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Inherent Occupational Health Assessment of Biobutanol Separation Processes during the Conceptual Design Stage

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Occupational health assessment on chemical processes is a crucial step in the workplace management system. Constant exposure towards harmful chemical substances can be detrimental to worker's health and the resulting medical compensation is often costly. Despite this, health performance of chemical processes was often being neglected as compared to safety and environment, and the assessment, upon conducted, was usually not carried out comprehensively. To bridge this existing gap, occupational health hazards assessment was conducted on biobutanol separation process - a biomass-based fuel that has the potential in replacing fossil fuel as the source of energy. For this, a method called the Inherent Occupational Health Index (IOHI) was used to assess eight biobutanol separation processes during the conceptual design stage. Chemical substances involved in the processes were evaluated based on their operating conditions, physical and chemical properties. Each of these elements was assigned with penalties depending on the degree of the potential health hazard they may pose. Based on the cumulative hazard level, the processes were ranked by the healthiness level. Following the assessment, the appropriate counter measures to reduce the hazards were then proposed.

1. Introduction

The element of safety and health in chemical process is not something that should be addressed lightly. Previous devastating incident - Bhopal toxic gas leak incident in 1984 for instance, is by far one of the worst man-made disasters that had cost thousands of innocent lives. This incident has grabbed global attention and efforts have been made since then to create a safer working environment in chemical process plant. The main concern now is not on 'how we can reduce hazard' but 'how far can we go in order to reduce hazard'. It is impossible to surpass the probabilities of human error and equipment failure in hazard management. To rely on add-on control systems and human factors is not a wise strategy in ensuring a sustained attainment of safety workplace and process operation. However, we are capable of avoiding the hazards, by reducing or eliminating the hazards fundamentally in the process if efforts are done in much earlier stages of process development and design. By integrating the chemical substance properties with the process plant design (including operating conditions etc.), it is possible to inculcate the principles of inherent safety in reaching the ultimate goal of having an inherently safer design of process plant. Biofuel, a fuel derived from living matter is one of the alternatives for production of renewable energy. It has grabbed global attention due to their renewable features to ensure continuous production, faster recovery as natural bio-resources are being used as the feedstock, as well as being more sustainable and environmentally friendlier when compared to the use of fossil fuels as the main source of energy. Extensive studies have been conducted on biofuel pertaining to its production, safety and efficiency. Unfortunately, researches on occupational health issues in biofuel industry are very limited, in comparison to the researches that have been conducted on economical, safety and environmental impacts. As green as it may seem to appear, biofuel production does pose potential health

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hazards due to various factors including workers' exposure to chemical substances including particulates, dust and alcohol; extreme operating condition; as well as the issue of fugitive emissions in the process production. It is important to conduct assessment on these processes.

2. Literature review

2.1 The concept of inherent safety

Misconception about the cost involved in safety-related practices has led to lack of efforts and poor compliance among the organisations. Safety is often deemed as something 'costly' (Kletz, 2009) and not practicable, especially in small and medium enterprises (Legg et al., 2015). Level of compliance among organisations is mainly influenced by behaviour and attitude towards safety, also known as the 'safety culture' in an organisation. Hayes (2015) has concluded that engineers do acknowledge their primary responsibility for choices and designs of chemical plants, but the final result depends highly on project managers. It is difficult to come up with a solution that recognises all the elements of cost, schedule and safety. This is agreeable to a certain extent, as protective equipment like interlocks, valves and other add-on tools are often costly. This approach is reactive in nature, as the financial allocation for protective equipment depends on the structure of devices and chemicals involved in the process. In other words, hazardous chemicals and complicated devices employed in the process require higher number of protective equipment and investments. This is contrary to the concept of 'Inherent Safety', which is a proactive safety approach as it handles the issue from the initial stage. The main principle is to avoid hazards fundamentally, hence reducing dependency on add-on safety control equipment (Kletz, 2009). Khan and Amyotte (2005) pointed out an interesting fact that maintenance and safety measure costs for conventional systems are actually more expensive than that of inherent safety. The inherent safety ideology holds a more promising and practical solutions to safety problem, besides having credits from the financial aspect as well.

2.2 Challenges in biofuel industry

Limitation of fossil fuel resources have led to development of using renewable feedstock for production of fuel and power generating materials. This technology is claimed to be more sustainable and environmental-friendly (Cheali et al., 2016). The most studied biofuel is bioethanol, mainly produced by sugar fermentation. Another alternative, biobutanol, is claimed to be more efficient in terms of energy production. A study done by Yun et al. (2016) has showed that performance of biobutanol-diesel blend is much higher than conventional diesel. Combustion pressure and heat release are much higher and nitric oxide, carbon dioxide and soot production is much lower. The presence of inhibitor during fermentation process leads to low yield of the desired product. Acetone-butanol-ethanol fermentation (ABEF) is not viable due to the low yield, sluggish fermentation, uneconomical product recovery and degeneration of production organism (Garcia et al., 2011). Alternatives in the form of pre-treatment of feedstock promises a better yield of biobutanol. Su et al. (2015) claimed that pre-treatment of feedstock is proven to be more effective than pure glucose fermentation for production of biobutanol. Unfortunately, most of the process equipment involved in the biofuel separation processes are costly and new designs at cheaper cost are in demand. Due to the continuous change in design, it is important to assess the new hazards that may appear to the new technology. This includes inherent occupational health hazards.

Chemical substances involved in this work are derivatives of alcohol (acetone, butanol, ethanol) that are irritants in nature. Short-term exposure will cause acute health effects including skin inflammation and eye irritation. Repeated and long-term exposure will lead to end-organ damage as they are toxic to central nervous system and reproductive system. Thorough assessment of the process occupational health hazards are very important to ensure a healthier process for the protection of workers' well being. Unfortunately, researches on occupational health issues in biofuel industry are very limited. Despite being more sustainable, biofuel production does pose potential health hazards due to various factors in the production processes. These include workers' exposure to chemical substances such as particulates, dust and alcohol; extreme operating condition; as well as the issue of fugitive emissions in the process production. The chemical substances involved in the biofuel production may be in contact with the workers through various routes of entry including inhalation and dermal/eye contact; resulting in deterioration of the workers' health condition. It is crucial to conduct an occupational health assessment in biofuel production process as the process does potentially pose health threats to the exposed workers. The use of chemical substances as solvents such as methanol and acetone can be hazardous to workers health if not being assessed properly. The process is actually more challenging in a way that they also involve solid materials e.g. particulate matters and fibres, that can be easily inhaled by the workers within the production area. In this study, a comprehensive work on inherent occupational health assessment will be performed on the biobutanol separation processes from the ABE fermentation.

3. Methodology

The main objective of this study is to conduct comprehensive inherent occupational health assessment on biobutanol separation processes from the acetone-butanol-ethanol (ABE) fermentation. This is part of the efforts towards bridging the gap between chemical processes and their health performance.

3.1 Inherent occupational health index selection

In conceptual design stage, the process is mainly still in the research and development phase. Hence, detailed data on the processes is not yet available. Despite the limited information available, it is crucial to perform early screening to select fewer viable processes to be further developed. Previous works have focused mainly on economic interest while selecting the routes, creating a research gap in their safety, health and environmental (SHE) performance. And among the three SHE aspects, health is the least being considered due to its more complicated underlying principles when being considered from the context of chemical based processes. The selection of routes determines the types of chemicals and the operating conditions in the process (Hassim, 2010). At this stage, the assessment will have to make do with the very limited information available i.e. operating conditions and properties of the chemical substances present in the process. With such constraint a method called the Inherent Occupational Health Index (IOHI) is seemed to be suitable for the assessment. This index takes into consideration all the possible factors that may pose occupational health hazards towards workers by making into the maximum use of the limited data available at this stage. According to the method, the hazard level of the selected factors is represented in the form of numbers (which is called as penalty) - higher number represents greater hazards (toxic level and potential for exposure). Summation of the factors will contribute to the final index and the value is used to represent the hazard level of the process route under study. In comparing several routes, the higher the index value, the more hazardous the process route is. The IOHI for each process route is obtained through the summation of two factors as shown in Eq(1). These two factors are Physical and Process Hazards Index (I_{PPH}) and Health Hazards Index (I_{HH}) (Hassim and Hurme, 2010).

$$I_{IOHI} = I_{PPH} + I_{HH} \quad (1)$$

Physical and Process Hazards Index (I_{PPH}) represents the potential of chemicals being exposed to the workers (influenced by the physical properties of the chemicals) and the operating conditions of the process. The final score for Physical and Process Hazards Index (I_{PPH}) is obtained through the summation of the five sub-indexes. These sub-indexes are material phase (I_{MS}), volatility (I_V), corrosiveness (I_C) and temperature (I_T), pressure (I_P) and process mode (I_{PM}). The physical and process hazards sub-index is obtained as shown in Eq(2) (Hassim and Hurme, 2010). For material phase (I_{MS}), volatility (I_V) and corrosiveness (I_C), they are penalized based on the most hazardous chemical in the process step.

$$I_{PPH} = I_{PM} + \max(I_{MS}) + \max(I_V) + I_P + \max(I_C) + I_T \quad (2)$$

Health Hazard index (I_{HH}) is contributed by two factors. These factors are Exposure limits (I_{EL}) and R-phrase (I_R). These two factors represent the level of chemical hazards towards human health upon exposure. The allocation of the penalty depends on the level of health hazards to the workers. The higher the health hazard, the higher the penalty will be. I_{EL} represents the chronic hazards of the chemical in the working air. I_R represents the health effect to the workers. The health hazard sub-index is obtained by Eq(3) (Hassim and Hurme, 2010).

$$I_{HH} = \max(I_{EL}) + \max(I_R) \quad (3)$$

For both exposure limits (I_{EL}) and R-phrase (I_R), they are penalised based on the most hazardous chemical in the process step. The list of the sub-indexes with their respective penalty scorings are in Hassim and Hurme (2010).

4. Case study: Biobutanol separation processes from acetone-butanol-ethanol fermentation

4.1 Process description

Biobutanol mixture is obtained from acetone-butanol-ethanol fermentation and the mixture will be separated further to obtain the desired products. In this study, a total of 8 options of separation processes have been assessed. The alternative designs consist of 3 distillation processes, 1 liquid-liquid extraction process and 4 intensified configurations derived from the liquid-liquid extraction process. The purpose of including extraction process in the proposed designs is to eliminate heterogeneous and homogenous azeotrope between butanol/water and ethanol/water, by using N-heyxl acetate as the extractant agent. Aside from the extractant agent, the other 3 main chemical substances that were assessed in this study are acetone, butanol and ethanol.

4.2 Physical and chemical properties

Chemical substances involved in the processes were identified and their properties are tabulated in Table 1 and the process conditions for each design were summarised in Table 2.

Table 1: Physical and chemical properties of chemicals involved in the processes for IOHI calculation.

Properties	Chemicals			
	Ethanol or Ethyl alcohol	Acetone	Hexyl acetate or Acetic acid	Butanol
Material phase (atmospheric conditions)	Liquid	Liquid	Liquid	Liquid
Volatility	BP: 78.5 °C VP: 5.7 kPa at 20 °C	BP: 56.2 °C VP: 24 kPa at 20 °C	BP: 118.1 °C VP: 1.5 kPa at 20 °C	BP: 117.7 °C VP: 0.6 kPa at 20 °C
Corrosiveness	Requires stainless steel material	Requires stainless steel material	Requires stainless steel material	Requires stainless steel material
Exposure limit 8 h (TLV–TWA ACGIH)	1,000 ppm (1,880 mg/m^3) TWA	500 ppm (1,188 mg/m^3) TWA	10 ppm (25 mg/m^3) TWA	20 ppm (61 mg/m^3) TWA
R-phrase	R-11	R-11, R-36	R-10, R-35	R-10, R-22, R-38, R-41

BP: Boiling point, VP: Vapour pressure.

Table 2: Process conditions for IOHI calculation.

Designs	Process mode, I_{PM}	Pressure (bar), I_P	Temperature (°C), I_T
1	Continuous	0.5 - 5	70 - 150
2	Continuous	0.5 - 5	70 - 150
3	Continuous	0.5 - 5	70 - 150
4	Continuous	0.5 - 5	< 70
5	Continuous	0.5 - 5	70 - 150
6	Continuous	0.5 - 5	70 - 150
7	Continuous	0.5 - 5	70 - 150
8	Continuous	0.5 - 5	< 70

5. Results and Discussion

For each chemical substance, it is assigned with penalty for the sub-indexes based on its' degree of hazard (Hassim and Hurme, 2010). Chemical health hazard factors for Physical and Process Hazards Index (I_{PPH}) and Health Hazard index (I_{HH}) were evaluated separately, in order to get the total score of each sub-index. These two sub-indices were then being totalled up to give the final score for the IOHI. Since each route may have several process steps, the IOHI score for the whole route can be calculated using one of the three index calculation approaches (additive, average and worst-case type) as proposed by Hassim and Hurme (2010). Additive scoring system involves the summation of all the sub-processes (process steps) indexes. Route with higher number of sub-processes will get a higher final score. To eliminate this additive effect, average scoring system was proposed where the average of IOHI for the route is calculated (the total IOHI score is divided by the number of process steps in the route). The worst-case scoring system involves the summation of the maximum sub-index penalties of the route (Hassim and Hurme, 2010). The detailed calculations are summarised in Table 3.

Based on the ranking presented in Table 3 using the three scoring systems, Design 3 scored the lowest making it the healthiest process among all. Design 5 scored the highest and ranked the lowest, making it the most hazardous route towards workers' health. Based on the ranking, distillation processes (Design 1 - 3) scored much lower than liquid-liquid extraction process and its' intensified configurations (Design 4 - 8).

Table 3: Overall ranking of health performance of biobutanol separation processes

Designs	IOHI (Additive)		IOHI (Average)			IOHI (Worst)		
	Score	Rank	Score	Standards	Rank	Score	Standards	Rank
1	139	4	10.69	Moderately safe	3	11	Moderately safe	3
2	128	3	10.67	Moderately safe	2	11	Moderately safe	2
3	117	1	10.64	Moderately safe	1	11	Moderately safe	1
4	126	2	11.45	Moderately safe	4	13	Moderately hazardous	4
5	140	5	11.67	Moderately hazardous	5	13	Moderately hazardous	5
6	188	8	11.75	Moderately hazardous	8	13	Moderately hazardous	8
7	164	7	11.71	Moderately hazardous	7	13	Moderately hazardous	7
8	152	6	11.69	Moderately hazardous	6	13	Moderately hazardous	6

*Rank 1 represents the healthiest route among the alternatives.

The result shows that intensified configurations designs are more hazardous to workers' health in comparison to distillation-based processes. This is due to the use of n-hexyl acetate as the extractant agent in the liquid-liquid extraction process and its' intensified configurations. N-hexyl acetate is highly toxic to skin and eye, and can cause internal organ damage upon inhalation. Furthermore, the operating temperatures in liquid-liquid extraction processes are higher than distillation processes. This increases the risk of exposure of workers' towards vapour inhalation. Hence, these processes scored higher than the alternative distillation processes. Besides ranking, the IOHI also is capable of determining the 'status' of health performance of a process based on the calculated IOHI value (see Table 3). This is a great feature since there are also cases where the assessment is performed on one particular process only, without the intention to compare alternative processes.

Table 4: IOHI standards according to the final IOHI score (Hassim and Hurme, 2010)

Category	I_{IOHI} scales
Safe	0 – 7
Moderately safe	8 – 11
Moderately hazardous	12 – 15
Hazardous	16 – 26

Table 4 shows there are four categories in this standard: safe, moderately safe, moderately hazardous and hazardous. Mind that the IOHI score here must be based on the average-type and worst case-type. Designs 1, 2, 3 and 4 fall under the 'moderately safe' category and designs 5, 6, 7 and 8 belong to the 'moderately hazardous' category. Details of the hazard causes are explained by the scoring received for each sub-index.
To improve their health performances, future work can focus on finding the healthier alternatives for the extractant agent being used in liquid-liquid extraction process as well as looking for potentials to further moderate the operating conditions (e.g. operating temperature) to make the processes healthier. Previous works have shown promising economic, safety and environmental performances of liquid-liquid extraction and its' intensified configuration. However, in terms of health performance, these designs are not healthy as compared to distillation processes. A healthier alternative for extractant agent will be beneficial as it helps to improve the overall health performance, and making it easier to select processes that satisfy economic, safety, health and environmental interest.

6. Conclusion

An occupational health assessment was conducted on eight biobutanol separation processes from acetone-butanol-ethanol fermentation during the conceptual design stage. This was done to bridge the gap between chemical processes and their health performances assessment. For this, an index that is frequently used for petrochemical based industry was used since there is no specific index available to conduct the assessment on biomass-based fuel. Future work can be directed towards developing new indices specifically for assessing health performances of biomass-related processes.

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Reference

Cheali P., Posada J.A., Gernaey K.V., Sin, G., 2016, Economic risk analysis and critical comparison of optimal biorefinery concepts, Biofuels, Bioproducts and Biorefining 10 (4), 435-445.

Garcia V., Päkkilä J., Ojamo H., Muurinen E., Keiski R.L., 2011, Challenges in biobutanol production: How to improve the efficiency?, Renewable and Sustainable Energy Reviews 15, 964-980.

Hassim M.H., 2010, Inherent Occupational Health Assessment in Chemical Process Development and Design, Plant Design Report Series, Aalto University School of Science and Technology, Aalto, Finland.

Hassim M.H., Hurme M., 2010, Inherent occupational health assessment during process research and development stage, Journal of Loss Prevention in the Process Industries 23 (1), 127-138.

Hayes, J., 2015, Taking responsibility for public safety: How engineers seek to minimise disaster incubation in design of hazardous facilities, Safety Science 77, 48-56.

Khan F.I., Amyotte P.R., 2005, I2SI: a comprehensive quantitative tool for inherent safety and cost evaluation. Journal of Loss Prevention in the Process Industries 18 (4), 310-326.

Kletz T., 2009, What Went Wrong? Case Histories of Process Plant Disasters and How They Could Have Been Avoided, 5th Ed., Elsevier Inc., Massachusetts, United States.

Legg S.J., Olsen K.B., Laird I.S., Hasle P., 2015, Managing safety in small and medium enterprises, Safety Science 71c, 189-196.

Su Y., Du R., Guo H., Cao M., Wu Q., Su R., Qi W., He Z., 2015, Fractional pretreatment of lignocellulose by alkaline hydrogen peroxide: Characterization of its major components, Food and Bioproducts Processing 94, 322-330.

Yun H., Choi K., Lee C.S., 2016, Effects of biobutanol and biobutanol–diesel blends on combustion and emission characteristics in a passenger car diesel engine with pilot injection strategies, Energy Conversion and Management 111, 79-88.