Thermodynamic Analysis for Nitric Acid Plant

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Abstract: A thermodynamic energy analysis based on the first and second laws were performed for small size nitric acid plant with a capacity of (20000 tons/ year) to produce (50 to 60) % nitric acid.

The lost work available energy to produce work was calculated for each unit and the total lost work of the plant was determined and found to be about (3.5MW), the lost work of the reactor unit represents (59.326%) of the total lost work. This means that irreversibility which causes lost work is severe for the reactor. Any improvement of the operating condition which reduces irreversibility of the reaction would improve the efficient use of energy of the overall plant, that is, reduce lost work or available energy for work.

This method of analysis can be used to pinpoint location of excess energy use in the chemical processes. However, it is the role of process engineers to recommend ways to reduce such waste of energy to the minimum possible and yet keep the process feasible.

Keywords: Nitric acid, thermodynamic, energy analysis, energy losses, plant efficiency.

INTRODUCTION

Nitric acid is an important chemical species for many industries. It is widely used in the production of fertilizers, explosives, etching of metals, wood finishing, and cleaning of food and diary equipment. On industrial scale, Ostwald's method is used to produce aqueous acid at about 60%by oxidizing ammonia with air. The following sequence of reactions takes place:

$$2NH_3\,(g) + 5/2\ O_2 = 2NO(g) + 3H_2O(g)$$
$$2NO(g) + O_2 = 2NO_2(g)$$
$$3NO_2(g) + H2O(l) = 2HNO_3(aq) + NO(g)$$

The production cost of nitric acid has a considerable effect on the cost of other products which use nitric acid as a raw material or otherwise. Therefore, any attempt to reduce the overall cost of nitric acid plants will contribute to the reduction of the cost of other products such as fertilizers (Chilton, 1931).

This study applies basic thermodynamic analysis to a 60% 20,000 ton/year nitric acid plant in order to assess energy utilization of this plant. The aim of this analysis is to evaluate energy losses (lost work) at each process step that otherwise could be partially recovered as useful energy instead of being wasted. It is then up to process engineers to come up with bright ideas to develop new process synthesis for new plants or carry out modifications on existing plants that cuts the energy cost of these plants. That is, this analysis pinpoint locations in the process where excessive energy losses take place, and therefore, concentrate efforts to reduce these losses. However, since real processes must always result in some energy losses, the target should be to reduce these losses while evaluating the economics of any process modifications which leads to the least feasible minimum cost design.

BASIC THEORY

Thermodynamic analysis of chemical processes is based on application of the combined equation derived from first and second laws of thermodynamics. For a steady state process, neglecting changes in potential and kinetic energies, the first law (energy balance) reduces to:

$$\Delta H = Q + W_s$$

And the second law (entropy balance) is given by:

$$\Delta S_{fs} - Q/T_0 = \Delta S^t \geq 0$$

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Where, ΔS_{fs} is the entropy change of the flowing streams, ΔS^t is the total system and surrounding entropy changes, and T_0 is the ambient temperature.

For a completely reversible (ideal) process Q is given by:

$$Q_{rev} = T_0 \Delta S_{fs}$$

Therefore, substituting this into the first law equation gives:

$$W_{s(rev)} = \Delta H - T_0 \Delta S_{fs}$$

Since the ideal work ($W_{id} = W_{s(rev)}$) and the real work ($W_{real} = W_s$) the lost work (W_{lost}) is defined as:

$$W_{lost} = W_{real} - W_{id}$$

Substituting W_{real} and W_{id} by their values above leads to:

$$W_{lost} = T_0 \Delta S^t \geq 0$$

This last equation states that the lost work (energy available for work) is either zero for ideal processes and positive for practical (real) processes. This equation is used to calculate the lost work for each step or equipment of the chemical process and then summed up to give the total lost work of the plant (Smith *et al* 2001).

RESULTS

The first step of this analysis is to carry out detailed calculations of the material and energy balances on the plant flow sheet Fig. 1. The results are given in Table 1. Then entropy changes for each process step (unit operation) are carried out using well known thermodynamic relations (Perry's Chemical Engineers Handbook, 2008). However, in order to use these relations hypothetical paths from the initial to the final state must be devised so that these relations may be applied. An example to illustrate this point is given by Fig. 2 for the absorption unit which produces the aqueous acid. reaction. Table 2 summarizes the lost work of the plant units. Fig. 3 and Fig. 4 compare the lost work calculated for different units percent-wise and in quantities of kW, respectively.

DISCUSSION AND CONCLUSION

The results of the thermodynamic analysis carried out for the nitric acid plant considered here indicate clearly that about 85% of lost work calculated for the whole plant comes from the ammonia oxidation reactor and the waste heat boiler to generate steam. This leads to the conclusion that the major source of the plant inefficiencies is located at these two equipments, and therefore, any process alteration regarding these two units may improve their efficiencies and reduce lost work of the plant. It is then the role of the process engineer to devise these alterations and check their improvements on the efficiency of the plant and evaluate these alterations economically to determine the most efficient and cost effective one. In this plant, since the oxidation reaction is exothermic, a possible alteration is to divide the reactor into zones so that the reaction may proceed progressively with intermediate cooling to reduce irreversibility which causes lost work.

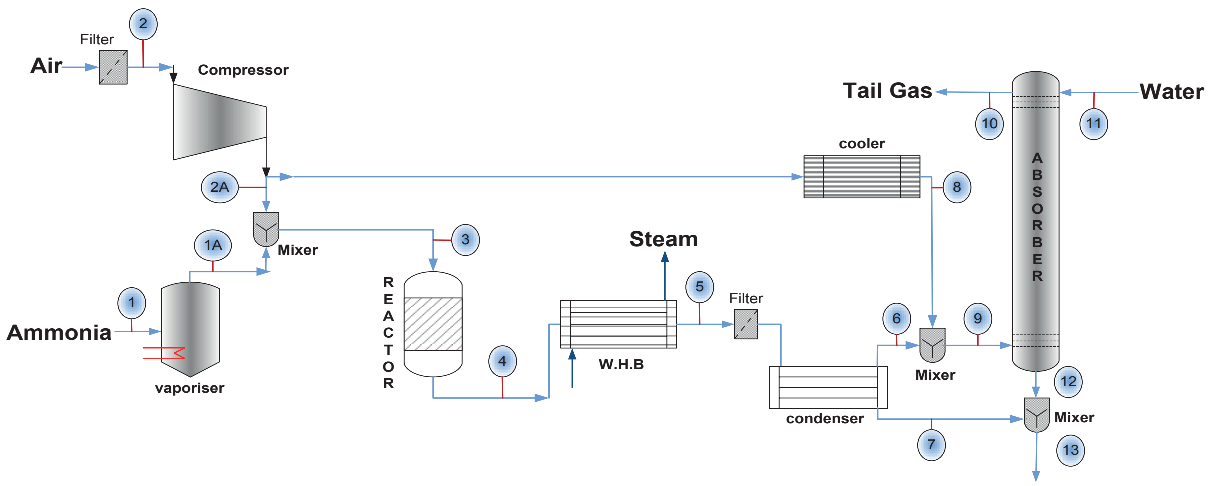

Fig. 1. Plant flow sheet.

Table 1. Mass balance {flows (Kg / hr)}

Line No. stream / Component	1 Ammonia Feed	1A Ammonia Vapor	2 Filtered Air	2A Oxidizer Air	3 Oxidizer Feed	4 Oxidizer Out let	5 W.H.B Out let	6 Condenser Gas	7 Condenser Acid	8 Secondary Air	9 Absorber Feed	10 Tail Gas	11 Water feed	12 Absorber Water	13 Product Acid
NH_3	731.0	731.0	----	----	731.0	----	----	----	-----	-----	----	----	----	----	----
O_2	----	----	3063.9	2628.2	2628.2	935.7	935.7	275.2	-----	408.7	683.9	371.5	----	----	----
N_2	----	----	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	-----	1346.1	10014.7	10014.7	----	----	----
NO	----	----	----	----	----	1238.4	1238.4	202.5	-----	----	202.5	21.9	----	----	----
NO_2	----	----	----	----	----	-----	----	967.2	-----	----	967.2	----	----	-----	----
HNO_3	----	----	----	----	----	----	----	----	850.6	-----	----	----	----	1704.0	2554.6
H_2O	----	----	----	----	----	1161.0	1161.0	29.4	1010.1	----	29.4	26.3	1376.9	1136.0	2146.0
Total	731.0	731.0	13027.7	11272.9	12003.9	12003.9	120039	10143.1	1860.7	1754.8	11897.7	10434.4	1376.9	2840.0	4700.6
Press (bar)	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1
Tem (c^0)	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43

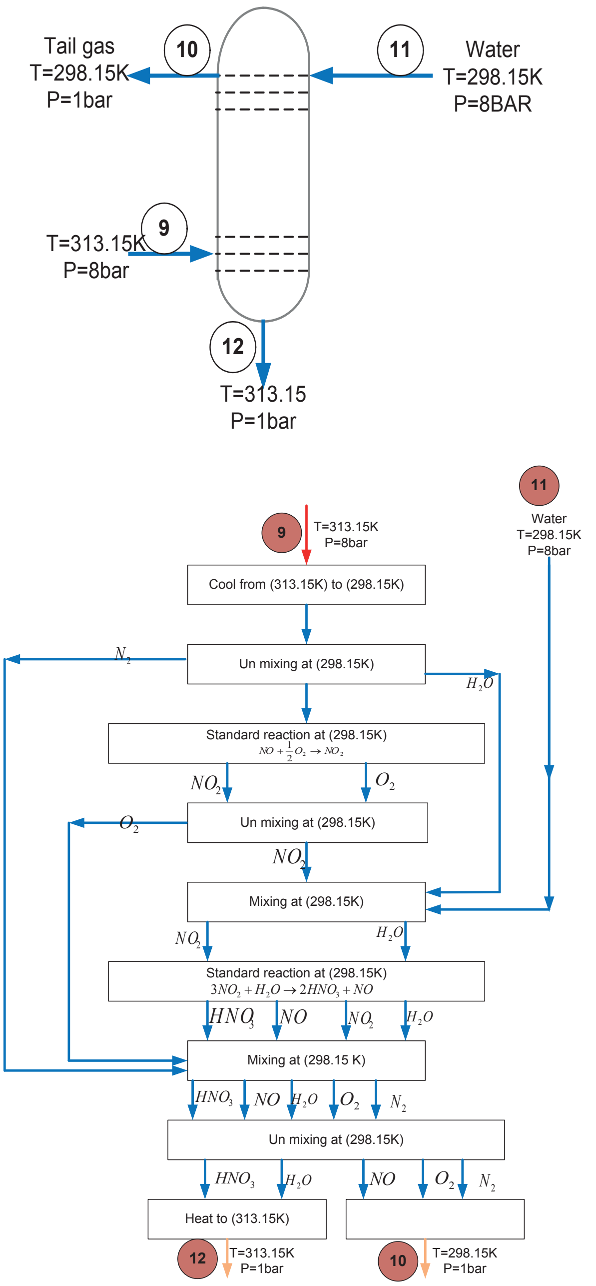

Fig. 2. Hypothetical path for ΔS calculation of the absorber

However, the increase in capital cost as a result should be compared to the savings on energy from lost work reduction. For the waste heat boiler unit, In general, maximizing feed water inlet temperature and reducing generated steam temperature will lead to less irreversibility, lower lost work, and higher thermal efficiency. On the other hand, the generated steam will be of lower quality.

Finally, the following concluding remarks regarding this thermodynamic method of analysis can be summarized:

Table 2. (Summary of lost work the plant)

Unit	lost Work (Kw)	% of total
Reactor	2304.22	59.326
W.H.B	969.59	24.96372
Mixer(1)	230.841	5.943388
Mixer(2)	165.8335	4.269661
Absorbed	81.67	2.102731
Mixer(3)	79.7445	2.053156
Cooler	21.5879	0.555817
Condenser	12.263	0.315731
Compressur	10.617	0.273352
Vaporiser	7.6298	0.196442

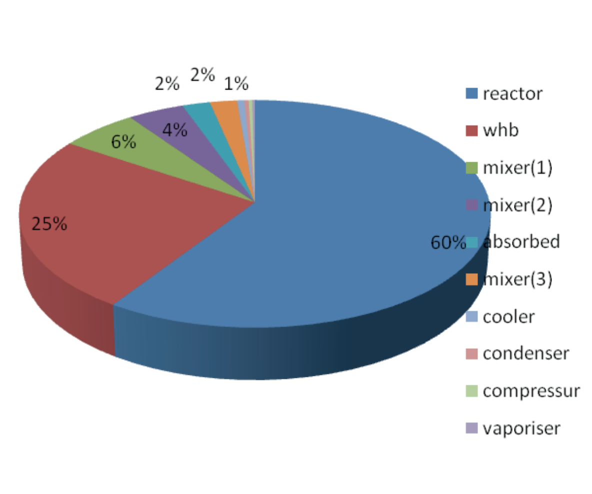

Fig. 3. Lost work percentage comparison

1 Lost work analysis is a powerful tool to evaluateprocess designs from the standpoint of energy utilization.
2 The method locates major sources of wasteful energy, but gives no hints on process changes to reduce them.
3 It directs the attention of the process engineer to the steps or equipments where process modifications can lead to considerable energy savings.
4 For newly designed plants, application of the analysis can result in highly efficient and environment-friendly processes.

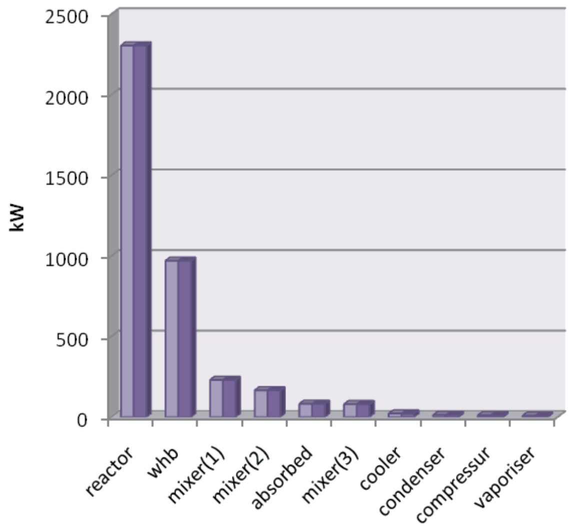

Fig. 4. Lost work (kW) comparison)

5 For existing plants, however, any feasible process modifications based on this analysis must be assessed considering plant layout, safety, controllability, etc.

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