which should be paid during the production and utilization period. Supplying energy in simulated unit includes providing electricity and cooling water. Evaluation of simulated unit shows that 1246200 m^3/yr cooling water and 1165800 kW/yr electricity is required. As repair and maintenance costs at initial years are less than final years, the prediction of repair and maintenance costs in the first five years relative to equipment costs would be 10 % which will be increased 5 % every 5 years. For calculating depreciation, Direct Method was utilized[13,14]. In this method the assumption is based on the fact that constant possession during its whole useful life has a consistent depreciation. Consequently, by utilizing COMFAR III software total production costs from 2010 to 2014 would be 441,664 Euro, from 2015 to 2019 would be 512,497 Euro and from 2020 to 2024 would be 583,330 Euro.

The amount of annual sales revenue of this simulated unit is provided by SO_3 and H_2SO_4 production. By utilizing Excel software the amount of produced SO_3 from oleum is about 20045.583 ton/year. The sale revenue per ton of SO_3 is *ca.* 40 Euro. Therefore annual sale revenue of SO_3 would be 801,561 Euro. The amount of produced H_2SO_4 from oleum is about 1087.808 ton/year. The sale revenue per a ton of H_2SO_4 is *ca.* 17.5 Euro, thus annual sale revenue of H_2SO_4 would be 19,057 Euro.

Concerning to the sales revenue which is not mainly cash and a plenty of produced product is used in the unit, paying taxes according to tax laws of Iran was not considered[8].

Sensitivity analysis examination of the simulated unit: Sensitivity analysis is applied for evaluation of uncertainty effect on economical projects.

In this analysis, if some key parameters - or all of them- to be significant, how these affect the economical indices. Economical indices such as IRR or NPV are used for sensitivity analysis[15-17].

Fig. 5 clarifies the sensitivity analysis by considering the relation between sales revenue, increase in fixed assets, operating costs (variation of -20 to +20 %) and IRR[9] in simulated unit. By 20 % decreasing in sales revenue, IRR[8] would be *ca.* 10 %. But with 20 % increasing in sales revenue, IRR[8] would be *ca.* 30 %. By 20 % increasing in constant investment costs, IRR[8] would be *ca.* 15 % and by 20 % decreasing in constant investment costs, it would be *ca.* 26 %. For production costs, by 20 % increasing, IRR[8] would be *ca.* 23 % and by 20 % decreasing it would be *ca.* 17 %.

External costs of oleum emission from investigated sulphuric acid unit: In the present study, by removal of oleum from 0.917 to 0.498 m^3/h, the amount of reduction (0.418 m^3/h) can be calculated in cash and to be considered as revenue. This revenue is the result of external cost decrease. As it mentioned before, oleum is an aggressive and corrosive material whose major hazard potential comes from the clouds of H_2SO_4 mist produced when reaction between moisture and sulphur oxides is occurred.

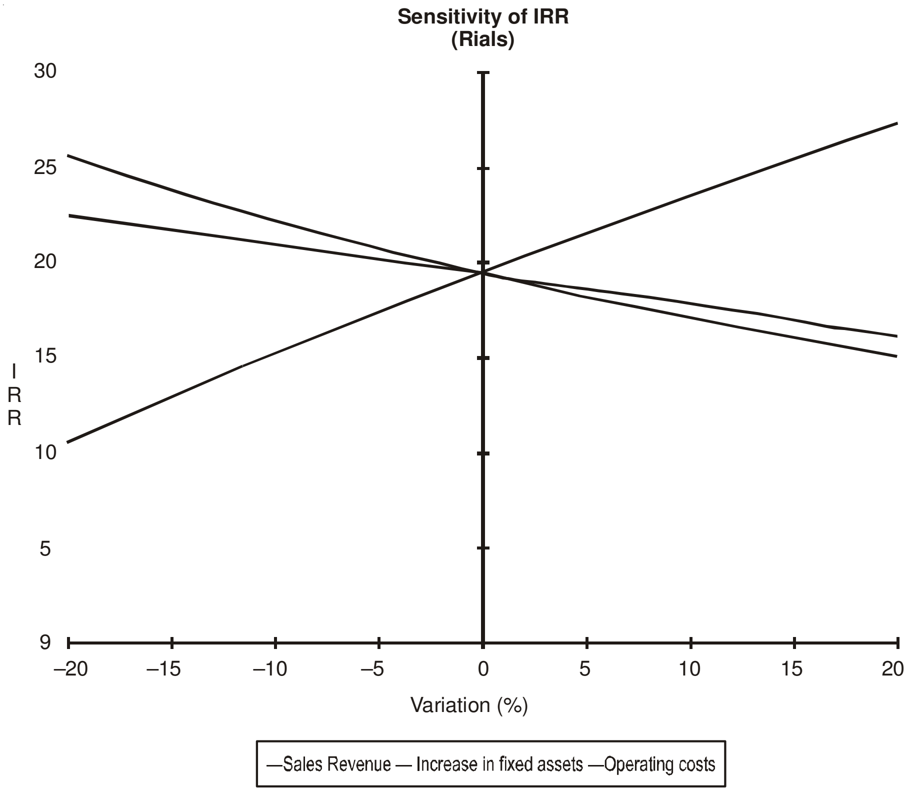

Fig. 5. Sensitivity analysis; the relation between sales revenue, increase in fixed bed, operating costs (variation of -20 % to +20 %) and internal rate of return (IRR) in simulated unit

Accordingly, external costs decrease of oleum can be considered as sulphur oxides emission into the environment which react with the moisture and produce sulphuric acid mists. The decrease of external costs of SO_x for each tone is about 1065.7 Euro in Iran[18]. Therefore, the gained annual revenues of decreasing in external cost of oleum removal in this simulated unit would be 1,254,852 Euro. Economical indices considering external costs of oleum removal from simulated sulphuric acid unit by using Excel software was gained as follow: NPV was gained up to 31,985,781 Euro, IRR was gained about 74% and PBP was gained 2.3 years.

Conclusion

The lack of a feasible system for removing moisture from sulphur combustion air is the main reason to produce oleum. By employing HYSYS v 3.1 software, the existing condition of this unit was simulated. On the basis of the simulating results analysis, using a proper refrigeration cycle for drying sulphur combustion air is indispensable. By utilizing the refrigeration cycle, the amount of moisture was reduced from 0.658 m^3/h in existing condition to *ca.* 0.391 m^3/h in simulated sulphuric acid unit. As a result, the amount of oleum of the stack outlet after reduction of moisture was reduced from 0.917 m^3/h in existing condition to 0.498 m^3/h in simulated sulphuric acid unit.

To gain the extra amount of oleum produced before the absorption tower, a cooler was installed after all of the catalyst beds. The temperature, therefore, was decreased from 216 to 120 °C to convert oleum into liquid. Then, a liquid-vapour separator was utilized to separate the liquid oleum and free SO_3 gas. The achieved liquid oleum which was *ca.* 8.376 m^3/h was transmitted to an endothermic reactor to heat oleum up to 200 °C.

After heating oleum, SO_3 was produced up to 7.130 m^3/h and liquid H_2SO_4 up to 0.387 m^3/h. Consequently, nearly all achieved liquid oleum before absorption tower was recovered to initial valuable material which can be used in the investigated sulphuric acid unit.

The results of economical analysis through utilizing COMFAR III software were as follows: internal rate of return was 19.49 %, payback period was 5 years and net present value was 148,928 Euro. By considering external costs, the mentioned values would be 74 %, 2.3 year and 31,985,781 Euro, respectively. Consequently, emission of oleum from this sulphuric acid production plant would be cost-effective with or without considering external costs.

Based on the results of present study, there are some suggestions to reduce more amount of oleum and to boost sulphuric acid production process as follow:

Using mist eliminators to remove acid mists from the gas stream to control stack emissions to the atmosphere, reduce damage of equipment caused by corrosive or fouling acid mists, improve purity of the vapour or gas for next processing, improve overall process economics of the operation and remove hazardous liquid mists from reactive gases to yield safer operations[3].

Using a scrubber tower, SO_2 gas can be dried in a scrubber tower by direct contact with weak sulphuric acid (usually 93 %) before entering catalytic beds. This contact provides additional cooling and cleaning of SO_2 gas. Thus the amount of moisture of SO_2 gas will be reduced which is conducted to oleum reduction. But using a scrubber needs more initial investment costs and longer time to reach for utilization[3].

REFERENCES

1. W.G. Davenport and J.K. Matthew, Sulphuric Acid Manufacture, South African Institute of Mining & Metallurgy, Elsevier (2006).
2. E.L. Douglas, Industrial Chemical Process Design, McGraw-Hill Inc. (2002).
3. J.A. Moulijn, M. Makkee and A.V. Diepen, Chemical Process Technology, John Wiley (2005).
4. G. Grint and G. Purdy, *J. Loss Prev. Processes Ind.*, **3**, 177 (1990).
5. M.D. Koretsky, Engineering and Chemical Thermodynamics, John Wiley (2004).
6. M.P. Singh, M. Kumari and S. Ghosh, *Atmos. Environ.*, **24**, 735 (1990).
7. T. Kapis and R.F. Griffiths, *J. Hazard. Mater.*, **67**, 9 (1999).
8. Iranian Petrochemical Company (IPC), Annual transcript of National Petrochemical (IRR) (2007).

9. G.M. Cameron, Generation of Sulphur Trioxide from Oleum. United State Patent 4915912, C-I-L Inc (1990).
10. R.M. Stephenson, Introduction to the Chemical Process Industries 3, Reinhold Publishing Corp (1996).
11. C. Soares, Process Engineering Equipment, McGraw Hill Inc. (2002).
12. Stanford Research Institute (SRI), Section of Sulphuric Acid from Sulphur (2006).
13. R. Brockington, Financial Management. DP Publications, Softcover ISBN-13: 9781858050256, ISBN: 1858050251 (1990).
14. R.P. Neveu, Managerial Finance, South-Western Publication Co. (1989).
15. R.A. Jarrow, Finance Theory, Prentice-Hall International Editions (1988).
16. L.D. Schall and C.W. Haley, Introduction to Financial Management, McGraw-Hill Inc. (1988).
17. C.H.J. Van, Financial Management and Policy, Prentice-Hall International Editions (1989).
18. Ministry of Energy, Energy Balance Report, IRR (2005).

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