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Hazard and Operability (HAZOP) study of wastewater treatment unit producing biohydrogen

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Abstract: Risk assessment is an important activity carried out in chemical process plants to ensure health and safety of all concerned. This paper deals with the risk assessment of a particular case study by using reliable technique of HAZOP (Hazard and Operability). The HAZOP study can be used as basic source of information for the design of any commercial plant and to provide positive impacts on the project before and after implementation. The main objective of this work is to apply this tool in a theoretical scenario for which a typical modern industrial wastewater unit producing biohydrogen was selected. For reliable HAZOP study whole process design was done on the basis of Process flow diagram (PFD), Piping and Instrumentation diagram (PID) and standard key words. Then the hazards of whole process were identified and initially some basic safety techniques have been applied to address these issues. Lastly, the results were evaluated indicating that an overall assessment yielded about 57 risks. However for safer system design, about 63 actions were recommended whereas most of them (71%) will need to install new devices.

Keywords: HAZOP, Process Flow Diagram, Waste Water Treatment, Bio Hydrogen Piping and Instrumentation Diagram

1. INTRODUCTION

The Hazard and operability (HAZOP) study forms an integral part of most process safety and risk assessment programs applied worldwide as a methodology for identifying and studying not only hazards, but also operability problems of a system. A HAZOP study is a proper, organized, and critical examination of the process of new or existing facilities to evaluate the potential for malfunctioning of equipment and property in terms of the resultant impacts (Dunjó, *et al.,* 2011). (Denti, 2010). The concept of a HAZOP study originated with the goal of identifying possible hazards present in chemical industries and process plants. (Angel *et al.,* 2015). . The purpose of the study was to eradicate any source leading to major accidents, such as toxic releases, explosion, etc. (Dunjó, *et al.,* 2010) (Galante, *et al.,* 2014). HAZOP analysis helps identify the safety issues as well as the hazards that can cause damage to the property and the personnel in addition to the operability problems which may lead to production losses due to inferior product quality or the process inefficiency. Therefore, HAZOP recognizes both problems that may compromise facilities' safety as those that may cause loss of continuity or loss of the product specification. The application of HAZOP is concerned with making relevant questions in the form of critical points, also called as nodes. The method involves a detailed study of the entire process from beginning to end with the help of Process variations in process conditions in relation to temperature, pressure, material or energy flows. The initial HAZOP study then help identify the protection measures that may be put in place to avoid impending accidents (Ashok, *et al.,* 2014) (Khan , *et al.,* 1997).

In this work use of HAZOP study was taken in account for the case study of proposed waste water treatment unit. The unit used an innovative biological conversion of the same waste water to bio-hydrogen production. Bio-hydrogen is produced from waste water through fermentation process including combined thermophilic or dark fermentation and photophilic fermentation process, where energy is produced in form of Bio-Hydrogen and waste water treatment takes place simultaneously. This research attempts to introduce suitable method of HAZOP analysis for the given process as compared to more conventional method such as qualitative matrix method (Habibi, *et al.,* 2008).

2. HAZOP METHODOLOGY

The proposed case studies for HAZOP study contain waste water treatment unit of chemical industry. Briefly, Bio-hydrogen is produced through biological conversion in the proposed waste water treatment unit of chemical industry. The feed for the plant was prepared by adding glucose, KOH_{aq} solution, recycle and nutrients. The purpose of addition of glucose was to enhance the conversion of waste water into Bio-Hydrogen. The process includes the feed stream which is pumped to heat exchanger exchanging heat with the bottom product (acetic acid solution) of Thermophilic Fermentation or Dark Fermentation Reactor. The outlet stream from heat exchanger then passes through the furnace for maintaining temperature of feed stream

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required in to Reactor, and then fed to the Reactor. The product stream from the reactor contains gaseous stream which leaves from top of reactor and consist of hydrogen, carbon dioxide and water vapor and liquid stream leaves from bottom which consists of acetic acid, water and solids which enters in Clarifier after heat exchanger. Solids separate as under flow and clear liquid as up flow from the Clarifier which then pumps the to Storage tank, as Photophilic Fermenter operates only in day time. From the storage tank the liquid after mixing with alkaline solution, recycle and nutrients cools in a cooler and pumped to photophilic fermenter. The product stream from Photophilic Fermenter contains gaseous stream that leaves from top of reactor consisting of hydrogen, carbon dioxide and water vapor and liquid stream which leaves from bottom consist of unreacted Acetic acid, Water and Solids which enters in Clarifier. Solids are separated from Clarifier as under flow and clear liquid as up flow from which 50% is wasted and remaining 50% is recycled into both Thermophilic and Photophilic Fermentation reactors. **(Fig-1)** shows the schematic of the waste water treatment unit. The documents required initially in the HAZOP study includes, proposed Process Flow Diagrams (PFDs), proposed Piping and Instrumentation Diagrams (P&IDs), proposed plant Layout and technical details were gathered by the team members.

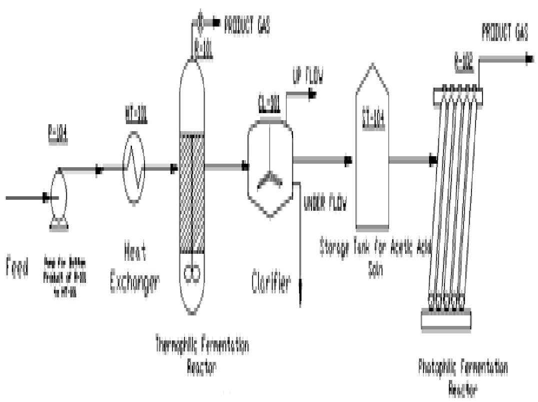

Fig-1: Schematic of Proposed Waste Water Treatment Unit for HAZOP Study

The critical nodes of the process included storage tank containing waste water, thermophilic fermentation reactor, photophilic Fermentation Reactor, Heat Exchanger, Clarifier or Settling tank and Pump were chosen as the subject of HAZOP study. To accomplish the hazard analysis, a "HAZOP Matrix" was constructed for each considered node. For the considered nodes the process parameters such as flows, pressures and temperatures were examined to determine possible deviations which could lead to ultimate hazards. For each deviation, the HAZOP study identified all the possible causes for that deviation. The consequences for each deviation were then listed, and finally recommendations were made to minimize the effect or to prevent the consequence. Common recommendations from the HAZOP study included the installation of high and low alarms (to warn the operator about deviations). Changes in P&IDs have been done after HAZOP study.

3. RESULTS AND DISCUSSION

The procedure of HAZOP followed the steps already described above and the HAZOP spread sheet was prepared. For simplification, each important subsystem and the auxiliary equipment were considered as a node. First node was Thermophilic Fermentation Reactor to produce Bio-Hydrogen and Acetic acid, second was Heat Exchanger which exchanges heat with cold feed and hot reactor bottom product, third was Clarifier or Settling tank to separate solid mass with acetic acid, fourth was Photophilic Fermentation Reactor which converts the remaining acetic acid into Bio-Hydrogen, fifth was Storage Tank which was used to store acetic acid solution during night and sixth was pump which was used to transfer the Thermophilic bottom product to heat exchanger. This makes a total of 6 nodes which were recognized, evaluated and HAZOP study was documented in 12 pages, summarized in Table 1. The team members primarily focused on the operational problems and more attention was focused on the deviations with negative influence on the operation of the system resulting in financial losses and personal injuries. Generally, in this study, 38 deviations or possible causes were identified in which 21% were related to first node, 18.4% were related to second node, 13.5% to third and 15.78% to fourth, 15.78% to fifth and 15.78% to sixth node. As the result shows one deviation can have several causes and effects, in the study, 57 causes of deviation were identified of which the main causes includes; Control valve malfunctions or failure results in fails open or fails close, malfunctioning of valves, blockage of outlet valves, Indicator and controllers fails causing variations in parameters (Temperature, Pressure, Flow, Composition), failure of Furnace and Cooler, malfunctioning of Pump, back flow in Pump, blockage of pathways or rupture in pathways, deviations in weather conditions like cold, hot or external fire, presence of different contaminant in feed and increased corrosion.

The causes were mainly related to equipment (72%), operation or manual (21%) and other (7%). A total of 63 actions and recommendations were suggested. Suggestions were mainly related to modification or improvement and installation of new equipment like alarming systems, strainers, supporting and by-pass valves, etc. (71%), proper inspection and periodic maintenance of equipment (20.6%) and correct operational methods (7.9%).

Table1: Summarized Table of Hazard and Operability (HAZOP) Study.

Guide Words	Deviation From operating conditions	Possible causes	Consequences	Action Required
None	No flow	1. Flow Control valve Failure (FCV-003) fails close. 2. Valve V-013 malfunctions 3. Failure of pump P-104. 4. Valve V-011 malfunctions. 5. Scaling in line (ASS-114) 6. (FIC-005) fails closing (FCV-005). 7. (LIC-002) fails closing (LCV-002). 8. FIC-008 fails closingFCV-008. 9. Scaling in line (L-118) 10. LIC-003 fails closing LCV-003. 11. Failure of pump P-105. 12. V-017 Closed or malfunctions. 13. FCV-004 Fails Closed 14. FIC-004 fails closing FCV. 15. LCV-001 fails Closed.	Reactor runs empty. Damage to the pump. Pressure increases in Line (MF-110). No heat transfer. Same exit and entrance temperature. Same as above. Pressure in line increases. No flow to the Clarifier (CL -101). No feed pass through the Clarifier (CL -101). No feed to Reactor R-102. Pressure in line increases. No flow to the Storage tank (ST -104). No flow to the Storage tank (ST -104) Pump Cavitation. Pump Cavitation. Deadhead Pump Pump Cavitation. Deadhead Pump	Use supporting valves with FCV-003. Check either FIC-003 properly working or not. Periodic Inspection of valve should be done. Stand by pump should present. Maintenance of valve V-011 and instrumentation. Proper inspection and maintenance of line should be implemented. a. Use supporting valves with FCV-005, and Use alarming system. b. Proper inspection and maintenance of all equipment's should be implemented. Use supporting valves with LCV-002, and Use alarming system. a. Use flow alarming system. b. Proper maintenance of all control systems should be considered. Proper inspection and maintenance of line (L-118) should be implemented. Use supporting valves with LCV-003, and Use alarming system. Stand by pump should present. a. Regular checking of valves. b. Use stand by pump. Use Supporting valves with FCV. Use alarm system. FAH,FAL Use Supporting valves with LCV-001.
More of	More flow	1. Valve malfunction (V-013), results in fully open valve. 2. Flow control valve (FCV-003) fails open. 3. (FIC-003) fails due to which feed flow rate increases. 4. Control valve (V-011) malfunction. 5. Control valve 6. (LCV-002) fails open. 7. FCV-008 fails open. 8. Control valve 9. (LCV-003) fails open. 10. FIC-004 fails opening FCV-004 11. FCV-004 fails open. 12. LCV-001 fails open.	Pressure in line (MF-110) increases. More flow results in reactor R-101. Quantity of feed increases thereby increasing load on the tubes. Improper heat transfer Liquid carried to the overhead section of settling tank(CL -101) Overloading of Reactor R-102. a. Liquid carried to the overhead section of settling tank(ST -104) b. Flooding may occur More flow to pump causing damage to pump. Temperature and pressure increases. More flow to pump causing damage to pump.	Regular checking of valves. Use supporting valves with FCV-003 Use flow alarm high. Regular checking and maintenance of valve (v-011). Install high level liquid alarm in the settling tank CL -101) Use flow alarm high at HAS-130 line. Install high level liquid alarm. a.Use Drainage valve. b.Use alarm system. Use supporting valves with FCV-004 Use supporting valves with FCV-004
	More pressure	1. Blockage of outlet valves (V-014). 2. Outlet valve (V-025) malfunctions 3. Back flow occurs in pump, if pressure at discharge of pump increases. 4. FCV-004 fails open. 5. V-017 fully opens or malfunctions	Temperature and pressure Increases. Possible vessel failure may occur. Voids implode and generate intense shockwave. Damage to pump. Same as above	Use pressure relief valve. Use relief valve. Use check valve at pump discharge. Use pressure indicator at pump suction. Use drainage valve

	More temperature	**1. TIC-003 fails causing high feed flow. 2. External fire. 3. FCV-003 malfunctions causing increase in temperature of fluid entering in clarifier CL-101 4. Cooler (C-101) fails to operate. 5. Hot Weather or External fire. 6. FCV-004 fails open. 7. Too much increase in temperature in reactor R-101.**	**Too much increase in temperature effect activity of bacteria. Failure of HT-101. Settling efficiency may effect. Feed to Reactor enter at high temperature than normal. Material of construction of the storage tank (ST-101) may affected. Temperature and pressure Increases, causing pump damage. Possible Pump failure.**	**Use temperature alarm High. Use by-pass system. Feed temperature should be adjusted in Heat exchanger before it enters the clarifier CL-101. Use temperature alarming system in reactor R-101. Use proper material of construction for Storage Tank. Use supporting valves with FCV-004. Use temperature alarming system in reactor R-101.**
	High PH	**1. OIC-001 fails. 2. OC-002 fails.**	**Bacteria activity may affect if PH increases from the PH range of Bacteria. Reaction may be affected due to increase from the PH range of bacteria.**	**Use high PH alarm. Use high PH alarm.**
Less of	**Less flow**	**1. Inlet valve (V-013) malfunctions. 2. Blockage of line 108. 3. Inlet valve (LCV-002) malfunction. 4. Scaling or corrosion in line (ASS-114) 5. Flow Transmitter FT-002 malfunctions. 6. Rupture in line MF-129 7. Inlet valve (LCV-003) malfunctions. 8. Scaling in line. 9. V-017 partially closed.**	**Reaction rate affected. Improper heat transfer due to less flow of hot fluid (acetic acid solution). Less amount of feed entered into the clarifier CL-101. Less amount of feed entered into the clarifier CL-101. Incorrect information transmitted to FIC-004. Loss of material (Acetic acid solution). Less amount of feed entered into the Storage tank. Pump Cavitation. Damage to pump**	**Use flow alarm Low. Use By-pass system. Use supporting valves with LCV-002, and Use alarming system. Corrosion allowance of 2 mm should be considered in lines. Use alarming system. Proper maintenance of line MF-129 should be carried out. Use supporting valves with LCV-003, and Use alarming system. a. Proper Maintenance and checking of line. b. Corrosion allowance of 2 mm should be considered in pipes. Connect a stand by pump and start it.**
	Less Temperature	**1. Furnace F-101 fails. 2. Cold Weather. 3. Cooler (C-101) fails to operate.**	**Too much decrease in temperature effect activity of bacteria. Improper heat transfer. Feed to Reactor enter at high temperature than normal.**	**Use temperature alarm Low. Use Temperature Gauge. Use temperature alarming system in reactor R-101.**
	Lower PH	**1. OIC-001 fails. 2. OC-002 fails.**	**Bacteria activity may affect if PH decreases from the PH range of Bacteria. Reaction may be affected due to PH range of bacteria.**	**Use PH alarm Low. Use high PH alarm**
As well as	**Impurities**	**1. Presence of different containment in feed.**	**Affect the performance of heat exchanger.**	**Regular checking required.**
Others	**Maintenance Speed High solid content.**	**1. Accumulation in shell and tube side. 2. If speed of agitator increase from 1 rpm. 3. High amount of unreacted material arise from reactor R-101.**	**Resulting in corrosion. Improper effect of separation. Damage to pump**	**Regular inspection should be done. Make sure speed of agitator does not exceed 1 rpm. Use strainer or filter before pump suction.**

4. CONCLUSION

This study encompasses the use of qualitative analysis i.e. HAZOP in a hypothetical scenario of a proposed waste water treatment unit of chemical industry. In order to achieve the aim of this study, first task was to identify the nodes using proposed Process flow diagrams (PFD), Proposed Piping and Instrumentation Diagrams (P&ID) and proposed Unit layout. A total of 6 nodes were recognized and evaluated, on which HAZOP study was conducted. Possible deviations during the HAZOP study were generated by various questioning, encouraged by a series of guide words to the intended design. After the guide words were matched with parameters, a deviation is created for the considered system of chemical unit, it was essential to identify all deviations of operation parameters i.e. temperature, composition and flow rate and their consequences. As the deviations lead to several causes, a total of 57 causes were evaluated in which more than half of the identified causes were related to the equipment defects followed by operational error. In order to improve safety and reduce risk, 63 actions were recommended, however most of them (71%) involve installation of new equipment especially alarming system to warn the operator about any unusual situation. Although major consideration should also be given on the application of instructions for regular inspection and periodic maintenance of the equipment which plays an important part in reduction of hazards.

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