HAZOP STUDY OF ETHYLENE OXIDE (EO) SECTION IN A MONO ETHYLENE GLYCOL (MEG) PLANT

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(with specialization in Industrial Safety and Hazards Management)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"HAZOP STUDY OF ETHYLENE OXIDE (EO) SECTION IN A MONO ETHYLENE GLYCOL (MEG) PLANT"**, in partial fulfillment of the requirement for the award of the degree of **Master of Technology (M. Tech.)** in **Chemical Engineering** with specialization in **Industrial Safety And Hazard Management (ISHM)**, submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology, Roorkee**, is an authentic record of my own work carried out during the period from July 2006 to June 2007 under the guidance of **Dr. NIDHI BHANDARI**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology, Roorkee.

The matter embodied in this dissertation work has not been submitted by me for the award of any other degree of this or any other Institute / University.

Date: 28/06/2007
Place: IIT Roorkee, Roorkee

(SUANTAK KAMSONLIAN)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

(Dr. NIDHI BHANDARI)
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ABSTRACT

HaZard and Operability (HAZOP) study is the most widely used and preferred approach in the chemical plant to accomplish hazard assessment, qualitatively and quantitatively. This study is typically performed by a team of experts having specialized knowledge and expertise in the design, operation, and maintenance of the plant. The HAZOP team members examine the process P&ID systematically, identify every conceivable deviation from design intent in the plant using a 'guideword' approach; determine all the possible abnormal causes and the adverse consequences of that deviation.

The present dissertation work has been conducted in MEG plant at RIL, Hazira where EO (ethylene oxide) and MEG (mono ethylene glycol) are the main products. The HAZOP study is carried out in EO section of the MEG plant since EO is a hazardous material in terms of toxicity, flammability in air and chemically instability, it can be handled and stored with safety, provided appropriate precautions observed. The main raw materials such as oxygen, inhibitor, carbon dioxide, ethylene, nitrogen and methane, are used in the manufacturing process of EO. The operating units involved for the production of EO in the plant are given as EO reactor, EO absorption, EO stripper, EO purification, EO recovery and EO storage tank.

Deviation or changes in the process parameters (such as temperature, pressure, levels of chemicals etc.) of EO operating unit may lead to a serious accident (violent reaction, damaged by overheating, hot spot formation, etc) and undesirable product since the product quality is sensitive; therefore qualitative and manual HAZOP study has been carried out as a dissertation work for a better performance of the process system as well as safety. Moreover, MEG plant is a continuous process which operates in supercritical condition, hence proper monitoring of the unit operation is required against hazards.

The present HAZOP study report shows the possible abnormal causes and consequences of hazard in the plant. A brief result discussion is also performed based on the present HAZOP study report. And also preventive corrective measure and recommendation has been made to improve the safety performance of the process and production line as well.

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ABBREVIATIONS

BFW	Boiler Feed Water
CSS	Carbon dioxide Shut-down System
CW	Cooling Water
DPAT	Differential Pressure Alarm with Trip
EC	Ethylene Catalyst
ET	Ethylene Terminal
FTA	Fault Tree Analysis
FM	Flow Meter
FRC	Flow Recorder Controller
FMECA	Failure Mode, Effect and Criticality Analysis
HP	High Pressure/Pressure Head
HDG	HAZOP Digraph
HAZOP	Hazard Operability Analysis
KRM	Knowledge based Risk Management
LG	Level Gauge glass
LA	Level Alarm
LIA	Level Indicator with Alarm
LOPA	Layer of Protection Analysis
OSS	Oxygen Shut-down System
PMI	Potential Major Accident
PHA	Process Hazards Analysis

PBT	Probability Bow-Tie
PRC	Pressure Recorder Controller
PFD	Process Flow Diagram
PIDs	Piping and Instrument Diagrams
RO	Restriction Orifice
RPT	Recipe Petri Nets
SDG	Sign Direct Graph
TRA	Temperature Recorder with Alarm
TAT	Temperature Alarm with Trip
TPN	Task Petri Net

CHAPTER 1

INTRODUCTION

1.1 Definition

HAZOP study is a systematic procedure conducted by a team of experts of different disciplines to identify and assess hazard using brainstorming discussions of deviations in operational parameters from normal/standard conditions (khan and Abbasi, 1997c). These deviations are generated by using standard guidewords. Normally, the team of experts of different disciplines will sit together to identify and assess the hazards associated with each and every process/plant component by analyzing the behaviour of process/plant component under deviation from the normal operation. Moreover, HAZOP study is applied to a continuous plant and the modification of this study can also be applied to batch plants (Kletz, 1999).

1.2 Concept

The Hazard and Operability (HAZOP) study was originated in the late **1960s** and developed as a practical method for problem identification in the process industries in the early **1970s** at the ICI, UK (Kletz, 1999). HAZOP study is one of the most common tools to accomplish hazard assessment qualitatively. It involves a detailed study of each and every part of the entire process line from start to finish with the help of 'piping and instrument diagrams' (PIDs) covering each and every vessel, conduit, valve, and other control equipment employed in the process line. In HAZOP, these PIDs are studied in relation to the operation of the process, the causes that may lead to variations in the plant operation due to human errors, process, or material failures, and the likely consequences (khan et al., 1997c). HAZOP thus takes into consideration the conditions such as temperature, pressure, creep, fatigue, etc., under which the physical parts (piping and instruments) are used, the aspects of human interaction with the piping and instruments, and the possible aberrations that may occur due to human errors, loss of process control, or material failures.

1.3 Principle

The basic principle of HAZOP technique is that hazards arise in a plant due to deviations from normal behavior. In HAZOP technique, process piping and instrument diagrams (PIDs) are examined systematically by a group of experts (HAZOP team), and the abnormal causes and adverse consequences for all possible deviations from normal operation that could arise are found for every section of the plant, (Crowl, 1990). Thus, the potential problems in the process plant are identified. The HAZOP team is a multidisciplinary team of experts who have extensive knowledge on design, operation, and maintenance of the process plants. The HAZOP team members try to imagine ways in which hazards and operating problems might arise in a process plant. To cover all the possible malfunctions in the plant, the imagination of the HAZOP study team members is guided in a systematic way using a set of 'guide words' for generating the process variable deviations to be considered in the HAZOP study, (Khan and Abbasi, 1997c).

1.4 Guide words

The sets of guide words that are often used are NONE, MORE OF, LESS OF, PART OF, and MORE THAN (H.Leone, 1996). When these guide words are applied to the process variables in each line or unit of the plant, we get the corresponding process variable deviation to be considered in the HAZOP study. A list of guide words with their meaning and the parameters where they can be applied is presented in Table 1.

Table 1.1: The list of guide words and their meaning

Guide words	Meaning	Applicable to following parameters
NO/NONE	Complete negation to design intention	Flow rate, level, capacity
MORE	Quantitative increase temperature, level	Flow rate, pressure
LESS	Quantitative decrease	Flow rate, capacity, pressure, temperature, level
PART OF	Only part of intention is fulfilled	Concentration, signal
AS WELL AS	In addition to design intention, something else occurs	Concentration, signal
REVERSE	Logical opposition of design intention occurs	Signal, flow
OTHER THAN	Complete substitution	Concentration, signal

1.5 HAZOP study procedure

From the flow diagram Figure 1.1, it can be seen that the technique is very much an iterative process, applying in a structured and systematic way the relevant guidewords in order to identify the potential problems (Kletz, 1999 and Khan et al., 1997c). The HAZOP study procedure consists of four main activities (steps):

1. Selection of study team and procurement of relevant information
2. Brainstorming discussion
3. Preparation of uncleared points, and
4. Report writing

Steps 2 and 3 are the most crucial since the total study duration is depend on these steps as well as effectiveness and reliability of the results. The report writing step is again a dependent activity on the second and third step.

1.6 HAZOP study methodology

In simple terms, the HAZOP study process involves applying in a systematic way all relevant Guidewords to the plant in question in an effort to uncover potential problems (Kletz, 1999). The results are recorded in columnar format under the following headings:

Table 1.2: Columnar format of HAZOP study

GUIDEWORDS	DEVIATION	CAUSE	CONSEQUENCE	SAFEGUARDS	RECOMMENDATION

1.7 Requirements

1.7.1 **Assemble the data**: All relevant documentation should be collected beforehand (Crowl, 1990 and Khan 1997c). Typically this might consist of:

- A Process Flow Diagram.
- A comprehensive Process Description containing operating parameters, flow rates, volumes, etc., as well as a brief summary of how each plant item functions.

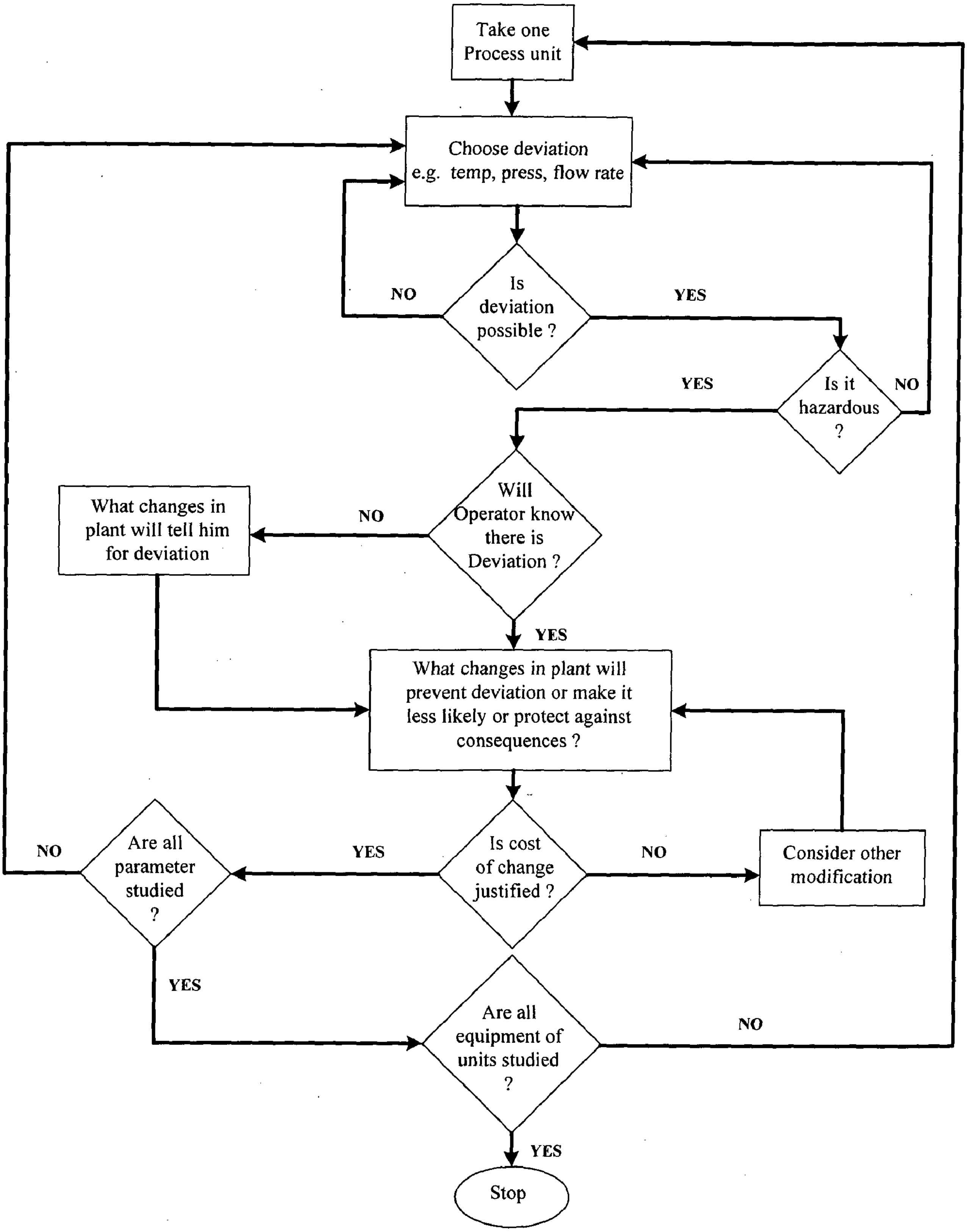

Figure 1.1: Procedure of HAZOP technique (Khan and Abbasi, 1997)

- P&IDs.
- Cause & Effect Charts setting out how control and trip systems operate.
- Details of vendor packages if available.
- Plant layout diagrams.
- Line arrangement either from isometrics or model if required.
- Pressure relief valve design data and design criteria.

1.7.2 **Understand the subject**: It is necessary to gain a good understanding of how the plant is meant to operate, by studying the assembled data. A proper note should be made during the course of the study. Without a reasonable understanding of how the plant functions, it will be impossible to plan a sensible study strategy, decide how long the review is likely to take, or who needs to be included in the study team.

1.7.3 **Subdivide the plant and plan the sequence**: If required, that subdivisions of the plant may be considered since it may be too burdensome for the study team to deal with all aspects and operations in the process simultaneously. Therefore, it must be split into manageable sections. Also, the sequence in which these sections are studied is important.

1.7.4 **Mark the drawings:** When the study strategy has been decided, a recording table is made where the plant items encompassed by each table should be marked in distinctive and separate colours, with the table numbers alongside in the same colour. Lines should be paralleled, and equipment and vessels outlined in the chosen colour.

1.7.5 **Devise a list of appropriate Guidewords:** Having completed the work above, it will be a simple matter to formulate a comprehensive list of the Guidewords required to cover all aspects of the process to be studied. Some companies, because most of the plant that they operate is of a similar nature, will have a standard set of Guidewords. Such a list should be checked to ensure that it is covers all aspects of the system to be studied.

1.7.6 **Prepare a timetable:** Timetable should be maintained for showing what needs to be accomplished at each study meeting. The speed of progress depends upon the complexity of the plant as well as the experience of the team.

1.8 Factors affecting the effectiveness and efficiency of HAZOP study

- Lack of experience of team members and leader
- Inappropriate team selection
- Incorrect scope of study
- Repetitious work
- Inadequate/inaccurate information
- Management shortcoming
- Poor loss prevention practice
- Shortage of technical information
- Lack of interest
- The ultimate limitation (human error, wrong documentation etc.)

1.9 Objectives of thesis

1. To present a comprehensive and literature review about HAZOP study and its variation

2. To carry out a HAZOP study in EO section of MEG plant and present the HAZOP study report

3. To suggest the preventive corrective action based on the HAZOP study result

4. To highlight the advantages and importance of HAZOP study

5. To give the future recommendations based on the HAZOP study report

1.10 Scope of thesis work

The scope of thesis work is to carry out the HAZOP study in EO section of the MEG plant at RIL, Hazira. EO is a hazardous material in terms of toxicity, flammability in air and chemically unstable, it can be handled and stored with safety provided appropriate precaution observed. The HAZOP study has been carried out to identify the potential hazards by finding out all the possible causes & the adverse consequences and preventive corrective measure are also implemented to safeguard the process units from future accident in EO plant.

CHAPTER 2

LITERATURE REVIEW

Since HAZOP study is vast and has ongoing research, significant literature is available for safety in the chemical plants against hazard. Some of the important papers which discuss advantages, methodology and application with their disadvantages and limitations are summarized below:

2.1. Khan et al. (1997a), has proposed the optimal and effective HAZOP (optHAZOP) which signifies the application of hazard study in such a way that the duration of the study should be optimum. Most of the hazards should be identified and assessed, better efficiency, good reliability of results, and the time of applicability should be such that the recommendations made by the study can be followed easily and economically. He discovered that the optHAZOP study procedure is same as a HAZOP study procedure that uses an expert knowledge base (henceforth called the information base). This information base is a large collection of facts, rules and information regarding various components of process plant. Along with the use of information it also follows some basic recommendations to give effective and reliable results.

Information base

The information base is an expert knowledge base consisting of information for process deviations, their causes, and their immediate consequences for various components (process/equipment/pipeline, etc.). The information regarding various aspects of the process plant is developed based on past experience, experimental study and the operational study.

Time of applicability

The best time for HAZOP study is just after the basic design. As the basic design is the final step of plant/process development (start of fabrication) and it can be executed only when all relevant information regarding the chemicals, process equipment and operating conditions has been made available.

Information required

As the HAZOP study is based on the brainstorming discussion of the available information regarding process, material and equipment used in the process, all the relevant information needed for the study should be collected before starting the HAZOP study. The total information needed for the HAZOP study can be characterized in three main groups namely - chemicals, process equipment, and off-and-on-site information.

2.2. Mushtaq and Chung (2000), were working on a project regarding about HAZOP procedure for batch processes in pipeless plants. According to them, the basic idea of a pipeless batch plant is to move the process vessel between fixed stations for mixing, separation and other activities. They made an arrangement of many units, such as movable reactors and other functional stations, which work cooperatively by avoiding collision or conflict. The elimination of their pipe work for the transfer of material offers a great flexibility for change, and allows a company to respond quickly to market demands and technological advances. Other benefits include reduced product loss, ease of cleaning, and reduced inventories. However, the flexibility that the pipeless plant offers, which allows changes to be made quickly and easily introduces new hazards. They also suggest that changes always need to be considered carefully before being implemented, as a change in a small section of a system could affect the safety of the whole system.

2.3. Venkatasubramanian et al. (2000), have proposed manual hazards analysis techniques and methodologies that can be leveraged by an intelligent systems approach to reduce the time, effort and cost involved, and to improve the consistency and thoroughness of the analysis. Such systems are not meant to replace the human team but to assist them in improving the overall efficiency and productivity of the team. Of the various PHA (Process Hazards Analysis) methodologies, the HAZOP analysis is the prime one for automation using intelligent systems due to its wide spread usage in the process industry and its systematic and comprehensive nature. The iTOPS, HAZOPexpert and Batch HAZOPexpert intelligent systems developed at Purdue University are now well beyond proof of concept and are ready for industrial applications and commercial exploitation.

HAZOPExpert models

HAZOPExpert is a model-based, object-oriented, intelligent system for automating HAZOP analysis in the continuous processes. The results of a HAZOP study may vary from plant to

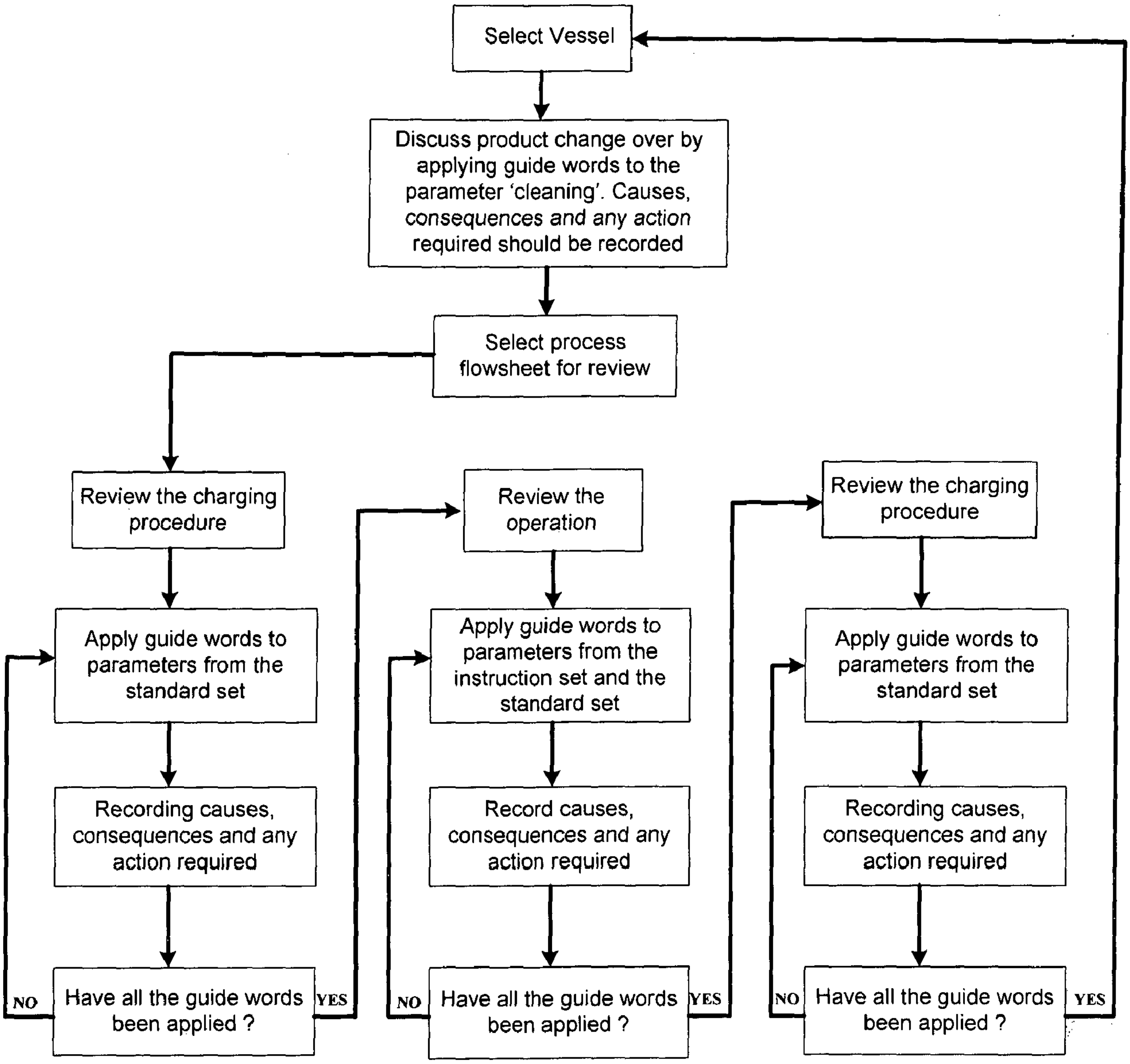

Figure 2.1: Flow diagram showing the HAZOP procedure for a batch process (Mushtaq and Chung, 2000)

plant; the model approach is systematic and logical, with many aspects of the analysis being the same and routine for different process flowsheets. Hence, focusing on these routine cause and effect analyses by developing generic models which can be used in a wide variety of flowsheets, thus making the expert system process-independent. It is also recognized that the process-specific components of knowledge, such as the process material properties and process P&IDs, have to be flexibly integrated with the generic models in an appropriate manner.

HAZOP-Digraph (HDG) models

The initial version of HAZOPExpert was modified into a HAZOP-Digraph (HDG) model-based framework to facilitate model development and refinement by the users as well as to tackle more complex process configurations. The HDG models are modified, signed, directed graphs (SDG) developed for the purpose of hazard identification. Hazard- Digraphs provide the infrastructure for graphically representing the causal models of chemical process systems in a transparent manner to the user. The knowledge about finding the abnormal causes and the adverse consequences are incorporated into these digraphs. The HDG models of the process units are used for propagating the process variable deviations and for finding abnormal causes and adverse consequences by interacting with the process specific knowledge. The HDG models are developed in a context-independent manner so that they are applicable to a wide variety of flow sheets. The user can build a new HDG model or add more knowledge to the existing HDG model using the graphical HDG model developer.

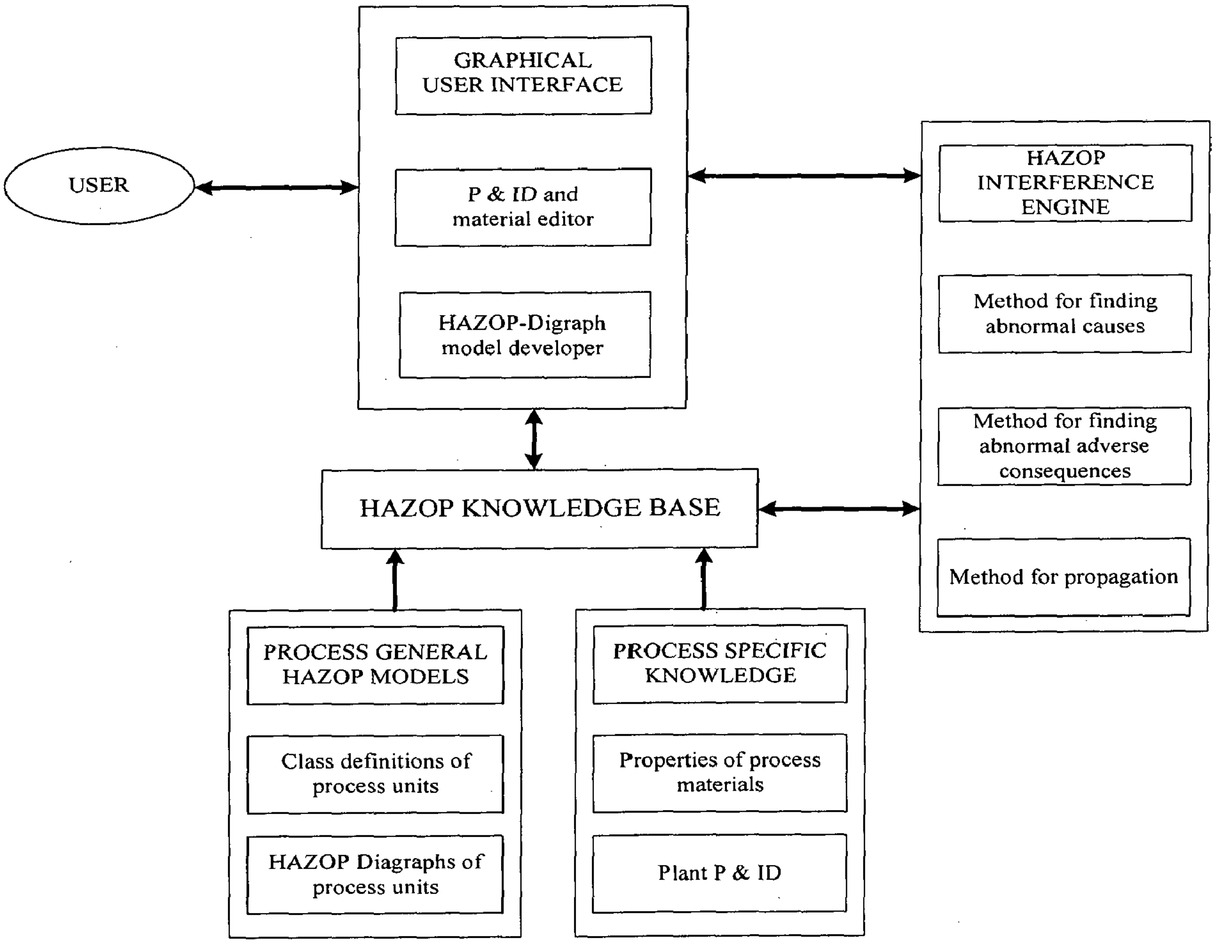

Figure 2.2: Architecture of HAZOPExpert (Venkatasubramanian et al., 2000)

2.4. Vaidhyanathan & Venkatasubramanian (1995), were working on digraphs model which have been used for representing causal models of chemical process systems. This digraph models were used in computer aided synthesis of fault trees and in process fault diagnosis. A digraph consists of nodes connected by directed edges. The nodes represent process variables and a directed edge connecting two nodes indicates the influence of the deviation in the first process variable on the second process variable. The process variables, and hence the digraph nodes, have the values +, 0, and - indicating whether the status of the process variable is high, normal, or low (compared to some normal value) and the directed edges connecting the digraph nodes can have the gains + or - indicating the direction of influence of one process variable deviation on another.

Vaidhyanathan et al. (2000) developed a HDG models of the process units in an object-oriented framework and were represented graphically in HAZOPExpert. The user can easily add new HDG models of process units or add more HAZOP knowledge to existing HDGs by using the HDG model developer in HAZOPExpert. These HDG models were stored in the HAZOP model library of the process units in HAZOPExpert and can be used in a wide variety of process flowsheets. HAZOPExpert has been implemented in an object-oriented framework using the expert system shell G2. Further research is also being pursued to include quantitative information in HAZOPExpert for filtering the HAZOP results and for hazard ranking of the adverse consequences identified by HAZOPExpert.

2.5. Bartolozzi et al. (2000), has proposed qualitative models of equipment units and their use in automatic HAZOP analysis since HAZOP analysis is mainly based on qualitative reasoning and the equipment models is essentially qualitative. In fact, qualitative unit models have to contain the knowledge to perform the HAZOP analysis of a chemical plant. In other words, equipment units must be considered from the point of view of their functionality, both in the normal and abnormal states. In particular, qualitative models must contain the information needed to propagate variable deviations from one unit to the previous one or to the next one and to evaluate the effects of operative faults and failures.

Bartolozzi et al. (2000), build the model library including the most common chemical units: this allows analyzing every plant configuration. The models that Bartolozzi et al.(2000) developed is similar to those proposed by Lees et al. (1997) to simulate the propagation of faults in chemical process plants, consisting of mini fault trees. This models of equipment units included in the library were set up specifically for the automatic HAZOP analysis;

separate types of qualitative models, named "cause models", "HAZOP models", and "consequence models", is also introduced in order to take into account the different phases of the HAZOP analysis and the distinct mental model used by the analysts during the methodical application of the guide words of the HAZOP analysis to the main variables of the plant units.

2.6. Heino et al. (1994), developed a KRM (Knowledge-based Risk Management) which is a general framework for safety and quality oriented process modeling and monitoring. It connects an object oriented model of the plant behavior to a set of databases for the conditional retrieval of relevant information. This framework has many applications, for example, in quality management, acquisition of experience, detailed diagnosis, 'living' safety analysis, etc.

KRM is a software system for documenting, handling and utilizing qualitative safety information. It consists of separate modules meant for various user categories in an industrial organization. The modules are integrated with each other and it is possible to run them in the same environment on the same physical machine. The structure of the system is presented in Figure 2.3.

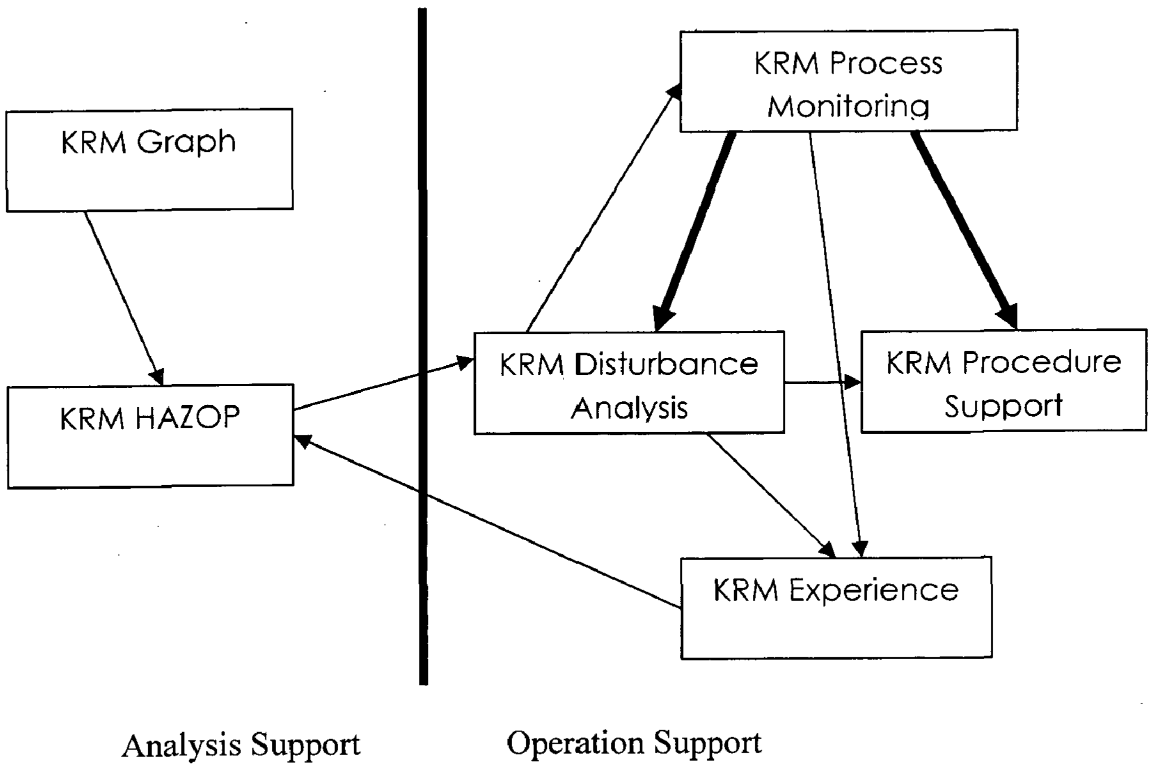

Figure 2.3: The modules of KRM and the flow information between the modules (Heino et al., 1994)

The important goal of the KRM system is to facilitate the exchange of information between process designers and operating personnel. Currently, the usual practice in process industry is that safety documentation created in investigations during the design phase is available to the operating personnel only in the form of a folder with no well-organized updating. Feedback from plant operation to the designers is not usually organized well either. KRM is able to contribute to the flow of information between different groups in the plant. KRM has two main objectives: analysis support and operator support. Deviations and their potential causes and consequences are the basic concepts in the knowledge-based operator support methodology of KRM. An advantage of KRMHAZOP is that it creates a structured database of HAZOP results.

2.7. Khan & Abbasi (2000), proposed a software tool called EXPERTOP for conducting a HAZOP study more effectively. The object-oriented architecture of EXPERTOP consists of: (a) knowledge base, (b) inference engine and (c) graphical user interface, as shown in Figure 2.4.

(a) ***Knowledge-base module***

Knowledge base is a collection of information set up in a pre-defined format which can be retrieved and used for HAZOP study. The knowledge base is created in two segments in order to cover all the equipment, process/ambient conditions, and typical problems that have been encountered in various industries. The knowledge base is developed in terms of rule network, where equipment is specified as the derived objects of the main equipment object class. These derived objects (different equipment) have various sub objects, functions and attributes attached to them. The knowledge base has the following four main features: (i) general process causes; (ii) general process consequences; (iii) process specific causes; and (iv) process specific consequences.

(b) ***Inference engine module***

The inference engine is a type of controller, which acts as a manager of the knowledge base, according to the user intention and requirements of the problem under study. The user interface enables the user to easily and swiftly interact with various modules of the software. It also provides on-line help for each option.

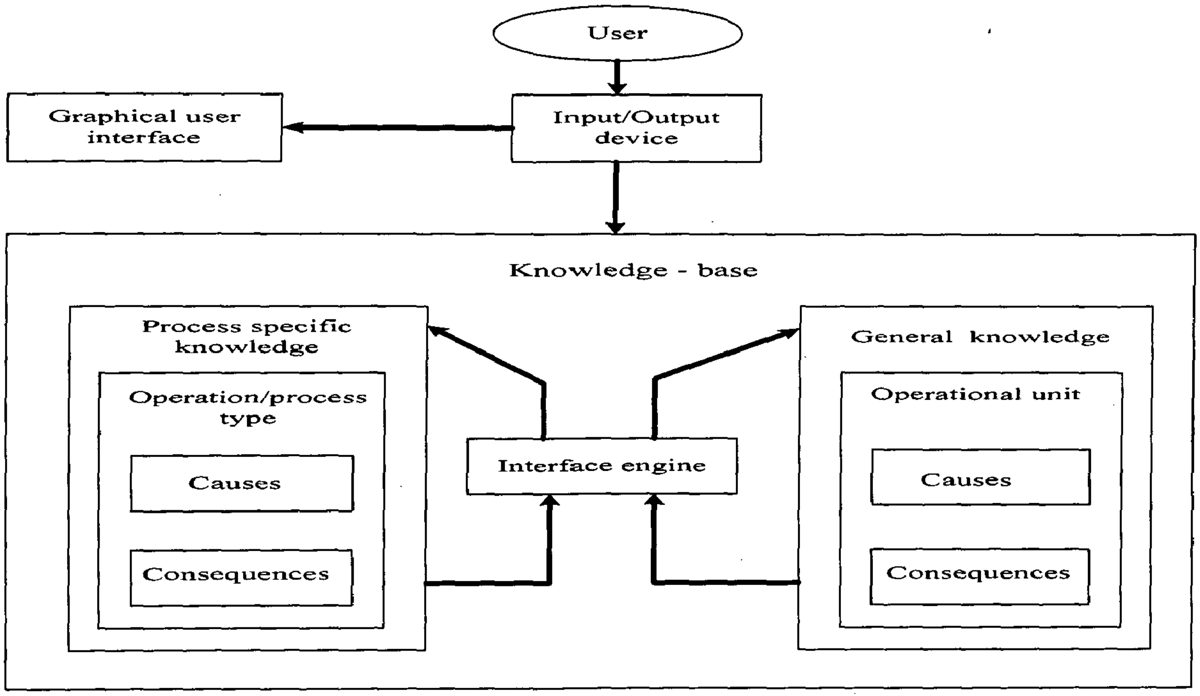

Figure 2.4: Architecture of EXPERTOP (Khan & Abbasi, 2000)

(c) ***Graphical user interface module***

This option provides a mode of external interface between the knowledge and the user. This option enables the user to draw industrial flow diagrams (process flow diagrams). It further extends the facility to select particular equipment from the process flow diagram (drawn earlier by using various industrial specific icons) with associated parameters and interacts with the knowledge base to carry out the HAZOP study. This option also provides a means of modification or upgradation of knowledge base according to the need and experience of the expert user.

2.8. Venkatasubramanian & Srinivasan (1996), developed a Petri net – digraph model Figure 2.6, for automating HAZOP analysis of batch chemical processes, called Batch HAZOPExpert, which has been implemented in the object-oriented architecture of Gensym's real-time expert system G2. From the plant description, the product recipe in the form of tasks and subtasks and process material properties, Batch HAZOPExpert can automatically perform HAZOP analysis for the plant maloperation and process variable deviation scenarios generated by the user.

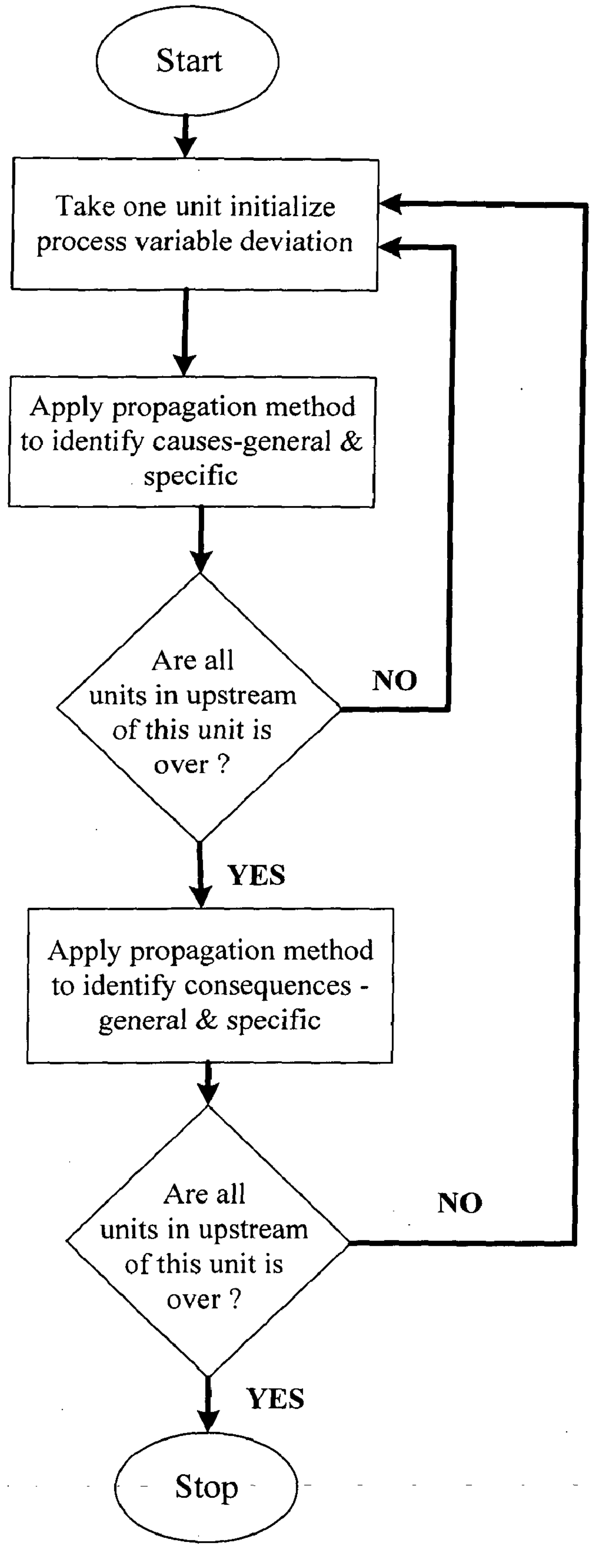

Figure 2.5: The inference engine for the knowledge base (Khan & Abbasi, 2000)

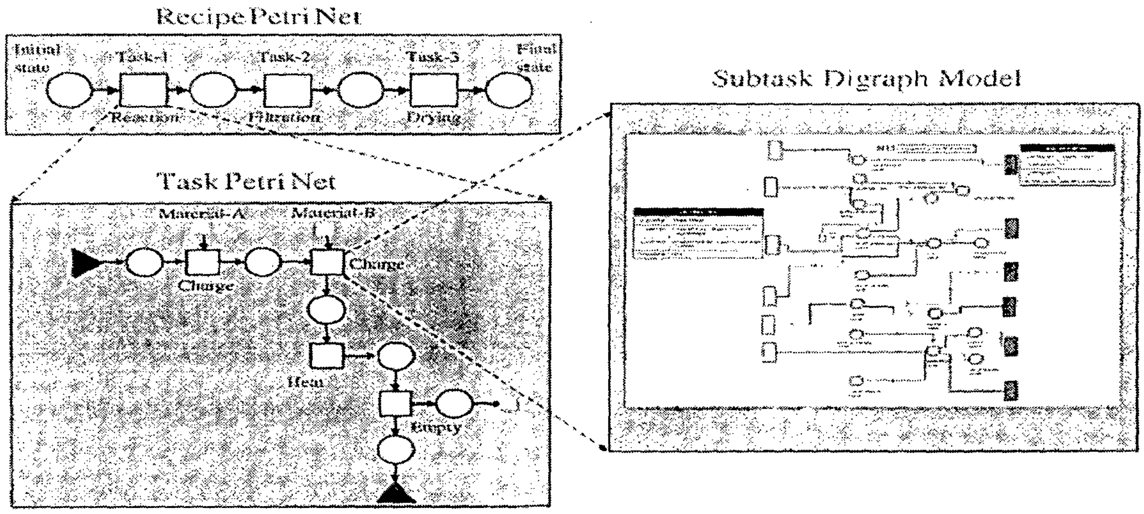

Figure 2.6: Hierarchical petri-net-based knowledge (Venkatasubramanian et al., 2000)

2.9. Khan & Abasi (1997b), developed a Mathematical model for HAZOP study time estimation. The total duration of HAZOP study were modeled as a combination of four different time steps (these four steps are further functions of many variables and sub-time steps.) as:

1) Preparation time

Firstly, the HAZOP team leader should plan and decide the schedule, duration of review meetings, and arrange the essential documents such as PIDs (process instrumentation diagrams), PFDs (process flow diagrams), plot plans, operating procedure, etc. Subsequently, the team leader has to decide the beginning point (scope of the study) and boundaries of study. A greater number of PIDs means more information collection, and identification of more unclear points, which requires a large preparation time. Hence, the preparation time is defined as a direct function of the number of PIDs and the degree of complexity of PIDs, and can be represented as

$$Tprep = 1.5(X_1 + 2*X_2 + 3*X_3 + 4*X_4) \qquad (2.9.1)$$

Where, X_1, X_2, X_3 & X_4, are number of PIDs of different class of complexity.

2) Study or meeting time

Study or meeting time is the duration of brainstorming discussion, which is the most important and main activity of HAZOP study. Hence, it is the main contributor to the total HAZOP study duration. This time step (duration of meeting time) depends upon three important parameters, namely: (a) effectiveness or skill of the team leader, (b) number of PIDs to be studied, and (c) the complexity of PIDs. The combination of different parameters for HAZOP meeting time estimation is represented as

$$T_s = (L_{eff} * f(Ci*Xi^{pi}) \qquad (2.9.2)$$

Where, L_{eff} = skill factor of team leader

Ci = the coefficient for different degree of complexity

pi = the effect of degree of complexity on number of PIDs (power factor)

Xi = the number of PIDs of each complexity

The expanded form of the meeting time function (total duration of brainstorming discussion) can be represented as

$$T = K*L_{eff}*(C_1*X + C_2*X + C_3*X + C_4*X) \qquad (2.9.3)$$

Where, K is a proportionality constant and equals to one for chemical process industries and higher than one (1.5) for petrochemical industries.

3) Report writing duration

A written report of the HAZOP study is the out-put of the team work. The report should be clear, concise so that one should understand what had been highlighted in the meeting and what are the outcomes of the study. The report should also consist of recommendations to eliminate or to control the problems identified by the study team. The time taken in writing a rough draft of report has been approximated as 45% of the preparation time. Hence it should be a function of total preparation time. This duration is only for the first draft of report preparation.

$$T\,report = 0.45 * Tprep \qquad (2.9.4)$$

4) Delay time

Every team member has his own responding time to understanding the problem and to propose the recommendations, there should be some provision to estimate the excess time to take care of the elapsed time in unforeseen activities and individuals responding time. This excess time has been defined as delay. This delay time includes the time lapsed due to non-availability of members, documents or any other essential items, and individuals responding time. The delay time can be categorized in two main groups as (1) delay in schedule of preparation and discussion, and (2) final report writing.

The first delay '1' signifies and quantifies the duration due to lack of any activity, information and responding time of individuals. This delay is estimated as 15% of the preparation time.

$$T_{delay1} = 0.15*T_{prep} \tag{2.9.5}$$

The second delay '2' is estimated to take into account the preparation of final report from rough draft. This is estimated as 25% of the draft report preparation time.

$$T_{delay2} = 0.25*T_{report} \tag{2.9.6}$$

The total delay is the sum of these two delays,

$$T_{delay} = T_{delay1} + T_{delay2} \tag{2.9.7}$$

Finally, the total HAZOP study time in hours is the sum of all available time (meeting, preparation, draft report and delay) and can be written as

$$T_{HAZOP} = T_s + T_{prep} + T_{report} + T_{delay} \tag{2.9.8}$$

The man-hours requirement for the HAZOP study can be estimated as

$$T_{man-hour} = T_{HAZOP} * \textit{number of team members} \tag{2.9.9}$$

The total duration of comprehensive HAZOP study in terms of weeks can be estimated as

$$T_{Weeks} = (1+1/W)*T_{HAZOP}/T_W \tag{2.9.10}$$

Where, W represents specifies frequency of rest and T_{weeks} represents hours per week assigned for study (number of hours per day **x** number of days per week).

2.10. Vaidhyanathan & Venkatasubramanian (1996), proposed a semi-quantitative reasoning methodology for filtering and ranking of HAZOP study results by using a HAZOPExpert. This filtering approach combines the qualitative digraph-based HAZOP models and the quantitative knowledge to eliminate the unrealizable consequences. A semi-quantitative methodology is based on some factors such as:

Design thresholds

During the design of the process units, certain safety thresholds have to be satisfied for the design specifications as compared to the operations specifications. The HAZOP team performing the analysis will compare the design and operating specifications of the process units with the safety thresholds, and will identify hazards such as, 'process equipment damage, fracture, major leak and loss of containment due to high pressure or high temperature' only when these safety thresholds are violated.

Fire hazard thresholds

In order to decide whether a high temperature deviation in a process unit will lead to fire/explosion hazards due to the presence of flammable process materials, a fire hazard threshold' is defined in HAZOPExpert. The 'fire hazard threshold' is the ratio of the auto-ignition temperature of a process material and the operating temperature of a process unit.

Toxicity hazards

Hazards also occur in process plants due to the loss of containment of toxic process materials. Thus, whenever loss of containment from a process unit is found as a consequence during HAZOP analysis, HAZOPExpert checks to find if there were any toxic process materials present in that process unit and the health hazards of the process materials and the occupational safety violations due to their release are determined from the process material properties. These hazards are then recorded as part of the HAZOPExpert's results.

Adequacy of protective devices

During HAZOP analysis, it is essential to check if the protective devices of the various process units are adequately designed. For example, if the set point pressure of the relief valve for a process unit is set equal to or higher than the design pressure of the vessel, then in the case of a high pressure deviation 'the unit will be damaged first protecting the relief valve'. In order to detect these design errors, whenever there is a deviation in a process variable of a process unit which is protected by a device like a relief valve or controller, the HAZOPExpert system checks if the set point of the protective device is set lower than the design specification of the process unit to ensure that there is adequate protection.

Resolving ambiguity using quantitative knowledge

The problem of ambiguity is inherent in qualitative causal reasoning. This is due to the fact that the result of adding qualitative 'high' and qualitative 'low' can be 'high', 'low' or 'normal'. Strategies such as using quantitative and design purpose information, and order of magnitude information have been proposed to tackle this problem. In HAZOPExpert, the quantitative operating specifications of the process units can be used to resolve ambiguities which arise during propagation of process variable deviations using the qualitative HDG models of the units

2.11. Khan and Abbasi (1997c), developed a TOPHAZOP as a knowledge-based software tool for conducting HAZOP in a rapid and efficient yet inexpensive manner. This TOPHAZOP consists of the following main modules: knowledge-base, inference engine, and user interface. The object-oriented architecture (OOA) of TOPHAZOP is presented in Figure below:

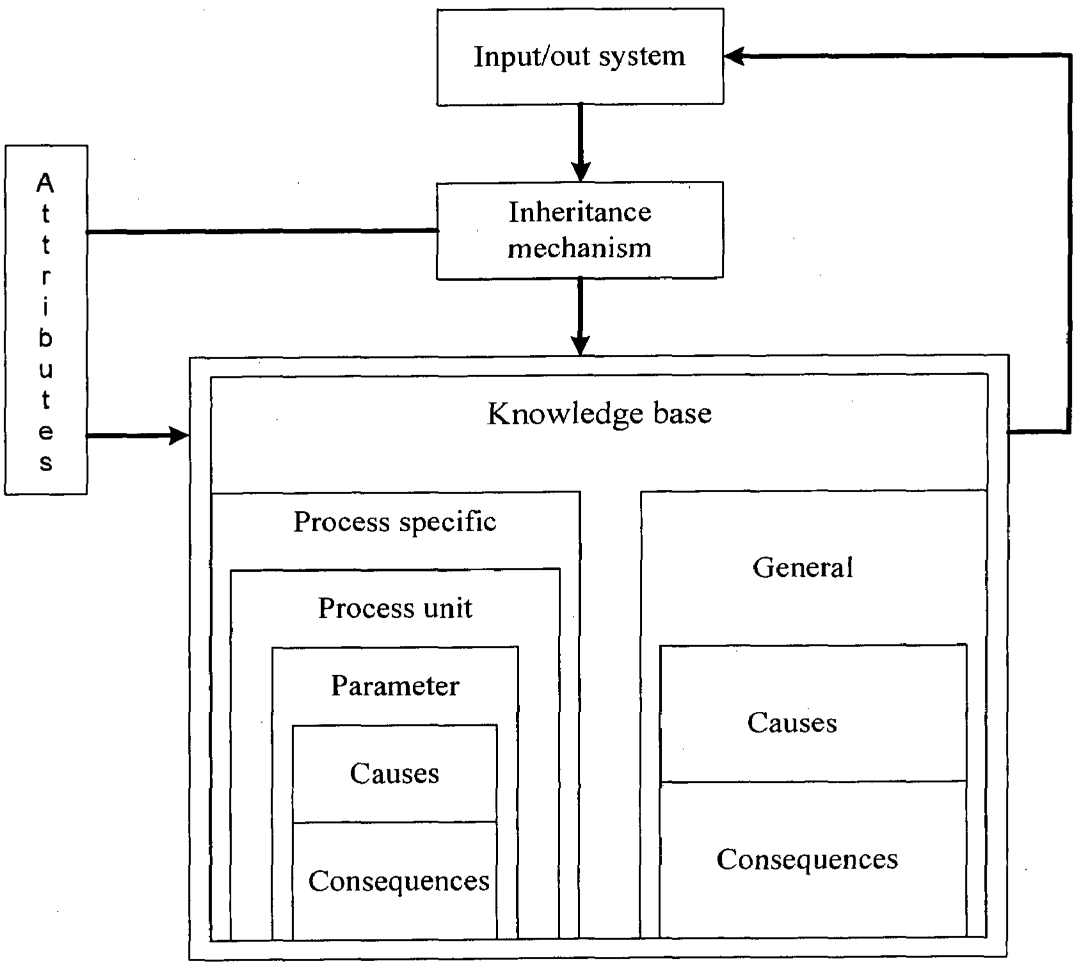

Figure 2.7: The object oriented architecture of TOPHAZOP (Khan and Abbasi, 1997)

Knowledge-Base

Knowledge-base is a collection of information set up in a pre-defined format which can be retrieved and used for HAZOP study. The knowledge-base is created in two segments in order to cover all the equipment, process/ambient conditions, and typical problems that have been encountered in various industries. The knowledge-base is developed in terms of rule networks with equipment specified as the derived objects of the main equipment object class. These derived objects (different equipment) have various sub-objects, functions and attributes attached to them. The architectural and message flow diagram of the knowledge-base is shown in figure below. The complete knowledge-base has been developed using a PC expert shell (G2 Gymsum expert shell). The knowledge-base has the following four main features: general process causes, general process consequences, process-specific causes and process-specific consequences.

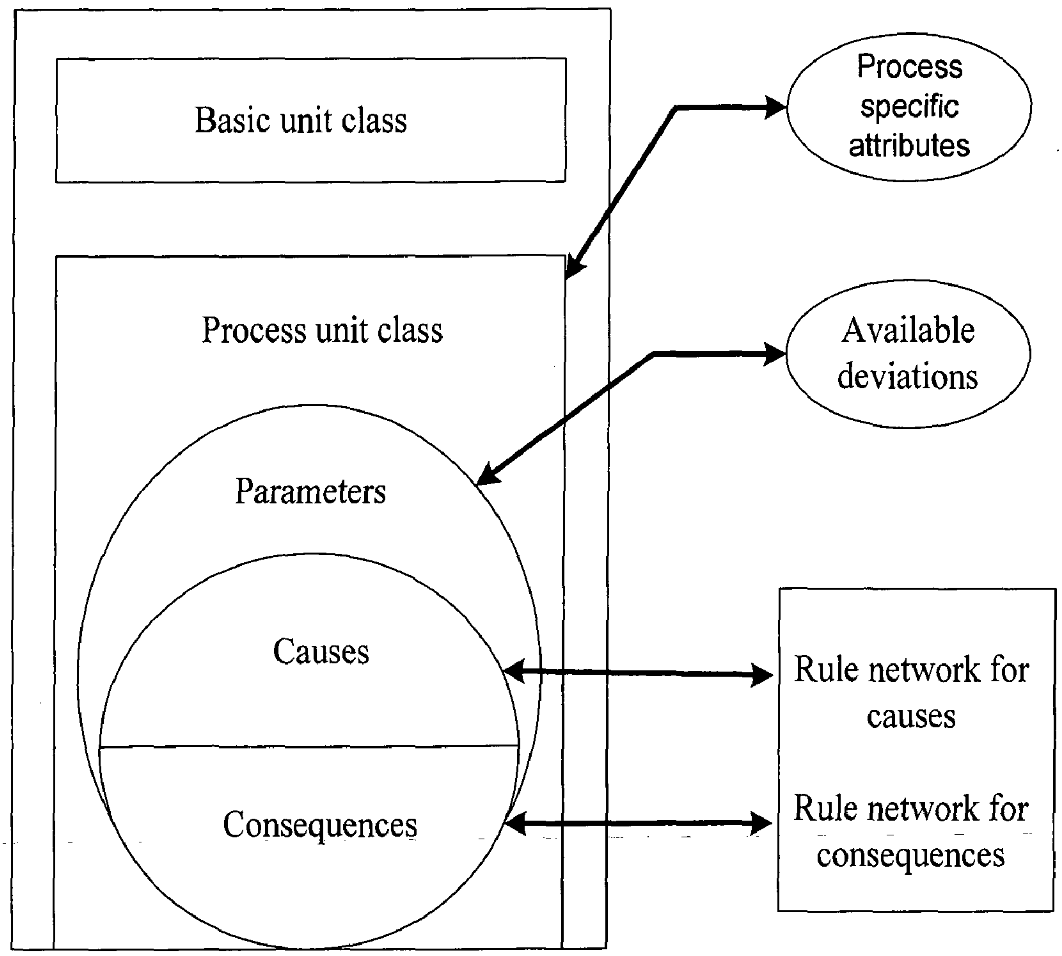

Figure 2.8: The architecture of knowledge base (Khan and Abbasi, 1997)

User interface

This option provides a mode of external interface between the knowledge and the user. This option enables the user to choose particular equipment from the set of equipment and associated parameters and interacts with the knowledge-base to carry out the HAZOP study. This option also provides a means of modification or upgrading of the knowledge-base according to the need and experience of the expert user. The user interface has two options: analysis and modification. Choosing one of these options will link the user to the appropriate module of knowledge and on keying in the necessary information the results of the HAZOP study will be obtained. The user has the liberty to check, and modify the knowledge-base or add new information to it. The output of TOPHAZOP is in the form of normal HAZOP reports and can be directly used in the presentation of the HAZOP study.

Remarks

The TOPHAZOP proposed by Khan et al. [15] is a knowledge-based user-friendly software for conducting HAZOP studies in a comprehensive, effective, and efficient manner within a short span of time. TOPHAZOP overcomes several major limitations (time, effort, repetitious work, etc.) of the existing HAZOP procedure. The software has an in-built knowledge-base which is extensive and dynamic. It incorporates process units, and works out numerous modes of failure for certain input operational conditions. It drastically minimizes the need of expert time. The knowledge-base has been developed in two segments: process-general knowledge, and process-specific knowledge. The process-specific knowledge segment handles information specific to a particular process unit in a particular operation, whereas the process-general knowledge segments handle general information about process units.

Further advancements are possible in the TOPHAZOP system in terms of incorporating: more complex process units, more efficient search methods, ability to handle more complex process situations such as reverse flow, recycle loop, purging, etc., and user interactive flow charting options.

Table 2.1: Summary of Literature Review

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL-OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
1.	**Khan et al. (1997a)** OptHAZOP- an effective and Optimum approach for HAZOP study	OptHAZOP technique for optimization of convention HAZOP study	Reduce the mutual execution load of experts by a half Better control strategies Produce more effective, efficient and reliable results	Requires past operation data for process monitoring Requires high level of expertise & substantial time commitment	Any type of industry such as refinery, Chemical, Petrochemical, Pharmaceuticals, Metallurgical etc.	Lack of past data may lead to incomplete process performance Human mistake may unable to recognize some simple hazards
2.	**Mushtaq and Chung (2000)** A systematic HAZOP procedure for batch processes, and its application to pipeless plants	A formalized approach to applying the HAZOP methodology to batch processes	Easy movement of the process vessel between fixed stations as mixing, separation and other activities Reduce product loss, ease of cleaning, and reduce inventories Offers great flexibility in change, and allows a company to respond quickly to market demands & technological advances	Time consuming Require special attention as they involve the connection and disconnection of pipework Require a computer support tool to guide and document the study	Pipeless plant (Batch process)	Defects in the design or construction of the plant may cause improper performance

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL - OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
3.	**Vaidhyanathan et al. (2000)** Intelligent systems for HAZOP analysis of complex process plants	PHA review Inherently safer design Real time fault diagnosis	Improve the reliability of HAZOP analysis results Filtering out consequence with low possibility Improve the quality of the analyses and reduce the time, effort & cost evolved	Requires high level of expertise Requires further quantification, including design modification and hazard minimization	All Chemical, Pharmaceutical and Specialty chemical companies	Large volume of data regarding process and equipment are to be keyed , in each time for analyzing a single deviation The acquisition of knowledge is limited
4.	**Vaidhyanathan and Venkatasubramanian (1995)** Digraph-based models for automated HAZOP analysis	A framework using diagraph-based model HAZOPExpert, implemented in an object-oriented architecture	HDG model add more knowledge to the existing models of the process units HAZOPExpert can able to find more causes and consequences than HAZOP team Improve effectively in terms of speed and reliability	Requires time and effort for risk assessment Systematically and critically examination of PIDs is required High computational load	Batch and Continuous process	Can not detect hazard fully , it needs quantitative analysis

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL - OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
5.	**Bartolozzi et al. (2000)** Qualitative models of equipment units and their use in automatic HAZOP analysis	Qualitative model in the system for HAZOP analysis	Better control strategies Reduce the analysis work and increase its reliability Simple spreadsheet can be used for producing std final report	Requires a large amount of work by the group of experts and time consuming	The models are conceived both for continuous and batch plants	Low success rate than mathematical model Depend on past operation data for process monitoring
6.	**Heino et al. (1994)** Monitoring and analysis of hazards using HAZOP-based plant safety model	KRM for documentation, handling and safety information Safety & reliability analyses	KRM system facilitate the exchange of information b/w process designer and operating personnel KRM-HAZOP creates a structured database of HAZOP results Reduce the complexity of process analysis Improve quality management, and monitoring & analysis of hazards	Requires revision of safety database and updates Require special attention for detecting deviations in real time Require CAD technology as a tool for efficient documentation	Heat transfer system Batch chemical reactor in fine chemical plant Oil refinery flare gas system	More emphasis on the identification of causes of deviations rather than the effects

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL - OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
7.	**Khan, & Abbasi (1999)** Towards automation of HAZOP with a new tool EXPERTOP	EXPERTOP system for performing HAZOP studies	Lesser costs and better accuracy than conventional HAZOP studies Improve production efficiency and minimized risks Minimizes the expert time and reduces the drudgery involved in conventional HAZOP studies	Requires a large volume of data for monitoring the process Requires more time and effort Requires experience professional to utilize the software	More complex process situations such as reverse flow, recycle loop, and purging, etc	No direct avenue to study fault propagation Modification or upgradation of knowledge-base depend on experts
8.	**Vaidhyanathan et al. (1995)** Peri net- Digraph models for automating HAZOP analysis of batch process plants	Petri-net digraph models as a multi-tier framework for batch process	Digraph based models gives easy identification of hazards Minimizes difficulty in analyses Labor and time intensive process can be reduced easily by automation Eliminates human error	Can not perform in the continuous plants Require proper control and interlocks	Only applicable for batch reactor	Limited to complex process unit and subtasks

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL - OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
9.	**Khan & Abbasi (1997b)** Mathematical model for HAZOP study time estimation	Proposed model for varying capacity and complexity of the problem Freeman model proper planning and management	Proposed model is simple Models can be automated with software More reliable estimation and less time consuming Improve production efficiency and minimized risks	Requires correct time(duration) for estimation Freeman model needs modification in terms of easy application and reliable parameter Require a proper planning and availability of information	Applicable in different stages of projects (conceptual design, star up, shut down, etc.) and different industries (chloralkali, chemical, petrochemical, fertilizer, etc.)	Efficiency, accuracy, and duration of the study are direct function of team leader's skill
10.	**Vaidhyanathan et al. (1996)** A semi quantitative reasoning methodology for filtering and ranking HAZOP results in HAZOPExpert	Semi-quantitative method for filtering and identification of consequence	Eliminates the unrealizable consequence Reduce time, efforts and expense involve in HAZOP review Lower human error	Requires a large volume of data & PID's information Require a high skill & expertise in the design operation and maintenance of the plant	Complex process units such as stripper, pressure relief-valve, controller etc.	Time is limited to perform successfully

Sl. No.	PAPER AUTHOR & TITLE	MAIN METHODOL - OGY	ADVANTAGE	DISADVANTAGE	APPLICATIONS	LIMITATION
11.	**Khan & Abbasi (1997c)** TOPHAZOP: a knowledge – based software tool for conducting HAZOP in a rapid, efficient yet inexpensive manner	TOPHAZOP for optimizing HAZOP analysis	TOPHAZOP could be completed by just one engineer Significantly reducing the requirement of expert manpower, HAZOP cost as well as margins of error Cutting short the total study time by more than 45% Capable to handle more complex process units	Require high skill professional to handle the software Costly and time consuming Require systematical examination of PIDs in relation to the process condition and human factors	Applicable in more complex situations such as reverse flow recycle loop, purging etc.	Large volume of data and previous information of the process is the much for successful performance

CHAPTER 3

OVERVIEW OF MEG PLANT

3.1 MEG plant introduction

Mono Ethylene glycol (MEG) is produced by direct oxidation of Ethylene and Oxygen over a silver catalyst by a two-stage process. A block diagram of MEG plant is shown in Figure 3.1.

1. Ethylene and Oxygen are reacted to produce Ethylene Oxide (EO).
2. Ethylene oxide is hydrolyzed in presence of excess water to make Ethylene glycol.

Some DEG (Di-Ethylene Glycol) & TEG (Tri-Ethylene Glycol) are also formed. The main use of MEG is in textiles, to make polyester, as antifreeze, to manufacture nitroglycerin etc.

3.1.1 Process Description

The plant is divided into various sections based on the function. They are as follows:

3.1.1.1 ASU section:

The oxygen required for producing the ethylene oxide and ethylene glycols are produced in the air separation units. These air separation units work on the principle of cryogenic distillation. The air is sucked from atmosphere and compressed by the air compressors. This air is cooled and passed through dryers to remove moisture and carbon dioxide. This dry air enters cold box and exchanges heat with the out going products and waste nitrogen streams and goes to the cryogenic distillation columns, where in Oxygen and Nitrogen are separated. These gases are compressed in compressor and send for usage. Small stream of Liquid Oxygen and Liquid Nitrogen is also produced.

3.1.1.2 Ethylene Oxide Reaction

Ethylene from the Ethylene terminal (ET) and Oxygen produced in the Air Separation Unit are used for making Ethylene Oxide (EO). Recycle gas replenished with Ethylene and Oxygen is preheated and fed to the reactor, which is a shell and tube exchanger. Ethylene Dichloride (EDC) or Ethyl chloride can be used as inhibitor to suppress the oxidation of Ethylene to Carbon dioxide. Methane is added to the recycle gas loop as diluent. Ethylene is converted to Ethylene Oxide as per following reaction

$$C_2H_4 + \frac{1}{2} O_2 \xrightarrow[\substack{18\ Kg/cm^2.g \\ \text{Catalyst containing 14\% Ag}}]{220^oC} C_2H_4O + 24\ Kcal/gmole$$

Some CO_2 is also formed as side reaction. To remove the heat of reaction, water is passed from shell side and steam is generated which is used as heating medium in other units.

3.1.1.3 Ethylene Oxide Recovery

The gas stream from the reactor contains CO_2, acidic compounds, formaldehyde, ethylene etc. apart from EO. Acidic compounds & CO_2 are removed from the gas stream & EO is recovered in this section using absorbers & strippers.

3.1.1.4 Light ends removal & EO purification

The stream containing EO from the above section still contains light ends, which are stripped using steam. Here traces of CO_2 remaining in the stream are also removed. EO stream is further purified to remove other impurities and pure EO is sold in the market.

3.1.1.5 Ethylene Glycol reaction & dehydration

The EO - water mixture coming from EO purification section is preheated to 196° C after adjusting the EO: H_2O ratio to 8.8:1 and sent to glycol reactor in which reactions take place in liquid phase. Here 99.99% of EO is hydrolyzed in 3 minutes. Mono ethylene glycol (MEG), Di ethylene glycol (DEG) & Tri ethylene glycol (TEG) are formed as per following reactions:

$C_2H_4O + H_2O \longrightarrow CH_2OH\text{-}CH_2OH$ (MEG)

$CH_2OH\text{-}CH_2OH + C_2H_4O \longrightarrow OH\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\,CH_2OH$ (DEG)

$OH\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}OH + C_2H_4O \longrightarrow HO\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}OH$ (TEG)

The reactor product contains 87.2% water. It has to be reduced to 0.01%. It is done in a triple effect evaporator. From the third stage the concentrated glycol (22.2% water) goes to dehydrator which operates under vacuum. Here the water content is reduced to 0.01%.

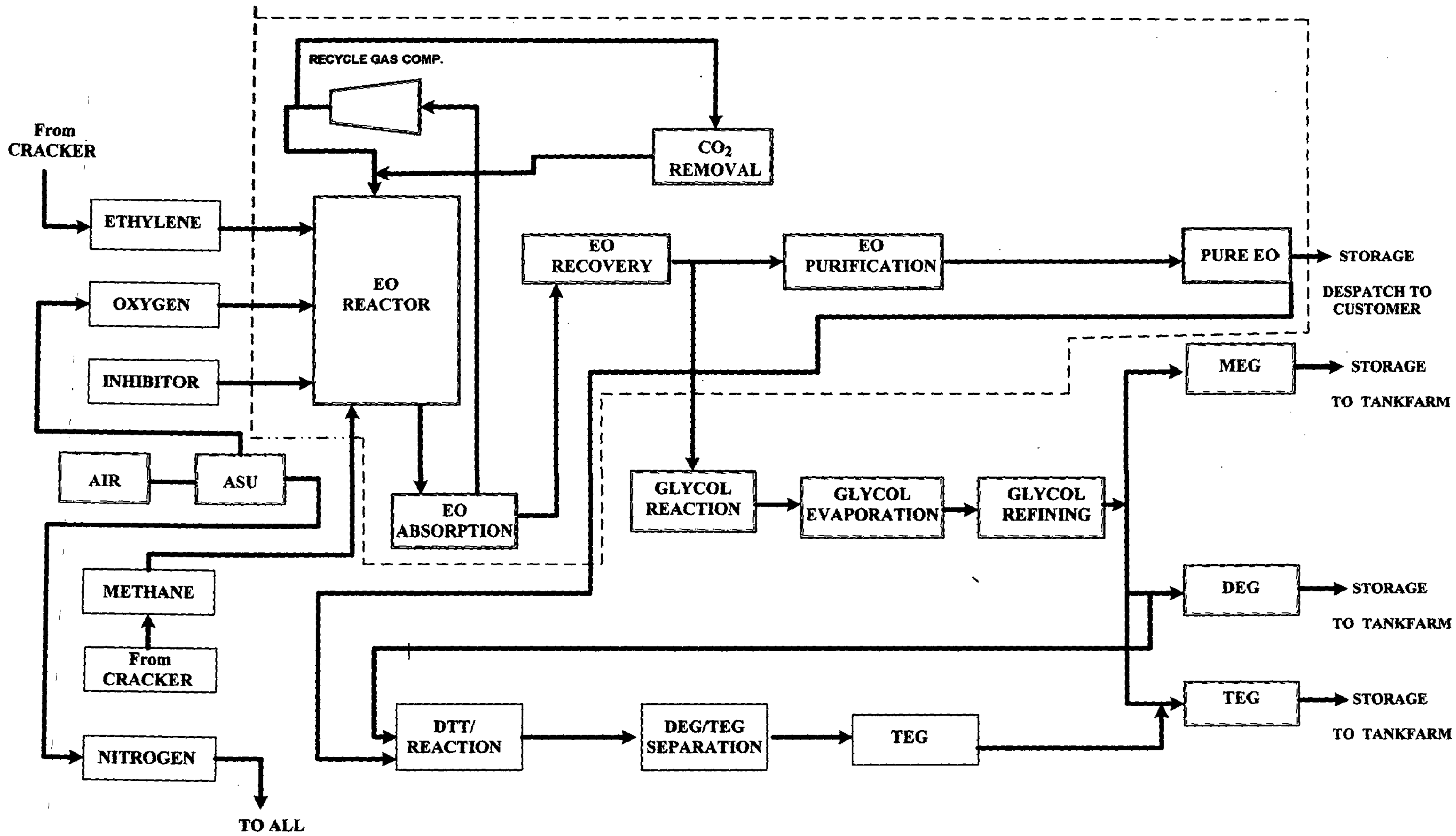

Figure 3.1: A Block Diagram of MEG Plant

3.1.1.6 Glycol purification

In this section MEG, DEG & TEG are separated in various distillation columns to obtain pure products.

3.2 DEG to TEG conversion facility (DTT)

In this section, DEG to TEG conversion has been taken place. Moreover, it is being operated as per requirement of TEG.

3.2.1 Process description

$$OH\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-})\text{-}OH + C_2H_4O \text{ --------}\rightarrow HO\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}OH + H_2O$$

(DEG) (EO) (TEG)

Pure ethylene oxide and Di-ethylene glycol are taken from storage tanks. Their respective feed pumps pump them to the mixing nozzle. The EO/DEG mixture is then heated and passed to the TEG reactor.

In the reactor the EO is completely converted to TEG and higher glycols. The reaction takes place in excess of DEG. The reactor product consists of about 70% wt DEG, 25% wt TEG and 5% wt heavier glycols. Then the reactor product is sent to the distillation section. In the first column, the DEG is recovered and recycled back. In the second column, TEG is produced as a top product and the column bottom mainly consisting of heavy glycol is sent to storage tank as Glycol residue.

CHAPTER 4

HAZOP STUDY OF EO SECTION IN A MEG PLANT

4.1 Scope of work

HAZOP study has been carried out in EO section of a MEG plant to ensure safe and environment-friendly operation. For conducting this HAZOP study in EO plant, data information of the plant is required such as the process description, safety consideration, PIDs and PFD of the plant. The facilities considered during HAZOP study in EO plant are 1) EC dosing system, 2) EO reaction, 3) EO recovery, 4) Quench loop make up, and 5) CO_2 removal section. A complete process flow diagram of EO section in MEG plant is shown in Figure 4.1.

4.2 Process description of EO plant

4.2.1 EO reaction and EO recovery:

Fresh ethylene is added to a recycling gas stream coming from the EO recovery section. O_2 is thoroughly mixed with the recycle gas in a specially designed mixing device (O_2 mixer). A sophisticated safeguarding system with an automatic O_2 cut-off and immediate N_2 purge ensures safe operation under all circumstances. The gas mixture is then preheated against reactor and moderator is added for reaction control and suppression of the oxidation of ethylene to CO_2 and H_2O. The gas enters the multi tubular reactor with the fixed bed silver containing EO catalyst. At elevated pressure (15-20 bar) and temperature (200-300°C), the following exothermic reaction takes place.

$$C_2H_4 + \frac{1}{2} O_2 \xrightarrow{Ag} C_2H_4O + 104.6 \text{ KJ/gmol, ethylene reacted}$$

The main by products formed are H_2O and CO_2 according to the reaction

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + 1322.8 \text{ KJ/gmol, ethylene reacted}$$

The heat of reaction is removed by evaporation of H_2O at the shell side of the reactor. The generated steam is used as heat medium in the glycol reaction and recovery section of the plants. Methane is added in small quantities as diluents gas for the gas phase reaction, allowing higher O_2 concentration in the gas loop as compared to N_2 as ballast gas.

The EO produced in the reactor is from the reactor product gases by absorption in water in the EO absorber. Then EO is stripped from the fat absorbent in the EO stripper. A portion of the feed ethylene is converted to CO_2 in the EO reactor. This CO_2 is further removed from the recycle gas by absorption under pressure in hot potassium carbonate solution. In order to recover the hydrocarbon gases from the carbonate absorbent solution, the absorbent is depressurized in a separate vessel. The CO2 is stripped from the potassium carbonate solution vented to the atmosphere.

4.2.2 LE removal and EO purification:

In the EO purification section, the EO-H_2O overheads from the EO stripper are condensed, then stripped in the light ends column to remove traces of CO_2 and light ends. From the incondensibles the EO is recovered in the residual EO absorber. The residual gas is recycled be means of the residual gas compressor to the EO absorber. The remaining aqueous EO is dehydrated and purified in the EO purification column. High purity EO product is stored and the low purity EO is added to the feed to the glycol reactor.

4.2.3 CO_2 removal section:

CO_2 is removed from the recycle gas by absorption in a potassium carbonate solution. The absorption of CO_2 in an alkaline is more correctly described as absorption followed by chemical reaction. At low temperature, the absorption equipment is favourable, but the slow rate of reaction is controlling. As the temperature increases, the unfavourable shift of the equipment is more than offset by increasing reaction rates. The use of hot potassium carbonate absorbent has further economic advantages. Heat exchangers to cool the absorbent are not required. In order to reduce the cooling of liquid descending the CO_2 absorber and therefore the steam requirement to heat up the same liquid in the CO_2 stripper, the gas feed to the CO_2 absorber is heated and saturated with H_2O in the CO_2 absorber feed preheater. This is achieved using the CO_2 stripper overhead as heating medium and high purity boiler feed H_2O to generate the stream. The CO_2 absorber gas feed is heated upto 85°C while the CO_2 stripper overhead is cooled to 91°C.

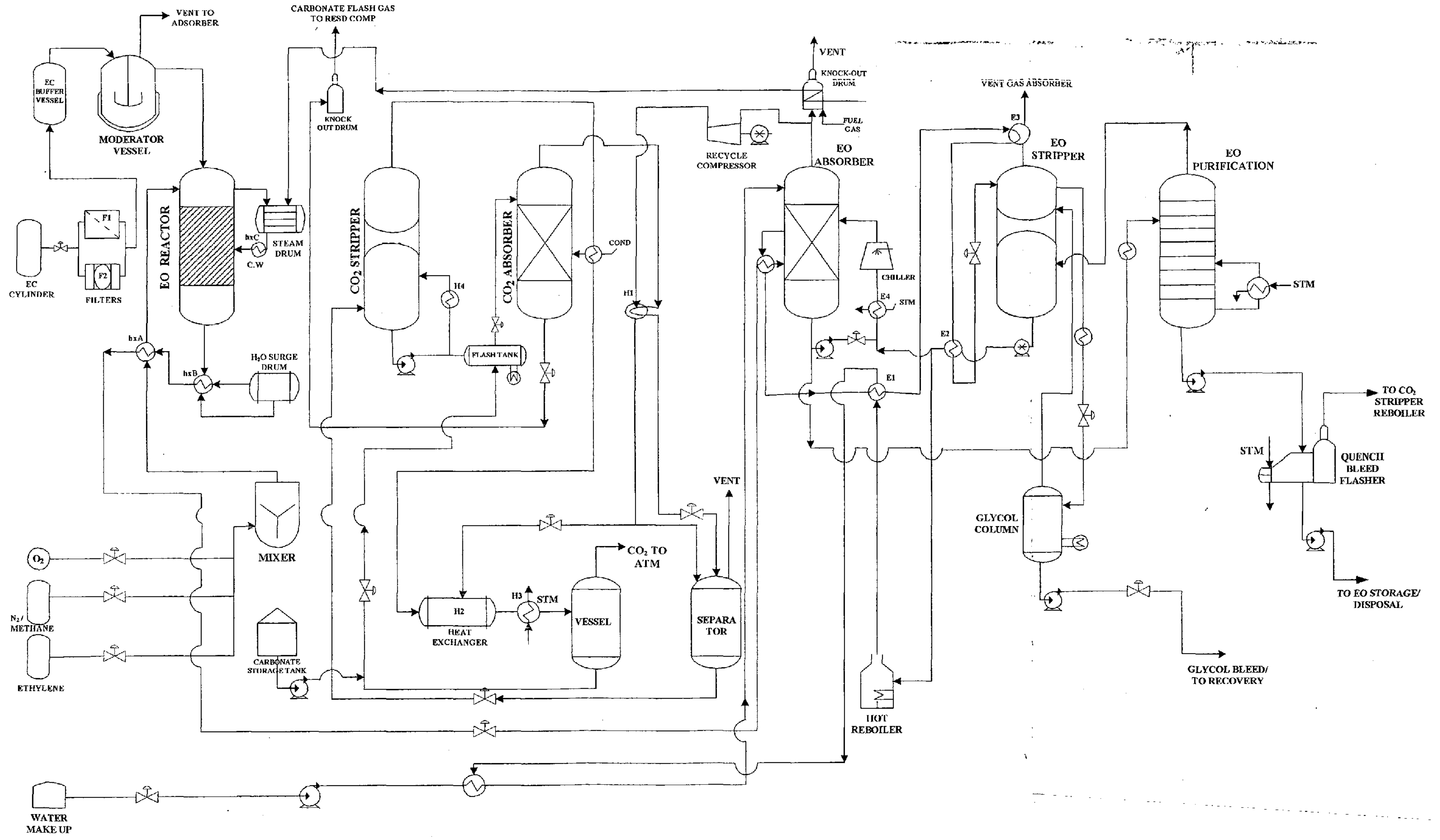

Figure 4.1: A complete Process Flow Diagram of EO section in a MEG Plant

4.3 Safety consideration

4.3.1 Run-away in the EO reactor & spontaneous exothermic reaction:

In a full run away situation, all of the O_2 entering the reactor is consumed to form CO_2, H_2O and small amount of CO. The design has been prepared and equipment selected so that a continued run away is not dangerous to the unit or personal. But this mode of operation is wasteful and may eventually result in the damage to the catalyst. A run away may be caused by any of the following circumstances: i) coolant temperature too high, ii) failure if moderator system, iii) reactor feed gas rate decrease without coolant temperature decrease, iv) failure of coolant supply and v) loss of feed O_2 control.

The majority of the pilot plant runaway was caused by deliberately increasing the coolant temperature to delineate the limits of operations. The commercial plant coolant temperature at design conversion is expected to be about 10-15°C below the temperature which could ease a runaway. The failure of moderator feed to the reactor will be indicated first by a slowly increasing reactor temperature profile, while the coolant temperature remains constant. A runaway is prevented by decreasing the coolant temperature and by observing reactor exit flammability limits frequently and reducing O_2 make up as required to maintained a satisfactory flammability limit margin.

Once the runaway has been stopped, the catalyst must be cooled back to the normal operating temperature by continuing the gas circulation, cooling the reactor further can be delayed by shutting off the reactor feed gas. Providing the O_2 below 17m, the reaction could then be re-started again without starting heating involved when the cause of the runaway has been found and remedied, the O_2 feed can be re-started, reactor brought back on stream at a controllable conversion level.

4.3.2 Post-ignition in the EO reaction system:

Post ignition is not very predictable, sometimes occurring at O_2 concentrations apparently below the normal flammable limit. It occurs in the reactor bottom head and exit line, and is detected by a substantial rise in temperature and CO content of the product gas stream. It is further characterized by production of excessive aldehydes and pyrolyser products which could become a problem if the post ignition is allowed to continue without stopping the O_2 flow. Subsequent post ignition seems to occur more readily shortly after the

1st one has occurred in directing a possible catalyst effect of the fresh residue left from the previous post-ignition.

When a post-ignition occurs, the reactor outlet temperature alarms and shut off the O_2 almost immediately otherwise trip manually. When the O_2 in the loop is depleted and the reactor exit piping cools to normal, the reactor may be started again as above, but the O_2 concentration in the reactor feed and the conversion should be reduced for several days. Lower moderator rates should also be tired.

4.3.3 Safety precaution for handling of chemical and health hazards:

Fire, explosion and health hazards of chemicals used in EO process are discussed below:

a) Ethylene is a colourless gas. It can form explosive mixture with air over a broad range of composition from three to about 35% V ethylene.

b) Recycle loop gas is not flammable but becomes flammable when mixed with air. The recycle or vent gas must be diluted with several volumes of air before the mixture is so dilute that it becomes non-flammable on the hydrocarbon lean side. Therefore, when equipment is scheduled to the opened for maintenance, it should be thoroughly purged with inert gas (nitrogen) before allowing air to enter.

c) O_2 under pressure or in liquid form reacts violently with hydrocarbons, such as oils and grease. The lines, valves, pressure gauge, etc. used in contact with O_2 should be cleaned of any oil contamination before use. This is often done with chlorinated solvent but these must be removed completely afterwards, since they deactivate the catalyst. Every effort must made to avoid the accidental entry of oil, such as might be contained in valve packing compound, pipe thread sealants, etc. Finally decided carbon, which is used in graphitized valve packing or gasket is also reactive with O_2 and should never be used for O_2 service. Air enriched with O_2 is also a hazard, since the burning rate of combustible materials (eg. Oil, clothing) is greatly increased in such an environment.

d) Methane is a clourless gas which forms explosive mixture with air at 5 to 15% V methane.

e) Reactor moderator may be either vinyl chloride or dichloroethane vinylchloride is normally extremely flammable and form explosive mixture with air from 3.6 to 33%V vinyl chloride. Dichloroethane is a liquid and forms explosive mixture with air from 6.2 to 15%V dichloroethane.

f) Glycols are flammable liquids of moderate fire hazards. Since the glycols in the EO unit are handled as aqueous solution, the fire hazard is small.

4.3.4 Health hazards:

a) Ethylene, methane and nitrogen are simple asphyxiants, victim should be moved to fresh air and artificial respiration applied, if necessary.

b) The moderator 1.2 dichloro ethane is pleasant smelling material which is toxic by inhalation or by contact with skin.

c) Ethylene oxide vapour is toxic upon inhalation and is highly irritating to the respiratory system, eyes and skin.

d) Potassium carbonate and sodium hydroxide are strongly alkaline and will burn skin tissue and damage eye tissue on contact. Protective clothing should be worn when handling these materials or their solution.

4.3.5 Protection of equipment against overpressure and vacuum:

In this design the relief valves location and dimension will be the responsibility of the contractor. Some remarks are following as

a) In view of the maximum allowable coolant operating temp of 270°C corresponding to a steam pressure of 55 bar g, a mechanical design pressure of atleast 60 bar g is recommended.

b) In case of complete off take blockage if the generated HP steam the relief valve at the reactor steam drum will protect the system. This relief valve is sized to handle a runaway at end of cycle conditions.

c) In case of cooling of the cooling system below 100°C, N_2 can be introduced into the reactor steam drum and the reactor water surge vessel to prevent vacuum in the coolant system. The recycle gas loop is safeguarded by specially sized relief valves, i.e. (i) the relief valve on top of the EO absorber, designed for releasing the total quantity of ethylene, methane and residual gas at the condition prevailing in a gas loop, (ii) the relief valve on top of the CO_2 absorber, designed for releasing the total quantity of ethylene, methane and residual gas at the condition prevailing in the gas loop. Other equipment is safeguarded by relief valves calculated in the conventional way.

4.3.6 Preparation of equipment for maintenance:

Portions of the system containing hydrocarbon vapour should be depressured to the relief system, and thoroughly purged with nitrogen before being opened. Before any equipment is entered, the N_2 should be purged with air and a supply of fresh air assured within the working spaces. Systems containing liquid EO have to be vented to the EO vent absorber or flushed and diluted with large quantities of water and at least blown with nitrogen. Glycols containing systems should be drained and flushed with water.

4.3.7 Fire and gas explosion hazards:

a) *Recycle loop gas (flammable limits):* The concentration of O_2 in the reactor feed can be raised indiscriminately. The increased in O_2 concentration resulting in reduced percent O_2 conversion will increase the reactor selectivity at a given ethylene conversion. The O_2 concentration at the flammable limit is decreased by increasing the concentration of argon or ethylene or by adding EO to the gas. Increased pressure and tap also decrease the O_2 concentration at the flammable limit.

b) *O_2:* The danger in O_2 system lies in the fact that many materials, including most metals, will burn in an O_2 atmosphere (or in O_2 enriched air) in an explosion like manner. Ways to limit this danger to an acceptable level are threefold viz. i) Omit all materials which will react easily such as oil, grease, organic materials. Select materials which have proved to be safe in O_2 service and have a sufficiently high ignition temperature, ii) Avoid all sources of energy which could initiate a fire by reducing flow velocities, turbulence, temperature and avoiding dust or particulate matter, vibration, and uncontrolled adiabatic compression, iii) Safeguard personal and equipment against flames by applying fires shields and for remote operation of valves.

c) *N_2:* It is of prime importance that the N_2 used to purge the O_2 mix nozzle is not contaminated, therefore elaborate back-flow protection systems (pressure differential instruments, sometimes with double block and bleed system) are provided to avoid under all circumstances back flow of contaminated N_2 from other plant units.

4.3.8 The analyzer system:

This system gives continuous and fast analyses of reactor feed and product gas are essential for the safety of operation. The analyser system comprises a "primary fast loop" which brings a "fast" sample of the gas at reduced pressure to the analyser house. There a part of the sample is diverted to a secondary loop leading to the analyser instrument. The off-gas from the primary fast loop is recovered via the residual gas compressor. If the flow in the primary fast loop becomes too low, then the O_2 trip system is activated. Around the reactor the following on-stream analysers are installed

- O_2 analyser in the reactor inlet gas, with O_2 trip setting for maintaining O_2 concentration at a safe margin from the flammable limit. O_2 analyser in the reactor product gas of stream with O_2 trip setting for maintaining O_2 concentration at a safe margin from the flammable limit. O_2 analyser, spare for the reactor inlet and outlet analyser
- CO analyser in the reactor outlet for rapid detection of post ignition
- Ethylene oxide analyser in the reactor outlet for reactor selectivity calculation. Ethylene analyser in the reactor inlet gas to be used as a trend recorder

CHAPTER 5

HAZOP STUDY REPORT

5.1 HAZOP study Work-Sheet Index

First of all, the whole process of EO section in a MEG plant is divided into several units (as study nodes), where a unit is defined as a part of plant or process having an independent unit operation and linked with other units to complete the process. Then, HAZOP study has been carried out step by step for EO section of MEG plant in the following tables:

Table 5.1.1: HAZOP study for moderator feed system in EO section of MEG plant

Table 5.1.2: HAZOP study for EO reaction with steam drum in EO section of MEG plant

Table 5.1.3: HAZOP study for shut-down cooler system in EO section of MEG plant

Table 5.1.4: HAZOP study for product cooler with water surge vessel in EO section of MEG plant

Table 5.1.5: HAZOP study for quench water system in EO absorber of MEG pant

Table 5.1.6: HAZOP study for CO_2 absorber feed cooling system in EO section of MEG plant

Table 5.1.7: HAZOP study for EO stripper overhead chiller of MEG plant

Table 5.1.8: HAZOP study for lean flash tank in EO section of MEG plant

Table 5.1.9: HAZOP study for lean absorbent chiller in EO section of MEG plant

Table 5.1.10: HAZOP study for fat absorbent heat exchanger in EO section of MEG plant

HAZOP STUDY WORKSHEET

Table 5.1.1: HAZOP study for moderator feed system in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of EC through the EC filter F1	a) No N_2	a) No filling of EC into the EC buffer vessel. Discontinuous operation minor issue		
			b) EC cylinder empty	b) No filling of EC into the EC buffer vessel. Discontinuous operation minor issue		
			c) EC filter is blocked	c) No filling of EC into the EC buffer vessel.	c) Differential press indicator will send an alarm to the initial room in case of high differential pressure	
			d) Blocked valves	d) No filling of EC into the EC buffer vessel.	d) Sight glass in the EC buffer vessel monitored during the filling procedure	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	2. No flow of EC through the EC filter F2	a) No ethylene pressure	a) No EC into the process	a) Low flow alarm	
			b) Blocked filter .	b) No EC into the process	b) Differential press indicator will send an alarm to the initial room in case of high differential pressure	
			c) Blocked valves	c) No EC into the process	c) Low flow alarm	
			d) No EC in the feed vessel	d) Ethylene break through	d) Low flow alarm	
	No	3. No flow of EC through the flow recorder controller	a) Microfilter blocked	a) No EC into the process	a) Low flow alarm and standby control system	
			b) Maloperation of the control valve	b) No EC into the process		
			c) Maloperation of the mass flow meter due to vibration and /two phase flow	c) Incorrect dosing	c) Indication on the EC online analyser	c) Provide line up for proper filling of the EO system upstream and downstream
			d) Maloperation of the controller	d) No EC into the process	d) Indication on the EC online analyser	
	Part of	4. Pre-flow of EC from cylinder to buffer vessel	a) Fully open high pressurized N_2 line	a) To keep it emptying of cylinder and too much vent flow to the adsorber		a) Introduce restriction orifice on the N_2 line

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Reverse	5. Reverse flow from EC vessel through the filters	a) Disconnected HP N2 and open line to the atmosphere	a) Pollution of the environment of EC gas or liquid	a) A check valve in the line from the cylinder to the filter	
	Reverse	6. Reverse flow from EC vessel through the ethylene line	a) Loss of ethylene pressure	a) Recycled gas entering the EC feed vessel	a) Press recorder controller closes with OSS activation	a) Consider back flow protection instead of trip from OSS
Temperature	More	1. High temp of EC	a) Exposure to sun radiation	a) High temp of EC lead to higher losses	a) Insulation of equipment	
Pressure	More	1.High pressure in the filters	a) A blocked outlet	a) Full nitrogen press in the filter	a) Safety valves have been provided	a) Safety valves should be set at press of 30 kg/cm^2
	More	2. High press in EC provided feed vessel	a) Open line up from high press N_2 b)Closed vent outlet valve	a) Maximum N_2 press on vessel b) High press	a) Safety valves have been provided b) Safety valves have been provided	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
			c) Blocked adsorber bed	c) Restricted flow		c) Check if adsorber bed can be fully blocked and consider installation of RD to bypass the adsorber to remove the adsorber bed because the vent is now connected to the flare
	Less	3. Low press in the EC vessel	a) No ethylene feed available	a) Cannot feed EC into the process	a) A low press alarm on the feed vessel and low flow alarm on the EC feed system	
	Less	4. Low press in the EC provided vessel	a) Malfunction of the press controller	a) Fluctuating press in the feed vessel. Increase in EC losses through the vent system		a) Design system with a dead bond
Level	More	1. High level in the adsorber vessel	a) Overfilling	a) Liquid carry over to the vent adsorber	a) Level gauge does exist	a) Consider protection of adsorber bed

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Maintenance	As well as	1.Decommission-ing of all filter	a) Cartridges get blocked with rust particles	a) Necessity to vent/drain the filter		a) Provide discontinuous chain connection through EC vessel and vent to the adsorber b) Discontinuous connection to N_2 line

Table 5.1.2: HAZOP study for EO reaction with steam drum in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	Less	1. Low flow of reactor gas	a) Compressor problem	a) Less flow on the EO reactor increase of O_2 in the loop	a) OSS activated on low flow and high O_2 concentration	
			b) Bypass full open	b) Less flow on the reactor increase of O_2 in the loop	b) OSS activated on low flow and high O_2 concentration	
			c) Maloperation of FRC	c) Less flow on the reactor increase of O_2 in the loop	c) OSS activated on low flow and high O_2 concentration	
	Other than	2. Compressor trips	a) Mechanical compressor problem	a) O_2 in the reactor will fully react (limited runway)	a) O_2 supply is shutdown	
	No	3. No flow from steam drum to EO reactor	a) No thermosyphon due to low heat load		a) Low flow trip on OSS activation	a) Time delay of 10 seconds is recommended to avoid nuisance trip. A override switch should be provided with a annunciation on the enunciator

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
					b) Low flow alarm for switch over to the pump	
			c) Thermosyphon loop is closed	c) No cooling/dry out of shell side of the reactor	c) Low flow trip on OSS activation	c) safety valve should have provision for hand operation
			d) Steam drum is empty	d) No cooling/dry out of shell side of the reactor	d) Low flow trip on OSS activation	
	No	4. No flow from steam drum to EO reactor through pump	a) Pump failure	a) No cooling in the EO reactor		a) Automatic opening of the safety valve to allow natural thermosyphon in case of pump failure and manual opening in case of power failure b) Remove the check valve in the discharge of the pump to failure free circulation through the volute of pump in case of power failure

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Part of	5.Insufficient flow in the shell side of the reactor overhead piping	a) HS(sulphur) catalyst operation with all four risers open	a) Unstable thermosyphon operation/vibration of the rises		a) Standard operation procedure to be followed
			b) HA(acetylene) catalyst operation with only 2 risers open	b) Restricted flow resulting into higher vaporization rates in the reactor shell sides		
	No	6. No flow of BFW in steam drum	a) Failure of pump	a) Loss of level in steam drum	a) Low level alarm and a low level trip which activates OSS	a) Add low flow alarm to FRC b) Consider auto and manual start of the pumps c) Provide adequate back flow protection on individual pumps
			d)Failure of controller	d) Loss of level in steam drum	d) Low level which activates OSS	
			e) Blocked valves	e) Loss of level in steam drum	e) Low level alarm and a low level trip which activates OSS	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
			f) No water in WPH header g) High press in the steam drum due to run away and safety valve pop up	f) Loss of level in steam drum	f)) Low level alarm and a low level trip which activates OSS	g) The press in the discharge vessel for the pump hydrolysis should be considered
	No	7. No flow of steam from steam drum to header	a)Blocked outlet	a) Increase of press in steam drum and risk of run away	a) High press alarm b) High press trip c) Relief valves	a) Connection to the silencer to be reconsidered
	No	8. No flow of the HP steam to the steam drum		a) Minor issue normally not in operation		
	More	9. High flow in the BFW	a) Failure of controller	a) Possible carry over of the liquid in other system	a) High level alarm b) High level switch	a) The BFW control valve should be fail close

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	More	10. More flow of the HP steam to the steam drum	a) Failure of controller or maloperation	a) Minor issue design press of the vessel is higher than the design press of steam line		a) Check size of the bypass and size it for 10-15 tons/hrs b) Add black valve upstream of flow orifice
	More	11. High flow of steam to the header from steam drum	a) Maloperation of the controller c) Run away situation	a) Reduce steam import c) Reduce steam import	a) Control system of header will compensate b) Relief valves present on the header c) Relief valves present on the header	a) Relief capacity of the safety valve on header to be checked
	More	12. High flow of steam from steam drum through manual valve				a) Reconsider design flow for start up situation only

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Reverse	13. Reverse flow from steam drum to the WPH header	a) Press loss in the header	a) Draining of inventory steam drum	a) Check valve in the bypass through the pumps and at the entrance to vessel b) Back flow protection	a) Check valve to be provided in the discharge of the pump
			d) Loss of header pressure	d) Draining of the vessel and excess press in the header	d) Non return valve on the stream line and a black valve	d) Block valves to be moved upstream of flow meter and downstream of the check valve
	Reverse	14. Reverse flow from the header to during start up and down	a) Low press in steam drum		a) Back flow protection and non return valve on steam header	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Temperature	More	1. Higher temp in reactor feed	a) Preignition and cool flame mixture phenomenon	a) Possible soot deposition on the catalyst c) May cause runaway in the reactor and high temp in the feed pipe metal	a) OSS is activated b) Trip on mixing nozzle outlet high temp c) OSS activated on reactor inlet temp	c) Thermal stresses to be considered for the preignition case
	More	2. High temp in reactor bed	a) Runaway reaction	a) Catalyst damage b) Post ignition	a) Shutdown will occur for the logic of two out of three tubes high temp (at multiple location) in two sets	
	More	3. High temp in primary product cooler side	a) High temp from the reactor b) Loss of cooling	a) Increased steam production b) Increase in the outlet temp of heat exchanger A	a) Reactor outlet temp trip b) Level trip on water surge drum c) Trip on the heat exchanger B outlet	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	More	5. Higher temp in feed product exchanger (tube side)	a) Loss of cooling in the heat exchanger B	a) High byproduct formation	a) Trip on the heat exchanger B outlet	
	Less	6. Low temp in the steam drum	a) Insufficient preheating		a) BFW inlet in steam drum & steam drum down comer are at maximum possible distance	
			b) Pre heaters by passed	b) Less temp of BFW in the reactor. Minor influence on the reaction less steam production		
	More	7. Higher temp in feed product exchanger outlet pipe (tube side)	a) By pass valve open	a) Low inlet temp		a) High temp alarm to be provide
				b) Higher work rate of catalyst resulting into increased selectivity drop		
				c) Lower stream production		
			d) Fouling of heat exchanger A			d) Consider removal of by pass

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	8. Low temp in the reactor feed gas	a) Bypass heat exchanger A (tube side) remain open	a) Higher work rate of catalyst resulting into increased selectivity drop b) Lower steam production c) Possibility of unstable thermosyphon loop of reactor		a) Consider removal of by pass
			d) Fouled in heat exchanger A	d) Higher work rate of catalyst resulting into increased selectivity drop e) Lower steam production f) Possibility of unstable thermosyphon loop of reactor		d) Outlet temp of heat exchanger B to be observed
			g) Failure of press control in the reactor water surge drum	g) Higher work rate of catalyst resulting into increased selectivity drop h) Lower steam production i) Possibility of unstable thermosyphon loop of reactor	g) Low press alarm is provided	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	9. Low temp of reactor unit	a) Malfunction of press control in steam drum c) Open start up valve	a) Conversion reduces and oxygen concentration reduces	a) Oxygen trip of the oxygen analyzer b) Low press alarm	
	Less	10. Low temp of heat exchanger B outlet pipe	a) Failure of press control in the water surge drum	a) Higher work rate of catalyst resulting into increased selectivity drop	a) Low press alarm is provided	
Pressure	More	1. Higher press in steam drum	a) Blocked outlet d) Runaway	a) Excess pressure in vessel d) Excess pressure in vessel	a) Higher press alarm b) Higher press trip c) Safety valve d) Higher press alarm e) Higher press trip f) Safety valve	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	2. Low press in steam drum	a) Press recorder controller malfunction	a) Oxygen conversion will go down leading to higher oxygen concentration in the reactor outlet b) Reverse flow of steam from the header	a) Oxygen analyser in the loop which will trip on high concentration b) Back flow protection on the control valve	
Composition	As well as	1. New revamp design generates at higher EO & ethylene concentration				a) Equipment for the flammability calculations are still valid upto 300°C with use of high selectivity catalyst
Level	More	1. Higher level in steam drum	a) Runaway reaction b) Rapid increase in heat load c) Failure of level controller	a) Possible carry over in the steam system	a) High level alarm b) High level switch closing BFW supply	b) Consider auto reset of BFW supply

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	2. Low level in steam drum	a) Failure of BFW pump	a) Not enough water for the cooling of the rector	a) Low level alarm b) Low level shutdown	
			c) Runaway reaction	c) Not enough water for the cooling of the rector	c) Low level alarm d) Low level shutdown	
			e) Blow down/drain valves remain open		e) Blow down outlet nozzles are elevated to maintain & minimum inventory of the liquid	e) Emergency/start up blow line sizes to be reconsidered
			f) Major leakage	f) Higher BFW consumption	f) Visual observation	
Leakage	Other than	1.Tube rupture in EO reactor	a) Material failure/poor workmanship	a) More water in the recycle gas, higher quench bleed is detected and reduced steam production b) Possibility of post ignition		a) Proper inspection procedure and corrosion monitoring
			c) High vaporization rate			c) Maintain vaporization rate less than 10%
			d) Poor BFW quality			d) Monitor BFW quality

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Other than	2. Tube rupture in primary conduct cooler	a) Material failure/poor workmanship b) High vaporization rate c) Poor BFW quality	a) Recycle gas containing CO_2 & EO and ethylene enters the thermosyphon loop resulting in the P^H value of steam condensate		a) Check the P^H value of condensate

Table 5.1.3: HAZOP study for shut-down cooler system in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of BFW through heat exchanger C	a) Failure of pump	a) Cooling delay, Minor issue		
	No	2. No flow of cooling through heat exchanger C	a) Blocked line b) By pass valve open			a) Design temp on the tube side to be checked b) Design temp on the tube side to be checked
	Less	3. Less flow of BFW through heat exchanger C	a) By pass valve open	a) Slow rate of cooling of the reactor. Minor issue		
	More	4. High flow of BFW through heat exchanger C	a) Control valve maloperation	a) Fast rate of cooling of the reactor. This will cause high stresses in the reactor tubes		a) Temp difference controller should be fail close b) Bypass of cooler should be fail open

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Temperature	More	1. Higher temp pressure	a) Maloperation of temp difference controller	a) Fast cooling of the BFW		a) Consider alarm for high temp difference & alternatively automatic closing of the control valve
	More	2. Higher press on the shell side	a) Blocked outlet	a) Excess press on the shell side	a) Design press of the heat exchanger C is higher than the shut off press of pump	
	More	3. Higher press on the water side	a) Tube rupture	a) Excess press on the tube side	a) Safety valve on the CW line	

Table 5.1.4: HAZOP study for product cooler with water surge vessel in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of BFW from water surge drum to N_2 buffer vessel	a) Line is blocked by valve	a) No cooling of reactor gas		a) Remove isolation valve on the thermosyphon loop down comer from water surge drum to heat exchanger B
			b) No level in water surge drum	b) No cooling of reactor gas	b) A low level alarm and trip	
	No	2. No flow from water surge drum	a) Line cannot be blocked no issue			
	No	3. No flow of BFW in water surge drum	a) Line is blocked by valve	a) Low level in water surge drum	a) A low level alarm and trip	
			b) Maloperation of controller	b) Low level in water surge drum	b) A low level alarm and trip	
			c) Failure of BFW supply	c) Low level in water surge drum	c) A low level alarm and trip	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	4. No flow of steam from water surge drum to header	a) Blocked line	a) Excess press in water surge drum	a) High press alarm b) Safety valve	a) Consider removal of silencer
	No	5. No flow of condensate from H_2O surge drum to clean steam condensate drum	a) Blocked line c) Maloperation of controller	a) Level increase in H_2O surge drum c) Level increase in H_2O surge drum	a) High level alarm b) Relief valve c) High level alarm d) Relief valve	
	Less	6. Low flow to heat exchanger B	a) Maloperation of thermosyphon due to less duty	a) Disturbs heat. Removal & unstable thermosyphon		a) Check thermosyphon for lowest duty
	Less	7. Low flow of BFW in the H_2O surge drum	a) No condensate return from glycol section & no bleed from steam drum	a) More BFW required from header		a) Make the design for the maximum flow

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	8. Less flow of condensate from H_2O surge drum	a) Maloperation of controller	a) Level increase in H_2O surge drum	a) High level alarm	
	More	9. High flow of steam in the H_2O surge drum	a) Post ignition	a) Increase in the press in the vessel	a) This line floating free with the header	a) Check maximum flow for the operation condition
	More	10. More flow through the safety valve	a) Post ignition	a) Increase in the press in the vessel		a) Post ignition flow to be considered for the relief load of the safety valve excluding the vapour escape to the steam header

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	More	11. High flow of condensate from H_2O surge drum	a) Maloperarion of controller	a) Low level in H_2O surge drum b) Steam break through	a) A low level alarm & trip	b) For steam break through check the relieving capacity of the safety valve on CSC drum c) Provide dirty steam condensate lock on the set point of level controller
Temperature	More	1. Higher temp in H_2O surge drum	a) High press in H_2O surge drum			
Pressure	More	1. Higher press in H_2O surge drum	a) Blocked outlet c) Post ignition	a) Higher press in H_2O surge drum c)Higher press in H_2O surge drum	a) Safety valves b) High press alarm c) Safety valves d) High press alarm	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	As well as	2. vacuum in the vessel	a) Cooling of the vessel during shutdown		a) Vessel design for vacuum	a) To ensure the nitrogen connection during shutdown
Level	Less	1. Less level in H_2O surge drum	a) Maloperation of controller or leak	a) Possible overheating of the system	a) A low level alarm and trip b) Elevated outlet nozzles	
	High	2. High level in H_2O surge drum	a) Maloperation of controller b) Blocked valve open and excessive blowdown from steam drum	a) Flooding of the vessel & possible carry over of water in the steam header b) Flooding of the vessel & possible carry over of water in the steam header	a) High level alarm b) High level alarm	

Table 5.1.5: HAZOP study for quench water system in EO absorber of MEG pant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of the make up water into the quench loop	a) No water in the WPL header	a) Reduction of level in the quench section	a) We have a low level alarm in the bottom of the EO absorber	
					b) A low flow alarm	b) Consider auto reset of BFW supply
			c) Failure of booster pump	c) Reduction of level in the quench section	c) We have a low level alarm in the bottom of the EO absorber	
					d) A low flow alarm	
					e) Spare pump available	
			f) Failure of flow control	f) Reduction of level in the quench section	f) We have a low level alarm in the bottom of the EO absorber	
					g) A low flow alarm	
			h) Blocked line	h) Reduction of level in the quench section	h) A low flow alarm	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	2. No flow make up water in the pump	a) Blocked line	a) Possible damage of pump		a) Appropriate procedure to be followed b) Sizing according to manufacturing recommendation
	More	3. High flow of the make up water into the quench section of EO absorber	a) Wrong setting of the flow controller c) Open bypass	a) Increase in level in the quench section c) Increase in level in quench section	a) A high flow alarm b) A high level alarm & trip c) A high flow alarm d) A high level alarm & trip e) A high level alarm & trip	
	Reverse	4. Reverse flow from the quench loop to the WPL header	a) Loss of press in the header	a) Contamination of the DM water header	a) Back flow protection b) A check valve	

Table 5.1.6: HAZOP study for CO2 absorber feed cooling system in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of recycle gas in CO_2 absorption system	a) safety valve close due to CSS	a) CO_2 in the reactor inlet may increase reduction in the reactivity of reactor	a) Reaction system will cope up by tripping on higher O_2 concentration situation even if the operator does not react	
				b) Possible surge of the recycle gas compressor	b) Bypass valve is provided	b) Opening time of the bypass valve should be decided at the time of full commissioning in order to avoid compressor surge
			c) Blocked line due to isolation valves on the CO_2 absorber upstream	c) CO_2 in the reactor inlet may increase reduction in the reactivity of the reactor	c) Reaction system will cope up by tripping on higher O_2 concentration situation even if the operator does not react	
				d) Possible surge of the recycle gas compressor	d) Bypass valve is provided	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	2. No flow of recycle gas in heat exchanger H2	a) Blocked line	a) High flow in heat exchanger H4 c) Low temp in CO_2 absorber d) No condensation of stripper overhead on heat exchanger H2 e) Increase in load on heat exchanger H3 & more moisture content in CO_2 vent		a) Provide high flow alarm b) Check H4 for the maximum flowrate
	No	3. No flow of recycle gas in H4	a) Blocked line	a) High flow in heat exchanger H2 b) Low temp in CO_2 absorber of recycle gas c) Lean carbonate goes to the absorber at a higher temp		a) Add a low flow alarm

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	4. No flow of lean carbonate to H4	a) Pump failure b) Blocked line	a) No absorption of CO_2 in the absorber b) CO_2 in the reactor inlet may increase reduction in the reactivity of the reactor	b) Reaction system will cope up by tripping on higher O_2 concentration situation even if the operator does not react	
	No	5. No flow of recycle gas CO_2 absorbed through sensor H1 & separator	a) Safety valve close due to CSS b) Blocked line due to isolation valves on the CO_2 absorber upstream	a) No issue at this points b) No issue at this points		
	More	6. High flow of recycle gas in CO_2 absorption system	a) Maloperation (quick closing) of differential press controller	a) Flooding of CO_2 absorber and carry over of the carbonate solution to the recycle gas loop	a) Adjustable minimum stopper provided on site for differential press controller b) High press differential trip on CO_2 absorber will activate CSS c) Trip on separator	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	Less	7. Low flow of recycle gas CO_2 absorption system	a) Maloperation (quick closing) of differential press controller	a) CO_2 in the reactor inlet may increase reduction in the reactivity of the reactor	a) Reactor system will cope up by tripping on higher O_2 concentration situation even not react	
	More	8. High flow of recycle from CO_2 absorber through condenser and separator	a) Maloperation (quick closing) of differential press controller	a) Possible carry over of carbonate to separator	a) Knock out drum with level controller	
Level	More	1. Higher level in separator	a) High carry over from CO_2 stripper d) Failure of the outlet valve	a) Possible carry over of carbonate to separator d) Possible carry over of carbonate to separator	a) High level alarm b) High level switch dumping the inventory c) High level to shutdown the CO_2 redundant opening of the dump connection d) High level switch to shutdown the CO_2 removal system	a) Check altitude of the level topping
	Less	2. Lower level in separator	a) Maloperation of the level control	a) Possible gas break through the stripper	a) Lower level switch closing all bottom outlet valve	

Table 5.1.7: HAZOP study for EO stripper overhead chiller of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	More	1. More flow of brine through E2	a) Throttled globe valves in the line to E2	a) High duty on the exchanger E2		a) Provide alarm on high flow on both the exchangers b) Use of butterfly valve of throttle the flow with metal seat to be investigated
	Less	2. Low flow of brine through E2	a) Blocked line	a) Increase EO loses in the vent gas & higher load on the EO vent absorber possibly on the residual gas absorber	a) High temp alarm	a) In case of high gas vent flow then trip the residual gas compressor immediately & OSS with time delay of 5mins
			b) Maloperation of the control valve	b) Increase EO loses in the vent gas & higher load on the EO vent absorber possibly on the residual gas absorber	b) High temp alarm	b) In case of high gas vent flow then trip the residual gas compressor immediately & OSS with time delay of 5mins
			c) Failure of the brine supply in the chiller unit	c) Increase EO loses in the vent gas & higher load on the EO vent absorber possibly on the residual gas absorber	c) High temp alarm	c) In case of high gas vent flow then trip the residual gas compressor immediately & OSS with time delay of 5mins

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Temperature	More	1. Higher temp of vent gas from E3	a) Lack of cooling	a) Higher EO vent losses	a) High temp alarm	
	Less	2. Low temp of vent gas to E2	a) Low cooling water temp	a) Possible hydrate formation	a) Chiller controller is maintain to 13°C	a) Provide additional alarm in the chiller
Leakage	Other than	1. Any leakage in the E2	a) Failure of heat exchanger tubes	a) Contamination of aqueous EO with chilled water which may contain treatment chemicals (molybedate)	a) Rare occurrence & chilled water tested regularly for the presence of EO	a) Hazards of treatment chemical to be investigated

Table 5.1.8: HAZOP study for lean flash tank in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of steam from CO_2 stripper to the flash tank	a) Blocked line	a) High level of steam in the CO_2 stripper	a) High level alarm	
				b) Low level of steam in the flash tank	b) Low level alarm the CO_2 stripper	
			c) Low level in the stripper bottom	c) Low level of steam in the flash tank		
	No	2. No flow steam from flash tank to the CO_2 absorber	a) Blocked valve	a) Pump surge		
			b) Low level in the flash tank	b) Pump surge	b) Low level alarm	b) Consider to add low level switch to trip the carbonate pump considering the safety of the hydraulic turbine
	No	3. No flow of flash tank overhead back to the CO_2 stripper	a) Blocked line	a) No removal of CO_2 steam from the CO_2 stripper bottom	a) High press alarm	a) Change manual globe valve to get valve
			b) No driving steam for the jet	b) No removal of CO_2 steam from the CO_2 stripper bottom	b) High press alarm	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	4. No flow of steam to the flash tank	a) Blocked line	a) No removal of CO_2 from the CO2 stripper bottom	a) High press alarm	a) Add low alarm on the steam flow control
			b) Maloperation of flow controller	b) No removal of CO_2 from the CO_2 stripper bottom	b) High press alarm	
			c) Low press in the steam header	c) No removal of CO_2 from the CO_2 stripper bottom	c) High press alarm	
	More	5. High flow of steam from CO_2 stripper to the flash tank	a) Maloperation of level controller	a) Low level in the CO_2 stripper bottom	a) Low level alarm	
	More	6. High flow of steam to flash tank	a) Cause high setting of flow controller or malfunction	a) Too high load on the column trays	a) Maximum flow is restricted by the control valve	a) Restrict maximum flow through the bypass & consider reduction of the bypass or elimination
	Reverse	7. Reverse flow through steam line	a) Loss of pressure in the steam header	a) Pollution of the steam header		a) Add check valve

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Level	More	1. Higher level in flask tank	a) Failure of pump b) Blocked line	a) Over filling of the flash tank	a) High level alarm b) High level alarm	
	Less	2. Low level in flash tank	a) Failure of level controller b) No feed from the CO_2 stripper	a) Possible pump surge b) Possible pump surge	a) Low level alarm b) Low level alarm	a) Consider to add low level switch to trip the carbonate pump considering the safety of the hydraulic turbine

Table 5.1.9: HAZOP study for lean absorbent chiller in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of lean absorbent to the chiller	a) Failure of pump	a) Chiller trips (under equipment)	a) Press drop will activate OSS in 3 mins (approx.)	a) Consider additional safety of CSS trip with low flow of lean absorbent
			b) Blocked line	b) Chiller trips (under equipment)	b) Press drop will activate OSS in 3 mins (approx.)	
	No	2. No flow of steam to chiller	a) Blocked line	a) Chilling is not achieved and higher temp of the lean absorbent to EO absorber		a) Load of the plant through put to be adjusted according to EO absorber performance
			b) Loss of steam	b) Chilling is not achieved and higher temp of the lean absorbent to EO absorber		b) Load of the plant through put to be adjusted according to EO absorber performance
			c) Maloperation of the controller	c) Chilling is not achieved and higher temp of the lean absorbent to EO absorber		c) Load of the plant through put to be adjusted according to EO absorber performance

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	3. No flow of cooling chiller	a) Blocked line	a) Chiller trips (vender equipment)		a) Vender to conform the necessity of the trip
			b) Loss of CW press	b) Chiller trips (vender equipment)		b) Vender to conform the necessity of the trip
			c) Maloperation of the controller	c) Chiller trips (vender equipment)		c) Vender to conform the necessity of the trip
	More	4. High flow of steam to E4	a) Maloperation of the controller	a) More glycol formation in the E4		a) Add high temp alarm
			b) Open bypass in the control station	b) More glycol formation in the E4		b) Add high temp alarm

Table 5.1.10: HAZOP study for fat absorbent heat exchanger in EO section of MEG plant

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Flow	No	1. No flow of fat absorbent through exchanger E1	a) Blocked line	a) No feed to the EO stripper		a) Low flow alarm to be introduced
				b) Higher press in the feed line & equipment		b) Introduction of safety valve upstream of E1 and safety valve discharge line up downstream of E5 floating with EO stripper or removal of black valves
			c) Open bypass	c) Feed to the stripper at lower temp	c) Live steam input will compensate for the lack of heat d) Low temp alarm	
	More	2. High flow of flat absorbent through exchanger E1	a) Maloperation of flow controller	a) Over load of the stripper (minor cover)		
				b) Loss of level in the absorber with possible gas break through	b) Low level trip on EO absorber	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
	No	3. No flow of steam to exchanger E1	a) Blocked lines	a) Feed to the EO stripper at lower temp	a) Live steam input on will compensate for the lack of heat b) Low temp alarm	
			c) Loss of press in steam header	c) Feed to the EO stripper at lower temp	c) Live steam input on will compensate for the lack of heat d) Low temp alarm	
			e) Maloperation of the controller	e) Feed to the stripper at lower temp	e) Live steam on will compensate for the lack of heat f) Low temp alarm	
Temperature	More	1. Higher temp process side of E1	a) High steam flow with product side blocked	a) Glycol formation will lead to a higher temp		a) Change the design temp on the product/steam side
	Less	2. Less temp on process side of E1	a) Low heat input to E1	a) Feed to the EO stripper at lower temp	a) Live steam input on will compensate for the lack of heat b) Low temp alarm	

Process parameter	Guide word	Deviation	Causes	Effect of Hazard (Consequence)	Preventive corrective method (Safe guard)	Recommendation
Pressure	More	1. High press on process side of E1	a) Blocked outlet	a) Increase of press above design press	b) Thermal relief valve	a) Introducing of safety valve upstream of E1 and safety valve discharge lined up downstream of E5 floating with EO stripper or removal of blocked valves
			b) Double blocking	b) Increase of press above design press due to glycol formation and thermal expansion		b) Consider sizing of thermal relief valve at 180°C rise
	Less	2. Low press on the absorbent side of E1			a) Restriction orifice maintains the minimum press	a) Restriction orifice sizing to be checked
Phase	Other than	1. Possible flashing in E1	a) Too much heat input	a) Possible gas pocket	a) Inclined heat exchanger to avoid pocket of gas	

CHAPTER 6

RESULTS & DISCUSSION

A HAZOP study has been carried out for an EO section of the MEG plant. A complete process flow diagram of the EO plant is show in Figure 4.1. After collecting all the relevant information (such as P&ID, PFD, process description of the process, material properties, safety consideration) and identifying the different chemicals used in the process, the whole process has been divided into several units (as study nodes), where a unit is defined as a part of plant or process having an independent unit operation and linked with other units to complete the process. A unit can be further divided into sub-units so as to study the unit thoroughly.

The sets of appropriate guidewords/keywords (NO, MORE, LESS, REVERSE, PART OF, AS WELL AS, OTHER THAN) are implemented in each of the nodes while conducting HAZOP study in EO plant. Since EO plant is a continuous process, a manual and qualitative HAZOP study is performed effectively. EO is chemically hazardous, toxic and flammable in nature. The EO manufacturing process units are operated at supercritical conditions, therefore any deviation or changed in the parameter (as temperature, pressure and levels of chemicals) may lead to serious accident (violent reaction, damaged by overheating, hot spot formation, etc) and undesirable product since the product quality is sensitive (i.e. highly flammable & toxic).

After studying thoroughly the process description of EO plant, it is found that certain deviations are generate in the process unit which can cause serious accident and hazards to the environment. Now let us discuss HAZOP study in each of the selected nodes and a brief result of HAZOP study carried out in EO section of MEG plant as follows.

6.1 Moderator feed system of EO plant: In this system, ethylene catalyst (EC) has been filtered in the filters (F1&F2) before passing through the EC buffer vessel. Certain guidewords are applied in the parameter (flow) to find out any possible occurrence of hazards. If the flow is disturbed, deviation takes place and gives a certain consequences such as no EC in the buffer vessel or mal-operation of the process due to EC filter is blocked, mal-operation of control valve or EC cylinder empty. A preventive corrective method has been implemented to safeguard against the risks, like low flow alarm (LFA), differential pressure indicator (DPI), controller valve or indication on the EC online analyzer. Moreover, if the temperature and pressure deviation occur, it may lead to higher EC losses, high N_2 pressure in the vessel or no EC feed in the vessel. These are caused by high temperature of EC, mal-operation of the pressure controller or closed vent outlet valve. To safeguard from the dangerous consequence a safety valve has been provided and an insulation of equipment is also suggested.

6.2 EO reaction with steam drum: As exothermic reaction is taking place in the EO reactor, proper safety operation of the unit process is necessary against hazards. Any deviation or changes in the parameter (as temperature, pressure and levels of chemicals) may lead to serious accident (violent reaction, damaged by overheating, hot spot formation, etc) and undesirable product since the product quality is sensitive (i.e. highly flammable & toxic). In view of this effect a protective measures have been suggested as back flow protection, high/low alarm for pressure/temperature/level, relief valves and proper O_2 shut down system (OSS) should be activated.

Steam drum is used for controlling the parameters (both temperature and pressure) and concentration maintenance of the EO reactor. High/low parameter (temperature/pressure) may lead to excess development of pressure and higher/low concentration of O_2 in the reactor. A preventive corrective method has been initialized in this system as O_2 analyzer in the loop which will trip on high concentration, high pressure trip/alarm or safety valves. Moreover, any deviation or change in level of steam drum may cause hazardous effect such as less water for the cooling of the rector, runaway reaction in the reactor or rapid increase of heat load. All these effects can be avoided by implementing measures like safety relief valves, low level alarm & shutdown system, visual observation, proper inspection procedure and corrosion monitoring.

6.3 Shut-down of cooling system of EO plant: Heat exchangers are used for cooling and heating of unit operation systems in EO plant. As heat exchanger C has been implemented for cooling the reactor. If the parameter (flow/temperature) deviates from its normal operation due to malfunction of control valves, failure of pump, faulty of temperature difference controller, blocked outlet or any tube rupture occur in the exchanger C, it may lead to slow/fast rate of cooling of reactor and excess pressure may be developed in the tube/shell side of the exchanger C.

6.4 PRIM: product cooler with water surge vessel of EO plant: Boiler feed water (BFW) is required in the H_2O surge drum for maintaining the water level and cooling process of the reactor. Thermosyphon system is used in the exchanger B to heat up the cold water. If there are any changes or deviation in the process parameter (such as flow), there is a chance of no cooling of the reactor, excess pressure in the vessel, low level of water in the vessel and unstable of thermosyphon system due to the possible reason i.e. no water in the vessel as line is blocked by valve, failure of BFW supply, mal-operation of controller or mal-operation of thermosyphon system. Post ignition can also cause high pressure in water surge drum due to rise in high pressure and high temperature in the drum. Change in the level of H_2O surge drum is another factor, which can cause possible overheating of the system, flooding of the vessel & possible carry over of water in the steam header or high pressure in the vessel. This may be due to the mal-operation of controller, blocked valve open & excessive blow down from steam drum or failure of pump. Preventive measures have been implemented in the process unit viz. high pressure alarm, safety valves, relief valves or low level alarm & trip, from hazards and equipment damage.

6.5 Quench water system in EO absorber of EO plant: Make up water is supplied to the quench section of the EO absorber. The changes or deviation of flow process of the make up water into the quench section of EO absorber may lead to high/low level of water in the quench section. This cause is due to the failure of flow controller, failure of pump or the line is blocked. A preventive corrective device (such as a low & high flow alarm & trip) should be provided at the bottom of EO absorber and spare pump should be made available.

6.6 CO_2 absorber feed cooling system of EO plant: Any deviation in flow process of a recycled gas to the CO_2 absorption system through heat exchanger (H2 &H4), may cause a possible effect on the system as flooding of CO_2 absorber and carry over of the carbonate solution to the recycle gas loop, low temperature in CO_2 absorber of recycle gas or high/low flow of gas in the exchangers, the main reason for these causes are blocked line, maloperation of pressure difference controller/indicator or failure of pump & safety valves. Moreover, level deviation in the separator may also bring a possible gas break through the stripper and possible carry over of carbonate to separator, due to the fact mal-operation of the level controller, failure of outlet valves or high carry over of gas in the separator. Preventive corrective measures are introduced to safeguard the process system against the risks, such as by pass valve, high pressure differential trip on CO_2 absorber, high/low level alarm & trip, knock-out drum with a level controller, etc.

6.7 EO stripper overhead chiller of EO plant: A brine solution is fed to the EO stripper through the heat exchanger E2. Any deviation or changes in the process parameter (as flow) may effect the heat exchanger E2 badly i.e. high duty on E2 for high flow and increase EO loses in the vent gas and higher load on the EO vent absorber possibly on the residual gas absorber in case of low flow of brine through exchanger E2. The main reason behind these effects are throttled globe valves in the line to E2, mal-operation of the control valve, the main line is blocked and failure of brine supply to the chiller unit. Likewise rise and decrease of temperature may also affect the E2 as higher EO vent losses due to lack of cooling and possibility of hydrate formation due to low cooling temperature. Preventive corrective measures such as high temperature alarm & trip should be provided and a chillers temperature controller should be maintained at 13°C.

6.8 Lean flash tank of EO plant: As steam flows from the CO_2 stripper to the flash tank, if the flow process is changed from its normal function it may affect the unit operation as well, this may lead to high level of steam in the CO_2 stripper and low level of steam in the flash tank when no/less flow occur. On the contrary high load of steam on the flash tank and low level of steam on the CO_2 stripper may occur when more flow takes place. Usually this affect occurs if there is a mal-operation of flow controller, low pressure in the steam head or the main stream line is blocked. Moreover deviation in level may also result in overfilling of steam in the flash tank if excess level of steam occurs due to pump failure or if steam line is blocked, and also if the pump gets surge if low level of steam in the flash tank occurs due to no feed from the CO_2 stripper or failure of level controller. High level alarm/trip and low level alarm/trip are the right preventive measures that should be provided.

6.9 Lean absorbent chiller of EO plant: The main factor in this section is a flow pattern of lean absorbent & steam to the chiller. If there is no/less flow of lean absorbent to the chiller, then the chiller trips (under equipment), the consequence due to the failure of pump or stream line blocked. Similarly no/less flow of steam to chiller may give rise to no/less chilling effect to the chiller and high temperature to the EO absorber due to loss of steam, stream line blocked or mal-operation of the controller. For preventing the further affect on the process, a pressure drop indicator should be provided which will activate O_2 shutdown system.

6.10 Fat absorbent heat exchanger of EO plant: In this section of study, heat exchanger E1 plays a vital role. The lean absorbent from EO absorber is passed through the exchanger E1 for maintaining the required chemical property of the feed substance before entering into the EO stripper section. Any change or deviation in the flow pattern will effect the process badly viz. in the case of no flow in the E1 gives no feed to the EO stripper and higher pressure in the feed line & equipment, the case of high flow of lean absorbent in the E1 gives over load in the stripper and loss of level in the absorber with possible gas break through, and the case of no steam flow in the exchanger E1, will cause low temperature of feed to the stripper. Similarly, change in temperature and pressure may also give undesirable consequences i.e. glycol formation lead to high temperature due to more temperature in the E1 and feed to the EO stripper at lower temperature due to less temperature in the E1 and more pressure than the design pressure due to high pressure on process side of E1. All these undesirable and hazardous affect on the unit process can be minimized by implementing the safe and sound measures such as low temperature alarm, live steam input which will compensate for the lack of heat, low level trip on EO absorber and thermal relief valves.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

HAZOP study in EO section of MEG plant has been carried out successfully by showing all the possible causes and the adverse consequences of failure or malfunction of the process units. A preventive action and process modification has been performed after this HAZOP study, to safeguard the operating system from undesirable accident in future such as

1. High temperature alarm and differential pressure indicator are installed in the EC buffer vessel to alert the operator in the event of excess temperature of feed and pressure drop in the vessel
2. Since exothermic reaction is taking place in the EO reactor, proper O_2 shut down system (OSS) and relief valves has been installed to prevent the reactor from explosion or ignition in the event of high reactor temperature. And a steam drum is properly maintained for controlling the parameter (temperature) of reactor in the event of cooling malfunction
3. High pressure alarm, safety valves and low level alarm & trip, has been installed in the H_2O surge drum for maintaining the water level and cooling process of the reactor in the event of failure of BFW supply, mal-operation of controller system and valve failure
4. High pressure differential trip and high/low level alarm are introduced to prevent the CO_2 absorber from high pressure in the absorber and failure of level controller
5. High temperature alarm and trip has been installed in the heat exchanger E2 to prevent from EO vent losses and the chillers temperature controller is also maintained at 13°C
6. Flow meter and level controller are installed in the line where steam flow occur from the CO_2 stripper to the flash tank in the event of less/more flow
7. Pressure drop indicator and high temperature alarm has been installed in the chiller to alert the operator in the event of failure of chilling effect due to high pressure and temperature

8. Temperature controller, thermal relief valves and flow meter are installed in the fat absorbent heat exchanger E1 to prevent from excess temperature in the exchanger E1 and mal-operation of valves

HAZOP study is a qualitative approach, therefore it consumed less time and easy to carry out compared to quantitative analysis such as risk assessment, LOPA, risk ranking matrix, etc. and Moreover, this HAZOP study not only identifies the hazards but also increases the operating life and performance of unit process and makes it environmental-friendly as well.

7.2 Future work

The present work described and concentrated logically on identifying the possible causes and consequences of variable deviations, but further research and analysis may required to assess the hazards. LOPA (Layer of Protection Analysis), risk rating matrix, PHA (Process Hazards Analysis) etc. are the semi-quantitative analysis which required qualitative analysis (HAZOP study) results for conducting the analysis to assess the hazards.

Further, it is recommended that computer and artificial intelligence should be more extensively used for HAZOP studies as well as plant safety. Already a program (software) such as TOPHAZOP, iTOPS, HAZOPExpert etc. are being propose as easy and efficient way of doing HAZOP study. This is because such systems can facilitate HAZOP reviews at an early stage of process development and design. This means that problems can be identified and rectified during detailed design or while formulating operating procedures. Making changes once a plant is built are very expensive compared with changes at the design stage (Skelton, 1997). Early identification of hazards will also lead to effective avoidance or control of such hazards. HAZOP at this stage will also help to develop confidence that the desired process is safe. Along these lines, the longer-term aim may well be to move towards process conception and synthesis to create inherently safer designs and operating plants that tend towards zero defects. A more immediate development could be the use of online hazard reviews for the training of operators for abnormal situation management. The online hazard models can also be adapted for fault diagnosis applications. Intelligent systems are now well poised to make significant contributions to PHA in real-life industrial settings thus improving the quality of the analyses while reducing the time and effort involved.

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Electronic resources:

1. HAZOP guideline (http://pie.che.ufl.edu/guides/hazop).

2. HAZOP method(http://www.acusafe.com/Hazard_Analysis/HAZOP_Technique.pdf).

3. HAZOP manager V6.0 – software for a HAZOP study and other PHA reviews (http://www.lihoutech.com).

4. Safety, risk, safety audits, health and safety audits, chemical reaction hazards; UK safety (http://www.chilworth.co.in/hazop.htm).

5. HAZOP analysis block flow diagram (http://www.smsink.com/services_pha_hazop.html)

6. HAZOP – Wikipedia, the free encyclopedia (http://en.wikipedia.org/wiki/Hazop).

APPENDIX

Hazardous chemical/material data and Safety action:

1. Ethylene

- Ethylene is a colourless gas with a characteristic sweetish odour
- Ethylene burns with a luminous flame. It is a simple asphyxiant

Hazards:

- Ethylene spontaneously explodes in sunlight with chlorine
- Ethylene can react vigorously with carbon, tetrachloride, nitrogen dioxide, aluminium chloride & oxidizing substance in general. Ethylene air mixtures will burn when exposed to any source of ignition like static, friction or electric sparks, open flames or excess heat

Toxicity:

- Ethylene has a very low order of systemic toxicity. When used as a surgical anaesthetic, it is always used with O_2
- Prolonged inhalation of about 85% of ethylene in O_2 results in slow fall of blood pressure
- At about 94% in O_2, ethylene in liquid for reaction suffers "freezing burns"

Treatment:

- Persons affected by exposure to ethylene should be moved to fresh air, kept warm & comfortable
- If breathing has stopped, artificial respiration should be given immediately. If there is eye contamination with liquid ethylene, eyes should be flushed with water for atleast 15 to 20 minutes & medical attention obtained.

2. **MEG (Mono Ethylene Glycol)**

- It is a colourless, sweetish liquid, and soluble in water
- TLV for MEG in particular form is 10mg/m^3. TLV for MEG in particular form is 50 ppm
- STEL (short term exposure limit) for MEG in particular form is 20mg/m^3, for a maximum exposure period of 15mins. Lethal dose of MEG for man is about 100 cm^3 per person

Health hazards:

The primary health hazard of MEG is related to ingestion of large quantities

- Excessive intake of MEG causes narcosis, depression of the respiratory centre and progressive kindly damage
- Eyes & skin irritation is generally mild at room temperature
- MEG vapours inhaled at room temperature do not present a significant health hazard
- MEG if vigorously heated or agitated can present an industrial inhalation hazard

3. DEG (Di-Ethylene Glycol)

- It is a colourless syrupy liquid, soluble in water. It is quite similar to MEG in toxicity and mode of action
- Inhalation of vapours of DEG at room temperature does not present a significant health hazard

Health hazards:

- DEG if ingested in excessive does can diuresis , thirst, loss of appetite, narcosis, hypothermia, kidney failure and death progressively
- DEG if heated or agitated could generate an industrial inhalation hazards

4. EO (Ethylene Oxide)

- It is a hazardous material in term of toxicity, flammability in air and chemically unstable, it can be handled and stored with safety provided appropriate precaution observed
- "Active level" of EO means a concentration of air-borne EO of 0.5 ppm, calculated as an 8 hr time weighted average (TWA)
- " Permissible exposure limits" (PEL) of EO is one part EO per million parts of air (1ppm) as an 8 hr TWA

Properties of EO:

1. Formula: C_2H_4O
2. Molecular weight: 44
3. Boiling point: 10.5°C (range 10.4°C – 10.7°C)
4. Freezing point: -111.3°C
5. Flash point: -17.8°C
6. Density at 4°C: 890 kg/m3
7. Flammable limits in air (by volume): lower 3% & upper 100%
8. Miscible with water at all concentration
9. Auto-ignition temperature in air at atm press: 429°C
10. Density temperature in the absence of air: 560°C
11. Latent heat of vapourisation: 569KJ/kgK
12. Sp.heat - liquid: 1.95 KJ/kgK
13. Threshold limit valve (TLV): 5ppm (vol)
14. Sp.heat – gas (1 atm 34°C): 1.10 KJ/kgK
15. Heat of polymerization of liquid: 92,100KJ/kg mole

16. Heat of decomposition of gas: 83,700KJ/kg mole

17. Heat of combustion: 29,400KJ/kg

Health hazards:

- Acute effects: since EO boils at 10.5°C and vaporizes at atm temperature and pressure, exposure of personnel to vapour in the work environment is a more likely hazard than is content with liquid EO. The vapour is irritant to eyes and respiratory system and exposure causes headache. It may cause cancer and heritable genetic damage

- Long-term effects: resproductive effects have rated at a level of 100 ppm. EO has been shown to be a nitrogen in a wide variety of biological systems including experimental animals

- Effects of liquid EO on skin & eyes: although EO vaporizes rapidly at normal temperature and pressure under open condition, particularly at winter temperature

- Monitoring & records: regular personal monitoring is recommended, augmented where appropriate with area monitoring & leak-seeking

Chemical hazards:

- Very dangerous fire hazard when exposed to heat or flame, and a severse explosion when exposed to flame

- The vapour may be readily ignited into explosion decomposition in the absence of air

- As traces of acetylene in EO may produce metal acetylides able to detonate the vapour, metal fitting containing copper, silver, mercury or magnesium should not be used in EO service

- Heating & subsequent cooling may cause continuing exothermic polymerization leading to container pressurization and explosion

- Ignition and decomposition may occur if dilute EO vapour are rapidly compressed and violent decomposition of a polyester-alcohol prepared from ethylene oxide and propylene oxide with a polyhydric alcohol above 100°C

Uses of EO:

- EO is used as intermediate in the production of various chemicals, such as ethylene glycol, various non-ionic surfactants, polyethylene glycol, mixed polyglycols, glycol ethers, ethanol amines and lubricants
- It is also used in fumigation and sterilization of foodstuffs and medicals equipment

Safety precautions:

- Avoid exposure obtain special instruction before use
- Keep container tightly closed, in a cool well ventilated place
- Keep away from sources of ignition- no smoking
- Take precautionary measures against static discharge

Instruments and Safety devices:

- Level measurement devices must be of the float differential pressure (DP) or torque-tube types and fitted internally. Glass level gauge must not be used. Tanks must not be sampled or gauged through dip-notches.
- High level and high temperature alarms must be fitted to the reactor and storage tanks independently of the corresponding indicators or recorders.
- In order to monitor trends in the temperature of stored EO, recorders should be fitted for large vessels in which homogeneous mixing is difficult to achieve the temperature measurement should be made at several level and high temperature alarms should be provided for each level. Such precautions are necessary to ensure that the changes in temperature are quickly recognized and appropriate actions are initiated.
- Pressurized storage tanks must be fitted with pressure measuring devices and should give warning if excessive pressure builds up in the tank or vacuum condition are approached.
- Relief valves should be fitted as close as possible to the storage vessel to prevent possible polymer build-up.

- Relief valves and vent system should discharge to vent stack fitted with flame arrestor and if steam or N_2 are available, this stack should be fitted with a sparger.

- Fire relief valves should be fitted in accordance with recommendations made in the codes of practice relating to liquefied petroleum gases and liquefied flammable gases.

- Bursting disc must not be used for pressure relief because they could lead to uncontrolled emission until the vessel is empty.