

Hazop Analysis of a Continuous Biodiesel Production Plant

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Abstract

The imminent risk in the production of biofuels can cause damage to the environment and the health of the local community. Based on this premise, and given the scarcity of industrial safety studies aimed at biodiesel plants, this research aims to carry out a study of hazards and operability (Hazop Analysis) in a continuous industrial unit of biodiesel implanted in the Technology and Quality Center of Ceará (NUTEC), in order to identify the main risks and propose measures to minimize them. For this purpose, the PFD (Process flow Diagram) of the unit using Microsoft Visio ® software, eight "nodes" were defined for the study, parameters and guide words were established, and, finally, the hazop tables were constructed. Due to the nature of the process, the parameters that stood out were flow and temperature with an incidence of 100% and 75% in the tables, respectively, while the critical "nodes" of the process were Heating and Cooling. In view of this, preventive maintenance and the adoption of a precise control system were highlighted as the main necessary actions. The study stands out for presenting a continuous industrial unit of biodiesel production with different production routes. And, although the risk assessment using the Hazop methodology has enabled an assessment of the main causes and effects caused by failures in the unit, it is observed that a study applied using quantitative techniques, such as Fire and Explosion Index (F&EI), Chemical Exposure (CEI) and Layers of Protection Analysis (LOPA), will enable prevention measures to be applied more safely.

Key-words: Industrial Safety, Continuous Industrial Plant, Biofuel.

1. Introduction

The use of fossil fuels is associated with, above all, environmental issues such as global warming driven by the emission of greenhouse gases (Furtado, 2020; Jiang *et al.*, 2017; Río *et al.*, 2019). In this way, the development of new energies, especially renewable energies, is considered the focus of a new trend of promotion and progress of the industry and since 1993, the production of biodiesel has increased considerably worldwide (Mao *et al.*, 2018); Gumus; Kasifoglu, 2010; Azad *et al.*, 2015).

Biodiesel is a biodegradable fuel, derived from renewable sources and obtained through the processing of vegetable or animal fat, ethanol or methanol and catalysts (Petrobrás, 2014). The main raw material for the production of biodiesel is vegetable, such as soybean oilseeds, sunflower seeds, cotton, castor beans, among others (Dandu; Nanthagopal, 2019; Singh *et al.*, 2020). As a method to obtain it, Transesterification is widely used, which also produces the by-product glycerol, diacylglycerides and monoacylglycerides (Bet-Moushou *et al.*, 2016; Consoni, 2017; Meneghetti; Meneghetti; Brito, 2013).

Regarding the national context, biodiesel was introduced into the Brazilian energy matrix through the National Program for the Production and Use of Biodiesel (Brasil, 2020). In 2019, 5,902,461 m³ of biodiesel were produced in Brazil and until June 2020 the production was 3,000,000 m³, thus evidencing its great representation in the national energy matrix (Anp, 2020).

With the increase in the number of industrial biodiesel units, a more in-depth study on the prevention of risks to employees and the community arising from industrial activity became necessary (Baraza; Castejón; Guardino, 2015). Therefore, *HAZOP* (*Hazard and Operability Studies*) emerged as a tool for identifying possible scenarios (Sella, 2014). *HAZOP* analysis is a structural and systematic approach, carried out by a multidisciplinary team during a set of brainstorming meetings (Guo; Kang, 2015).

HAZOP analysis deduces the possible causes and consequences for a given process deviation by matching the guide words with the process parameters. This is characterized as a qualitative analysis method (Tian; Du; Mu, 2015; Kang; Guo, 2016). Hazop is a well - accepted procedure in the industry and has the advantages of being an easy-to-understand accident investigation tool in complex systems (Toungsetwut, 2012; Crowl; Louvar, 2015).

Therefore, the present study has as objective the concepts of industrial safety to carry out the *HAZOP analysis* in a continuous industrial unit destined to the production of biodiesel implanted in

the city of Fortaleza-CE, in the Fundação Núcleo de Tecnologia Industrial - NUTEC, in order to identify the main risks, as well as proposing mitigation measures for them.

2. Methodology

The development of this study was carried out through the elaboration of the process flowchart (PFD-*Process flow Diagram*) of the unit, in which Microsoft Visio ® *software was used* to allow a more complete view of the process. Based on this and aiming to qualify the intention of the process in order to identify possible deviations, the "guide words" "more, greater", "less, less", "no, none" referring to the process parameters "temperature", "level" and "flow". Therefore, by applying these guide words it is possible to identify probable deviations. Thus, for the Hazard and Operability Analysis (*HAZOP*), Table 1 was used, adapted from Aguiar (2008).

Table 1 - HAZOP Model

System subsystem	System/Subsystem:		At the:		Date:	
Parameter:				Page:		
v 1 ()	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	

Source: Adapted from Aguiar (2008)

This table allows the identification of possible process deviations, possible responsible causes and the respective consequences for production, safety and the environment. Necessary actions, therefore, are recorded from the analysis of the defined nodes.

3. Results and Discussion

3.1 Delimitation of Study Nodes and Process Flowchart (PFD)

Hazop tables, a priori the study nodes were delimited, which refer to the small fractions of the process. These are presented in Table 1 below.

At the	Occupation
1	Food
two	transesterification
3	Phase I Separation
4	Phase II separation
5	Purification of biodiesel I
6	Purification of biodiesel II
7	Heating
8	refrigeration

Table 1 - Nodes in the System and their Functions

Own authorship (2020)

Feeding node 01 is related to the storage of anhydrous alcohol, catalyst (NaOH or KOH) and vegetable oil, which are subsequently pumped to node 02 where the raw material will undergo the transesterification reaction step. The process starts with the input of the reactants directed either to the CSTR group of reactors (continuous stirred tank reactor), or to the static mixer, if the flow is directed to the PFR group (Plug Flow Reactor). Node 03 is Phase Separation I, where the ester and glycerin phases are separated through the horizontal decanter. In phase separation II, node 04, the biodiesel is separated from the glycerin and alcohol and is destined for node 05, Purification of biodiesel I, where the washing and acid treatment processes take place to hydrolyze the traces of glycerin. In node 06, Purification of biodiesel II, the biodiesel will undergo the dehumidification process in the evaporators. Node 07, Heating, is related to the generation and distribution of heat, while node 08, to water cooling, which are industrial utilities and influence various stages of the process. Figure 1 depicts the process flowchart of the unit and provides an overview of the continuous biodiesel production model.

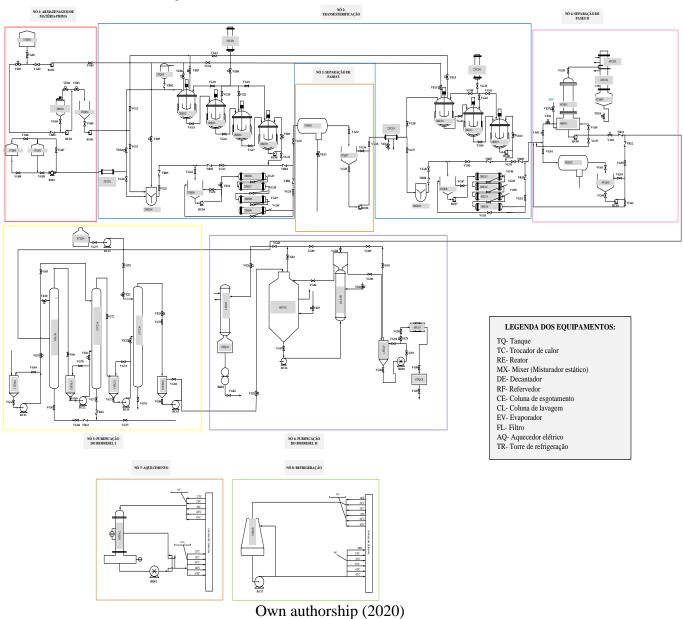


Figure 1 - Process Flowchart of the Continuous Biodiesel Unit

3.2. Construction of HAZOP Tables and Discussion of Results

The parameters level, flow and temperature were defined for the study, as well as the guide words "more/higher", "less/lower" and "none". Table 2, below, presents the *hazop analysis* for the power node, in which the study parameters are flow and level and the guide words are "more", "less" and "none". Using these guide words, evaluations are carried out regarding possible causes and possible effects that these may cause in the unit under study.

Unit: NU	JTEC					
System:	Raw material s	torage		Node 01: Food		
Paramet	Parameters: Flow and Level			Date: 09/01/2020		
Study point (node)	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
1	1 Flow rate	Most	Increased power load. Inefficiency in the flow control loop.	Catalyst dilution problem. Low conversion yield. Inefficiency in the dehumidification of vegetable oil.	Evaluate the pumping system and control loop of this node for flow.	
		Any less	Power load reduction. Problem in BC02 centrifugal pump and BS01 gear pump; pipe leakage.	Increase in processing time and reduction in final production.	Predictive and preventive evaluation and control of the pumping system and process valves.	
		None	No anhydrous alcohol and catalyst solution. Problems in the flow control loop. Stoppage of the pumping system, obstruction in pipes and valves.	Shutdown of the Plant's power system. Cancellation in the production of the Plant.	Perform evaluation in the control loop for flow corresponding to the respective node.	
	Level	None	Lack of anhydrous alcohol and catalyst solution or organic matter, problems with the node level sensors.	Shutdown of the Plant's power system. Cancellation in the production of the Plant.	Perform evaluation in the control loop for the level corresponding to the respective node.	

Table 2 - Hazop Analysis for Node 01

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Based on the table, it is noted that flow above the ideal volume could result in problems in catalyst dilution, low conversion yield and inefficiency in vegetable oil dehumidification, whereas flow below the ideal volume would cause an increase in processing time and reduction in final production, while the lack of flow could cause the unit's supply system to stop. Regarding the level, when non-existent, it can cause the plant to stop. The necessary actions to be implemented must be preventive maintenance of the equipment and evaluation of the control loop for level and flow. Since for node 1 the feed will be the study variable to be maintained and controlled, the techniques that involve surveys of parameters which can maintain the continuous flow of material should seek to maintain the flow stages throughout the unit. Laminar, turbulent regime parameters and unit stoppage can cause non-compliance in the final product or non-existence in production. Next, Table 3 presents the *hazop analysis* for node 02, Transesterification, in which temperature and flow were considered as the process parameters.

System:	Transesterifica	ation		Node 02: transesterification			
Parameters: Temperature and Flow			Date: 09/01/2020				
Study point (node)	Process Parameters	Deviations (guide words)	Possible ca	auses	Possible consequences	Necessary actions	
two	Temperature	Most	Greater hea thermal oil oil pumpin failure.	. Thermal	Power overheating. Deviation of physical-chemical parameters.	Carry out an evaluation in the Heating Node control system for flow and temperature, evaluate the effectiveness of the thermocouples used in the control loop of the Electric Heater GDC-007-001.	
		Any less	Low heatin thermal oil oil pumpin failure. TR heat excha bundle dan	. Thermal g system S-002-001 nger tube	Reduced process efficiency. Possible contamination of organic matter present in the exchanger.	Perform an evaluation in the Heating Node control system for flow and temperature. Perform preventive and predictive maintenance on the heat exchanger tube bundle.	
		None	Thermal of failure. Sto the therma pumping s	ppage of l oil	Plant stop.	Perform an evaluation on the Heating Node control loop fo flow and temperature. Analyze the effectiveness of the thermocouples used.	
	Flow rate	Most	Increase in speed of B BC05 pum Increase in reactor fee	C04 and ps. the	Poor conversion of reactants to product due to shorter reaction time.	Control on the input mass of the CSTR and PFR reactors, evaluation of the control loop for flow at the respective node.	
		Any less	Reduction motor spee and BC05 Possible of of piping o closure of valves.	ed of BC04 pumps. ostruction r partial	Reduction in process efficiency and reduction in final production.	Carry out an evaluation of the pumping system and the control loop, including flow sensors, actuated valves, piping present in this node.	
		None	Mass flow to non-rota BC04 and pumps. Va piping obst	tion of BC05 lves and	Possible plant shutdown.	Perform preventive and predictive maintenance so that the system does not stop working.	

According to Table 3, the flow above the ideal volume would lead to poor conversion of reactants into products, while the flow below the ideal could result in a reduction in the efficiency of the process, while the lack of flow could cause the plant to stop. Regarding the temperature, the overheating of vegetable oil can cause deviations in the physical-chemical parameters of the product, since when the temperature is below the ideal, the result is a reduction in the efficiency of the process and possible contamination of the organic matter, finally, when the temperature is zero, the plant stops. The necessary actions to be implemented are preventive maintenance of equipment and evaluation of the temperature and flow control loop. In relation to Node 03, shown in Table 4.

Unit: NI	UTEC					
System:	Phase Separati	on I	Node 03: Phase Separation I			
Paramet	ters: Level and	Flow	Date: 09/01/2020			
StudyProcesspointParameters(node)		Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
3 Level	Level	Most	Increase in the feed load from the reactors. Inefficiency in the control loop and level sensors.	Drag from the glycerin phase to the ester phase exit in the SEF-003-001 decanter. Inefficiency in phase separation.	Evaluate the level sensors and the level control loop in the phase separation process I.	
		Any less	Reduction of the feed load coming from the reactors.	Low product load and reduction in final production.	Evaluate the level sensors and the level control loop in the phase separation process I.	
		None	No power load being sent to the node under study. Level sensor problems.	Plant Stop.	Evaluate level sensors and monitor feed volumes.	
	Flow rate	Most	Increase in the supply load, opening of the actuated valve VE11, problems in the BC04 and BC05 centrifugal pumps.	Inefficiency in the separation of ester and glycerin phases. Poor conversion of reactants to product due to shorter reaction time.	Control on the inlet mass, evaluation of the control loop for Node flow.	
		Any less	Reduction of the reactor power load, problems in the actuated valve VE11. Pipe leak.	Inefficiency in the separation of ester and glycerin phases in the SEF-003-001 decanter.	Control on the inlet mass, evaluation of the control loop for flow.	
		None	No power load. Problems in the BC04, BC05 material delivery pumps.	Plant stop.	Control on the inlet mass, evaluation of the control loop and the control valve.	

Table 4 - Hazor	Analysis	Referring to	o Node 03
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Hazop analysis *of* this node, the study parameters level and flow and the guide words "more", "less" and "none" were established. From Table 4, it can be concluded that a higher flow rate and higher level can trigger the dragging of the glycerin phase to the ester phase exit in the decanter, in addition to the poor conversion of reactants into products and overload in the feeding of the reactors of the next node. Lower flow and level lead to a reduction in final production. Finally, when there is no flow and level, the plant will stop and its production will be canceled. Therefore, it is proposed the evaluation and predictive and preventive control of the pumping system and process valves, as well as the evaluation in the control loop, both for level and for flow, corresponding to the respective node. Table 5 presents the evaluation of node 04 regarding Phase Separation II. In this node, the flow and temperature parameters are evaluated.

System:	Phase Separatio	n II	Node 04: Phase II Sepa	ration	
Parameters: Temperature and Flow		Date: 09/01/2020			
Study pointProcess Parameters(node)		Deviations (guide words)	Possible causes	Possible consequences	Necessary actions
4	Flow rate	Most	Feed load increase, valve opening actuated VE11.	Inefficiency in phase separation.	Control on the input mass of the node, evaluation of the control loop and the control valve.
		Any less	Reduction of reactor feed load, problems in the actuated valve or leaks.	Inefficiency in phase separation.	Control on the input mass of the node, evaluation of the control loop and the control valve.
		None	No power load. Problems in the material sending pump BC07, BC08.	Plant stop.	Control on the input mass of the node, evaluation of the control loop and the control valve.
	Temperature	Most	Temperature control or thermocouple failure.	Rough vaporization of liquid alcohol increased vapor flow with possible excessive foaming.	Maintenance of the structure of the reboiler and evaluation of the temperature and pressure control system.
		Any less	Temperature control or thermocouple failure.	Inefficient separation of pure biodiesel and alcohol vapor.	Performing maintenance on the structure of the reboiler and checking the temperature and pressure control system.
		None	Breakdown in the temperature control system.	Stopping the process of breaking the ethanol emulsion in the present equipment.	Maintenance of the structure of the reboiler and evaluation of the temperature and pressure control system.

Table 5	- Hazop	Analysis	for Node 04	

Own authorship (2020)

In this node, biodiesel is separated from glycerin and alcohol and sent to the purification system. Based on the evaluation of Node 04, it appears that the flow and temperature variables for this node may affect, above all, the phase separation of the reacted medium from the previous node, in addition to the condensation of steam and eventual plant shutdown, if these variables deviate to "more, less, none". Therefore, it is necessary that the pumping elements, pipes and valves are constantly the focus of preventive and predictive maintenance in order to operate correctly. Table 6 below presents the *hazop analysis* for the biodiesel purification node I, where the study parameter is the flow rate and the guide words are "major", "small" and "none".

Unit: NI	U TEC					
System:	Purification of	Biodiesel I		Node 5: Purification of Biodiesel I		
Parameter: Flow			Date: 01/09/20			
Study point (node)	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
5	Flow rate	Larger	Pumping problem, flow and pH control failure.	Excessive water in the washing process; acidification of biodiesel and corrosion of equipment.	Maintenance of the pumping system and the valves and pipes; check in the pH control system.	
		Less	Pumping problem, valve and piping obstruction, flow and pH control system failure.	High soap content resulting from the saponification process; biodiesel with basic pH.	Perform maintenance on the pumping system and the valves and pipes; check the pH control system.	
		None	Stoppage of the pumping system, total obstruction in pipes and valves, failure of the flow control system.	Stop in the biodiesel purification process I.	Perform preventive and predictive maintenance on equipment.	

Own authorship (2020)

After analyzing the data, it is noted that a non-ideal water flow would result in excess water in the biodiesel washing process, inadequate biodiesel purification, or stoppage of the biodiesel purification system I. While, in the case of dilute acid above it could result in acidification of biodiesel and corrosion of equipment or biodiesel with basic pH. Therefore, the *hazop analysis* focuses on the maintenance of pumps, valves and pipes, and the monitoring of the water and acid flow control system. Table 7 below presents the *hazop* for the biodiesel purification node II, where the study parameters are flow and temperature and the guide words are "higher", "lower" and "none".

Unit: NI	UTEC					
System:	Purification of	Biodiesel II		Node 6: Purification	of Biodiesel II	
Paramet	ter: Temperatu	re, flow		Date: 01/09/20		
Study point (node)	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
6	Temperature	Larger	Electric heater resistors overload. Temperature control or thermocouple failure.	Structural damage to equipment; deviation of physical-chemical parameters in the final product.	Preventive maintenance. Evaluation of the effectiveness of the electric heater and evaporator thermocouples.	
		Smaller	Problems in the electric heater resistors. Temperature control or thermocouple failure. Encrustation or leaks.	Evaporator heating inefficiency; contamination of organic matter sent to the evaporator.	Perform maintenance on the coils. Evaluation of the effectiveness of the electric heater and evaporator thermocouples.	
		None	Failure of the heating resistors in the electric heater. Temperature control or thermocouple failure.	Stopping the biodiesel drying process.	Predictive maintenance.	
	Flow rate	Larger	Possible problem in the steam flow control system	Ineffective condensation of alcohol vapor.	Perform maintenance on the flow control system.	
		Smaller	Possible problem in the control system; clogged valves and pipes.	Inefficiency in the alcohol vapor condensation process that occurs in PBO- 004-003.	Maintenance of the valve and piping system; monitoring of the flow control system.	
		None	P ane in the flow control system; total obstruction of pipes and valves.	Cessation of the alcohol vapor recovery process.	Preventive maintenance on equipment and flow control system.	

According to the data in the table, overheating could affect the structural shape of the equipment and deviation of physical-chemical parameters in the final product, since temperatures below the ideal could affect the reduction of the efficiency of the drying process, and, finally, zero temperature would result in stopping the biodiesel drying process. Deviations in the flow of alcohol vapor in the heat exchanger, if above the ideal would result in ineffective condensation of the alcohol vapor, already below the ideal would cause inefficiency in the process of condensation of the alcohol vapor, finally, zero flow would result in cessation of the process of alcohol vapor recovery. The necessary actions are to carry out an assessment of the heating control system, maintenance of the pumping system, valves and piping of the electric heater. Table 8 below presents the *hazop analysis* for the heating node, in which the study parameters are flow and temperature and the guide words are "major", "minor" and "none".

Unit: NUTEC						
System: Heating				Node 07: Heating		
Paramet	Parameter: Flow and temperature			Date: 01/09/20		
Study point (node)	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
7	Flow rate	Larger	BD02 motor speed increase and flow control system failure.	Change in the structural shape of the equipment and rupture of pipes.	Check the current supply control, possible use of frequency inverters or speed reducers.	
		Less	Pumping problem; valve obstruction; Flow control system failure.	Inefficiency in heating the heat exchangers.	Check power supply control, pumping system problems and obstructions in pipes and valves.	
		None	Stoppage of the pumping system; obstructions; Flow control system failure.	Plant stop.	Carrying out preventive and predictive maintenance to prevent the system from stopping.	
	Temperature	Larger	Electric heater heating resistors overload. Temperature control failure.	Overheating in heat exchangers causing degradation of internal organic matter.	Implement periodic evaluations in the heating system control system, evaluate immersion resistances and the effectiveness of the thermocouples used.	
		Less	Problems in the resistors in the electric heater. Temperature control or thermocouple failure.	Heating inefficiency in heat exchangers and reduced process efficiency.	Implement evaluations in the heating control system, evaluate the immersion resistances and the effectiveness in the thermocouples used.	
		None	Problems in the resistors in the electric heater. Temperature control failure.	Plant stop.	Evaluations in the heating control system, to evaluate the immersion resistances and the effectiveness in the thermocouples used.	

Table 8 -	Hazop	Analysis	Referring to	Node	07
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In view of what is exposed in the table, it can be seen that a flow of thermal oil above the ideal could result in a change in the structural shape of the equipment and possible rupture of the pipes, since a flow below the ideal could cause inefficiency in the heating of the heat exchangers, finally, inexistence of flow would affect the stoppage of the industrial plant. Furthermore, very high temperatures could cause degradation of the organic matter inside them, while temperatures below the ideal could cause inefficiency in the heating in the heat exchangers and evaporator, resulting in a reduction in the efficiency of the process, in short, no heat supply in the heating process would result. at the plant stop. The fundamental actions are maintenance in the pumping system and unblocking of pipes and valves. Table 9 below presents the *hazop analysis* for the cooling node, in which the study parameters are flow and temperature and the guide words are "major", "minor" and "none".

Unit: NU	TEC					
System: Refrigeration				Node 08: Refrigeration		
Parameter: Flow and Temperature				Date: 01/09/20		
Study point (node)	Process Parameters	Deviations (guide words)	Possible causes	Possible consequences	Necessary actions	
8	Flow rate	Larger	Possible problem with the BC21 pump motor rotation.	Very high pressure drop and possibility of pipe rupture.	Perform maintenance on the pumping system.	
		Smaller	Possible pumping problem. Obstruction of valves and pipes.	Inefficiency in the refrigeration of vapors to be condensed.	Perform maintenance on the pumping system and valves and pipes.	
		None	Stoppage of the pumping system, obstruction of pipes and valves.	Cessation of the condensation and drying process.	Perform preventive and predictive maintenance of the refrigeration system.	
	Temperature	Larger	Cooling tower fan rotating motor inefficiency.	Inefficiency in the refrigeration of vapors to be condensed and dried.	Perform maintenance on the cooling tower with evaluation of your fan.	

Table 9 -	Hazon	Analysis	Referring	to Node 08
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Own authorship (2020)

Based on the table, it is noted that flow above the ideal volume could result in very high head loss and the possibility of rupture of pipes, flow below the ideal volume would cause inefficiency in the refrigeration of vapors to be condensed, while the inexistence of flow could take place at the cessation of the condensation and drying process. Regarding the temperature, when above the ideal, it can cause inefficiency in the refrigeration of vapors to be condensed. The necessary actions to be implemented must be to carry out preventive and predictive maintenance on the cooling tower, pumping system and unclogging the pipes and valves.

4. Final Considerations

The work stands out for presenting, in an integral way, a continuous process of biodiesel production with different production routes, as well as an analysis of several possible failures that could result in human safety or operational problems.

The analysis detected operational risks arising from deviations in operating standards, as well as the possibility of explosions and environmental contamination. It was found that because it is a continuous production unit, the inefficiency or stoppage of any system can compromise the operation of the entire unit, thus having a chain effect. However, of the eight study nodes, the critical points were Heating and Cooling due to their influence on the other processes. Furthermore, the parameters that stood out in the analysis were flow and temperature, with an incidence of 100% and 75% in the tables, respectively. While the level parameter had a 25% incidence during the construction of the Hazop tables. In view of this, it was concluded that the focus of the necessary actions should be aimed at the adoption of an effective control system and preventive maintenance of equipment, especially pumps and valves.

Although the risk assessment using the *Hazop methodology* allows an assessment of the main causes and effects caused by failures in the unit, it is observed that a study applied using quantitative techniques, such as Fire and Explosion Index (F&EI), Chemical Exposure Index (CEI) and Analysis of Protection Layers (LOPA), will make it possible to avoid possible damage to operators and equipment in this ethyl or methyl ester production unit.

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