1

Introduction

1.1 Research Overview

World’s primary energy consumption has grown by 45% over the past 20 years (BP Energy Outlook 2030, 2011). Total world energy use will rise from $580.73 \times 10^3$ PJ to $813.02 \times 10^3$ PJ in 2035. Worldwide industrial energy consumption will grow from $201.67 \times 10^3$ PJ in 2008 to $304.10 \times 10^3$ PJ in 2035 (International energy outlook, 2011). World energy related carbon dioxide emission will also rise to 43.2 billion MT in 2035.

Among all the industrial sectors, the chemical industry is one of the energy intensive industries with 33% share in industrial energy use. The increased cost of raw materials, infrastructure and energy, increase the production cost that increases the burden on the profit margin of the chemical sector. The Profit margin of chemical industry can be increased by improving process design and using energy efficient equipment. The chemical industry has successfully reduced its energy consumption after the oil crisis during 1970-1980. But in last few years energy efficiency improvement is almost constant (Chemical Bandwidth Study, 2004). The challenges ahead are increasing fuel cost and competition in international market. The chemical industry is looking forward to various alternatives to reduce production cost by improving process, modification of equipment and analyzing resource consumption. As shown in Fig.1.1 chemical industries are operating above the practical minimum energy requirement.

In such a situation, exergy analysis can be seen as an effective tool apart from an energy audit to reduce energy wastage. Exergy analysis provides insight for improvement in the process or equipment to enhance its energy efficiency by reducing the loss of exergy. It is also one of the tools to pinpoint true energy losses at various stages and equipments in a chemical plant. Exergy analysis can also be helpful in improving an existing process or design and developing new environmental friendly processes.
The major exergy loss in the chemical industry is in the reactors followed by distillation columns. In most of the cases heat released during highly exothermic processes is used for the steam production. High pressure steam contains higher exergy, but it is laid down to low pressure for an industrial requirement that causes more exergy loss. To investigate possible causes of exergy losses in actual process in the chemical industry, Nitric acid and Ethylene oxide/ethylene glycol production plants are selected. Overall energy and exergy analysis are carried for these processes. Apart from this, exergy analysis is also used as a tool to decide catalyst life on the basis of economic evaluation of the process. Coupling endothermic reaction along with exothermic reaction in the same reactor is a very important area of interest for researchers. Exergy analysis is used to find suitable thermally coupled reactor for the production of methanol.

1.2 Scope of Work
In the present work exhaustive literature survey is carried out to study the extent of work related to exergy analysis of chemical process and specific equipments. Improvement in the mono high pressure nitric acid plant is proposed in the study. A practical solution for heat recovery in running plant is suggested. Catalyst activity in ethylene oxide process is a key factor. Hence exergy analysis of EO/EG process is accrued out at higher selectivity
and lower selectivity. A catalyst replacement policy is suggested based on exergy destruction and cost. A new process, developed by Mitsubishi Chemical Corporation for the production of ethylene glycol, is compared with existing process on the basis of exergy analysis. Finally on the equipment level different thermally coupled reactors are analyzed. The heat liberated in methanol synthesis reaction is utilized for hydrogen production in various reactor combinations. These are compared and best combination is suggested. The overall scope of present work is shown in Fig. 1.2. Exergy analysis can be applied as an important tool to analyze the chemical production processes at various levels starting from individual equipment to complete plant economic analysis. It is expected that such study will be very much useful for enhancing the performance of existing and new chemical processes.

![Exergy analysis](image.png)

**Fig. 1.2** Scope of work

### 1.3 Research Objective
Some of the processes in chemical industry are exothermic in nature while some are endothermic. It is observed that most of the heat in the exothermic process is lost into the
atmosphere through cooling water. The quality of energy is lost due to processes irreversibility. Hence, exergy balance of process will pinpoint true losses. One step in this direction is to analyze the different processes based on exergy. Though some processes are previously analyzed, practical solutions to reduce exergy loss were hardly proposed.

The first objective of the present work was to take an exhaustive review of exergy analysis of process industries.

The second objective of the present work was to perform energy and exergy analysis of the selected processes to identify true losses in the processes.

The third objective of the present work was to suggest a practically possible solution to improve plant exergy efficiency and to define a new parameter based on exergy and cost to evaluate economic aspect of the process.

The fourth objective of the present work was to select suitable equipment based on exergy analysis.

1.4 Significant Contribution

The nitric acid production plant is generating large amount of energy along with nitric acid as bulk chemical. The efficient utilization of energy can improve the process performance and economics of plant. In the nitric acid plant, product gas leaving the reactor is passed through a train of heat exchangers and pipelines. While traveling oxidation reaction is taking place, hence pipes and heat exchangers are also acting as plug flow reactor. During simulating the nitric acid plant, all such pipes and heat exchangers are considered as a plug flow reactor for prediction of suitable conversion and temperature. The composition of the gas is changing with distance traveled. Energy balance and exergy balance of nitric acid plant are calculated. Saving of energy in the compressor and cooler condenser in the nitric acid plant is proposed for the first time.

For ethylene oxide and ethylene glycol production process, at start run and end run of ethylene oxide process temperature and heat released in oxidation process is changed. Steam generation is more at end run at the cost of ethylene consumption for the same amount of ethylene oxide production. Exergy balance at both runs will be helpful to find out true losses in the process. Catalyst activity at end run is deciding factor for economic consideration. Complete exergy balance is calculated for actual plant conditions.
Improvement in exergy efficiency by recovering ethylene from purge gas is proposed. A mechanism to decide catalyst life with the help of EXCEM method is also proposed. Exergy analysis is used to evaluate thermally coupled reactors to minimize exergy destruction during the simultaneous production of methanol and hydrogen. The overall aim of present work is to use exergy analysis in chemical industry and provide a solution to increase the profit of plant.

1.5 Thesis Organisation

Chapter-2 Exergy Analysis
Basic concepts of exergy, definitions of exergy efficiency are discussed in this chapter. Chemical exergy and reference environment are also included in the chapter.

Chapter-3 Literature Review
The aim of the literature review is to know the nature of work carried out by researchers in the chemical process industry. Various inorganic and organic products have been considered for this review. Exergy aspects for process improvement and pollution control are also considered for review.

Chapter-4 Minimisation of Exergy Losses in Mono High Pressure Nitric Acid Process
This chapter presents energy and exergy analysis of the mono high pressure nitric acid process and suggestions has been proposed to reduce exergy losses. First time attempt has been made for the recovery of heat from cooler condenser in the nitric acid plant.

Chapter-5 Exergetic and Exergoeconomic Evaluation of Ethylene Oxide /Ethylene Glycol Process at Start Run and End Run
This chapter discusses energy and exergy analysis of EO/EG process at start-run (higher selectivity) and end-run (lower selectivity). Two different processes of EG are compared based on exergy analysis. Finally, EXCEM method is used for exergoeconomic analysis of the process for selection of catalyst.
Chapter-6 Thermally Coupled Reactors for Methanol Synthesis – An Exergetic Approach

This chapter discusses the use of exergy analysis as a tool to evaluate the performance of thermally coupled reactors for the production of methanol. Exergy destruction per ton of methanol production and per ton hydrogen production is also calculated.

Chapter-7 Conclusions and Perspectives

All the findings in above chapters are discussed process wise and conclusion are drawn for them. Recommendations for further work are also suggested.
References

