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Inherently Safer Design Applied to the Biodiesel Production

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The implementation of the inherent safety principles could be ambiguous due to the strategies that are involved on. Optimization is one of the options that could be seen as the key to balance the risk reduction and the economic feasibility of the project. The utilization of safety index is another option, with lower time efficiency and related results. The present paper will focus on the implementation of inherent safety principles into the biofuels production. The starting point is related to the chemist modification, passing from the common trans-esterification reaction to a two steps process, a hydrolysis of the triolein and with the fatty acid obtained do an esterification with methanol. The software selected for the project development is Aspen Plus and the reduction on the process risk will be evaluated with process safety indexes. The latter involve the characteristics of the process, type of equipment and the most important thing the type of substance that is handled on each unit.

1. Introduction

Estimates of the global potential for biomass that can be converted into fuels vary widely. One recent study concluded that by 2050, biomass theoretically could supply 65% of the world’s current energy consumption, with sub-Saharan Africa, the Caribbean and Latin America accounting for roughly half of this global potential (Energy and Fundation, 2007).

A raise on the Biodiesel (BD) demand is associated with higher quantities of raw materials and higher volumes of hazards materials transported within the process plant. This could represent a risk to the process but it depends how it is managed, as it was said by Scott Berger on an interview: “it really don not matter in which process are you working on, any material has a certain conditions where it can be dangerous and if this hazard is not handled properly it could present a problem. The key is to know the materials, the process and the hazards that are involved on each of one of them”(domesticfuel.com, 2011).

Inherent safety (IS) is a modern term for an age-old concept: to eliminate hazards rather than accept and manage them (Center for Chemical Process, 2008). An inherently safer design (ISD) implicates the application of the four strategies of IS: minimize, simplify, moderate, and substitute; starting at the identification of the hazards and risks related to the operation, raw materials and product storage and handling (Gómez et al., 2012). The elimination of the hazards are so fundamental to the design of the process that they cannot be changed or defeated without changing the process (Hendershot, 2010). However, an ISD can make an incident inherently less likely to occur, although the consequence of the incident, should it occur would be unchanged (Hendershot, 2011).

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2. Biofuels grow and synthesis

The continuous grow on the fuels demand has raise the necessity for new process and new plants, therefore the appearance of unknown risk could be vital to the process operation. According to the biofuels platform, the world production of biofuels on 2009 was 51.2 Mt (Biofuels), and there is an approximation that over 35 billion gallons (thousandmillion) in new capacity, or more, is going to be required by 2022 (Rosenthal, 2011).
On Europe This behavior has been observed on the BD production, from the latest 90's, where the biofuels production was less than a million of tones, at 2011 this number has been risen to about 22 millions of tones (EBB). In Colombia, the biodiesel, as the global behaviour has been trying to expand its boundaries, increasing the planted area of Palm oil from the 18,000 on 1960 to 404,104 to date (Fedepalma, 2010), converting Colombia in one of the first five countries that produce palm oil and has the technology as it can be seen on Figure 1. Nowadays there are six BD plants in operation, with a combined production capacity of 536,000 t/y.

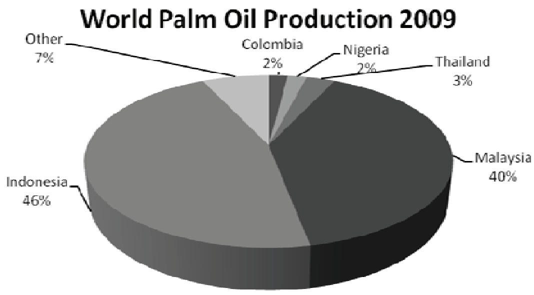

Figure 1. Palm oil production (Ong et al., 2011)

This economical grow leads to an intensification to the process, leaving an empty space for the new production alternatives. The trans-esterification of vegetable oils to biodiesel is a relatively slow reaction, mainly because the reactant (alcohol) needs to be excessive in order to drive the reversible reaction in the preferable reaction (Zhang et al., 2003). Therefore enhanced mixing will be beneficial to achieve smaller reactor size and shorter residence time (Mannan et al., 2006). Moreover, improved mixing performance will require less alcohol to achieve the ultimate conversion, thus reduce the hazards from excess alcohol. The approach presented on this work (Figure 2), involves a modification to the reaction system. Over the classification of first generation biofuels, the trans-esterification of triglyceride with methanol was changed into two reactions, the first one is the hydrolysis of the triglyceride to obtain the fatty acid (Octanoic Acid) that reacts forward with the methanol through an esterification reaction to produce BD.
The project has into account three variations to the process. The first one is the base case, the production of BD using the same synthesis (two reactions) with a Plug Flow Reactor (PFR, R-102 on Table 1) as the esterification reactor; involving the use of a mixer (M-102 on Table 1) of the oleic acid and the methanol streams and reactor previous to the first column presented on the Figure 2. The second and third options is the process presented on the Figure 2, where the only variations between them is that the second option can be considered as the base case and the third option involves the economic optimization of the process, changing the flow of methanol into the recirculation cycle, the reflux ratio and the distillate/feed ratio on the reactive tower and its operating conditions (temperature and pressure). These three alternatives could be used as an example to show the effects of the economical optimization into the variation of the risk based on the operational changes.

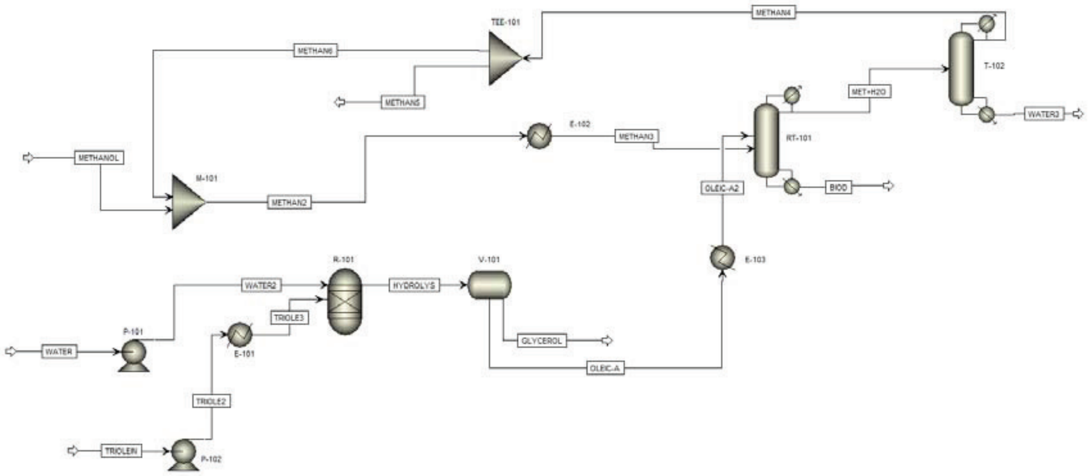

Figure 2. Equipment and streams of the biodiesel process

3. Inherent safety

ISD are based on an informed decision process. An option may be inherently safer with regard to some hazards and inherently less safe with regard to others; decisions about the optimum strategy for managing risks from all hazards are required. The decision process must consider the entire life cycle, the full spectrum of hazards and risks, and the potential for transfer of risk from one impacted population to another (Hendershot, 2011).

From the incident information of BD process plants like the ones presented by several authors and data bases (Moss, 2010, Salzano et al., 2010, Fire World, 2011), there are two critical steps: Reaction and Neutralization. The reaction involves the handling and separation of the methanol, a highly volatile material, very flammable, and classified as a Class I according to NPFA. The neutralization process, where the acid is mixed with glycerol that have traces of methanol that can ignite if the heat released overcome the activation energy. One of the inherent safety strategies (limiting of the effects) is present on the modification performed to the process (two reactions), the neutralization of the glycerol is eliminated, reducing the occurrence of an undesired event. Also the presence of the methanol is limited to the second reactor and its purification process.

The inherent safety principles are widely known but is evident the ignorance of its appropiate implementation. This is the opportunity of exploring others methodologies, Faisal Khan on several works (Khan et al., 2002, Khan et al., 2003, Khan and Amyotte, 2004, Khan et al., 2004, Khan and Amyotte, 2005, Khan et al., 2001) has worked on this aim, presenting plenty of attempts to state a methodology. The safety indexes, a balance between hazard that is intrinsic to the substances kept on the equipment and the safety measures that have been used to control them; this is the case of the main tool used on the development on the project, the I2SI methodology (Khan and Amyotte, 2005), focused only on the risk evaluation not on the cost associated to the process. On Figure 3 there is a representation of the safety index implementation, it's based on three main indexes: I2SI (Khan and Amyotte, 2005), SWeHI (Khan et al., 2001) and iNdeX (Khan et al., 2004)

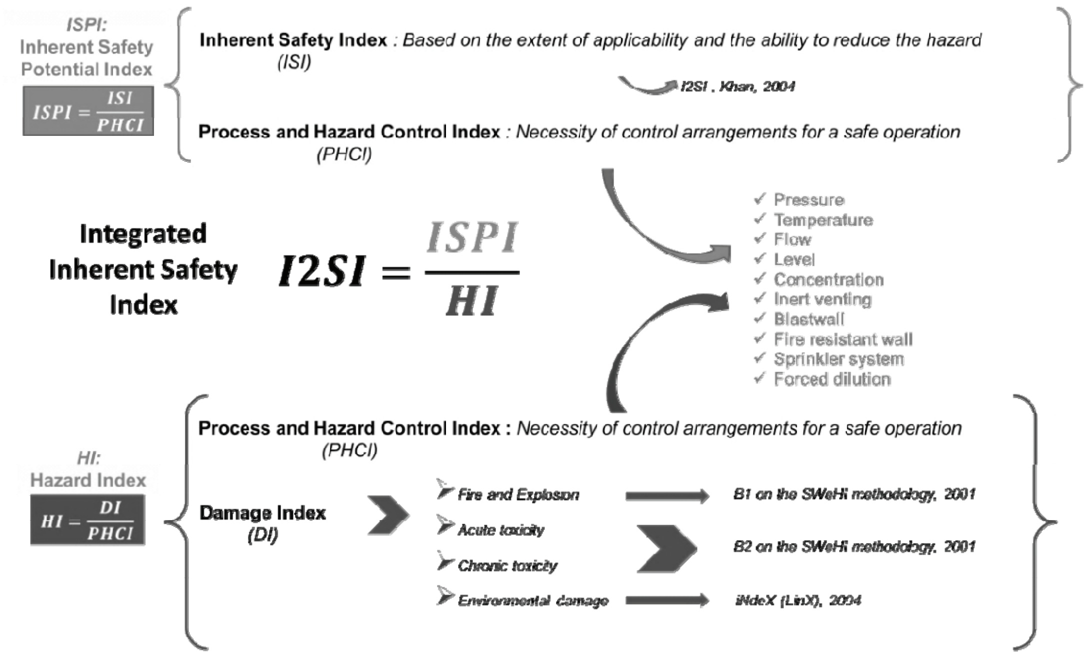

Figure 3. I2SI methodology

The integrated inherent safety index (I2SI) was the latest safety index developed by Khan et al, it is a recompilation of his previous works where it has an specific method for each type of equipment, classified as storage units, units involving physical operations, chemical reaction, transportation units and finally others hazardous units as flares and furnaces. It is mainly focused on the fire and explosion hazard and the toxic and corrosive hazards. The first part focused on the flash point, fire point and the auto-ignition temperature for each of one of the equipment. For the second part, the toxicity of the equipment is calculated from the NPFA classification of the substances. The affectation for both fire and explosion & toxicity load is quantified over an area in terms of the radius of the area (in m) that is lethally affected by a toxic load having a 50 % probability of causing fatality (Khan and Amyotte, 2005).

4. Results

Through the implementation of the safety index we obtained the following results presented on the Table 1. The simulations have similar values; therefore the modification to the reaction system has a slight improvement from the base case study (PFR reactor). The use of a reactive distillation system, improves the management of risk, lower pressure and lower temperatures on the recirculation streams and units that involve the handling of higher concentrations of methanol (main hazard of the process).
Additionally to the change of esterification reactor, we propose an optimization of the distillation process to show that an intensification of the process, do not necessary involves the increase of the risk on the plant. Although this results cannot be seen as an extensive investigation, because the aim of the optimization was to optimize the methanol recirculation flow, controlling the variables within the reactive distillation column (i.e internal pressure, reflux ratio) and the makeup stream.

Table 1: Integrated inherent safety index - I2SI

Units	Reactor PFR	Reactive Distillation	Reactive Distillation Optimized
P-101	1.314	1.387	1.390
P-102	1.063	1.147	1.152
E-101	1.062	1.146	1.152
E-102	1.152	1.669	1.657
E-103	1.134	1.204	1.195
M-101	1.163	1.809	1.811
M-102	1.122	-	-
Tee-101	1.170	1.824	1.831
V-101	1.144	1.211	1.216
T-101	1.128	-	-
T-102	1.147	1.639	1.637
R-101	0.667	0.772	0.773
R-102	0.123	-	-
RT-101	-	0.791	0.785

5. Conclusions

The economic optimization of a process do not necessary means that there is going to be an intensification of the risk involved on the process. Depending on the case (as it was seen on the present work) the modifications made, can slightly changes the hazards intrinsic to the process evident on the type of substances handled on the facility.

The implementation of the safety index into the process and plant design shows that is an important tool that can make evident hazards that are not so clear to the operation of the process. The possibility of make changes to the process on the design stages could lead to accomplish the mission of the inherent safety principles, the elimination of the hazard at the source.

The BD production through the reactive distillation can be seen as an attractive production alternative, taking into account that it involves lower production units involved on methanol handling. It is important to highlight the importance of the control into the tower, to assure that the operational risk of the reactive column will not be greater that other options as the case of the PFR presented on this work.

References

Biofuels, P. *Production of biofuels in the world* 2009 [Online]. Biofuels Platform • ENERS Energy Concept. Available: www.biofuels-platform.ch/en/infos/production.php?id=biofuels [Accessed July 2012].

Center For Chemical Process, S. 2008. Inherently Safer Chemical Processes: a Life cycle approach, John Wiley & Sons, Inc.

Domesticfuel.Com 2011. How to Properly Handle Chemicals in a Biorefinery. In: BERGER, S. (ed.). [Accessed June 2012].

EBB, E. B. B. 2011. The EU biodiesel industry [Online]. Available: http://www.ebb-eu.org/stats.php# [Accessed June 2012].

Energy, F. C. & Fundation, U. N. 2007. The Benefits of Biofuels: International Development [Online]. [Accessed July 2012].

Fedepalma 2010. Anuario estadístico. Bogotá, Colombia. [Accessed July 2012].

Fire World, I. 2011. Biodiesel Incidents Logs. 2012 ed. [Accessed June 2012].

Gómez, G., Rodríguez, S., Cadena, J. & Muñoz, F. 2012. Kletz's legacy for developing countries: Simple systems based on inherently safer design. *Journal of Loss Prevention in the Process Industries*, 25, 843-847.

Hendershot, D. C. 2010. A summary of inherently safer technology. *Process Safety Progress*, 29, 389-392.

Hendershot, D. C. 2011. Inherently Safer Design–Not Only About Reducing Consequences! *Progress Safety Progress*, 30.

Khan, F. I. & Amyotte, P. R. 2004. Integrated inherent safety index (I2SI): A tool for inherent safety evaluation. *Process Safety Progress*, 23, 136-148.

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, 310-326.

Khan, F. I., Husain, T. & Abbasi, S. A. 2001. Safety Weighted Hazard Index (SWeHI): A New, User-friendly Tool for Swift yet Comprehensive Hazard Identification and Safety Evaluation in Chemical Process Industrie. *Process Safety and Environmental Protection*, 79, 65-80.

Khan, F. I., Husain, T. & Abbasi, S. A. 2002. Design and evaluation of safety measures using a newly proposed methodology “SCAP”. *Journal of Loss Prevention in the Process Industries*, 15, 129-146.

Khan, F. I., Sadiq, R. & Amyotte, P. R. 2003. Evaluation of available indices for inherently safer design options. *Process Safety Progress*, 22, 83-97.

Khan, F. I., Sadiq, R. & Veitch, B. 2004. Life cycle iNdeX (LInX): a new indexing procedure for process and product design and decision-making. *Journal of Cleaner Production*, 12, 59-76.

Mannan, S., Wang, Y., Zhang, C. & West, H. H. Year. Application of inherently safer design principles in biodiesel production process. In, 2006. 982-989.

Moss, P. 2010. *Biodiesel Plant Safety*. Biodiesel Magazine.

Ong, H. C., Mahlia, T. M. I., Masjuki, H. H. & Norhasyima, R. S. 2011. Comparison of palm oil, Jatropha curcas and Calophyllum inophyllum for biodiesel: A review. Renewable and Sustainable Energy Reviews, 15, 3501-3515.

Rosenthal, M. 2011. Biofuels Mandates Around the World [Online]. Available: www.biofuelsdigest.com/bdigest/2011/07/21/biofuels-mandates-around-the-world/ [Accessed June 2012].

Salzano, E., Di Serio, M. & Santacesaria, E. 2010. Emerging Risks in the Biodiesel Production by Transesterification of Virgin and Renewable Oils. *Energy & Fuels*, 24, 6103-6109.

Zhang, Y., Dubé, M. A., Mclean, D. D. & Kates, M. 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology*, 89, 1-16.