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Screening of Sustainable Biodiesel Production Pathways during Process Research and Development (R&D) Stage using Fuzzy Optimization

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Biodiesel is recognized as an important renewable energy source to fulfill global energy demand and resolve environmental issues. Despite its known advantages, it is still very critical to assess the sustainability of biodiesel production prior to the greater expansion for commercialization. The sustainability assessment can be conducted during process screening on the alternative biodiesel synthesis pathways. This is in line with Responsible Care, which commits chemical industries to consider safety, health and environmental (SHE) aspects when designing a new process. According to inherent safety principle, early hazard assessment offers greater benefits compared to the latter phases of lifecycle since the opportunity for making process modifications is higher yet requires lower cost. In this study, inherent SHE analysis is conducted for biodiesel production during the earliest design stage called process research and development (R&D) design. The inherent SHE assessment is done based on the fundamental information available, i.e. reaction chemistry and process condition. In this study, eight biodiesel production pathways via continuous transesterification process, such as catalyzed, supercritical and enzymatic transesterification, are identified and evaluated. Since multiple pathways need to be assessed based on multiple sustainability criteria, fuzzy optimization is used as the multi-criteria decision making tool in selecting the most optimum pathway. Based on the optimized result, pathway of enzymatic transesterification using fresh vegetable oil is identified as the optimum pathway which has least hazard in inherent SHE assessment.

1. Introduction

According to World Energy Outlook (International Energy Agency, 2012), it is expected that there will be a 30 % increase in global energy demand from current to 16,730 Mtoe in year 2035. However, the reserve of conventional fossil fuel is continually depleted and this captures the world's attention because of the concern on energy crisis. Besides, the excessive usage of fossil fuel triggers environmental issues that threaten the sustainability of human and other livings. As mutual solution to energy crisis, IEA revealed that the renewable energy should be utilized to support about half of the new global demand by year 2035. Since 1980s, biodiesel which derived from non-fossil source is gaining considerable interest to become a potential fuel to substitute petroleum. Biodiesel possesses the chemical properties and energy content which is very close to diesel fuel. Besides, biodiesel also portrays the merits as an environmental-friendly, biodegradable and non-toxic fuel. Due to those advantages, biodiesel production has been increased tremendously since the last decade and further expansion could be foreseen. Meanwhile, as result of the rapid industrialization activities, public's awareness towards the risks posed by chemical industries has gradually increased. Later, under the force of social and voluntary initiatives such as Responsible Care, chemical industries are urged to improve the performance of safety, health and environment (SHE) (Hook, 1996). To achieve effective SHE improvement, this can be done by integrating the aspect of SHE in chemical plant and process design.

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Evaluation of SHE involves quantification of hazards, which is important for the later steps of comparison and screening of process alternatives. For SHE hazard quantification, traditional evaluation approaches are mostly used in implementing external control (such as instrumentation, mechanical and administrative system) to protect human from the existing hazards. Further, the traditional hazard evaluation often focuses on single aspect of the process, for instance, Hazard and Operability (HAZOP) studies, Quantitative Risk Assessment (QRA), Major Hazard Review Program (MHRP) are process safety analysis methods. Apart from that, traditional approach can only be applied during detailed engineering design or even during the operational stage. As an improved method of hazard assessment, inherent analysis emphasizes on reduction and elimination of intrinsic hazard without the need to use the external devices. Unlike the traditional approaches, the inherent analysis produces more cost-optimal option because it can be applied in any stages of plant design. The inherent principle was firstly introduced and applied to safety evaluation in chemical plants by Kletz (1984). Later, Kletz (1984) also proposed the inherent concept to be adapted to environment and industrial hygiene analysis, for purpose of providing more comprehensive protection to the people and the environment. As benefit, integration of inherent SHE into plant design could surely contribute to achieve more sustainable development. Besides, it is particularly important to conduct the inherent SHE evaluation during the early course of plant design. This is because it brings more advantages in terms of engineering modification and capital expenditure due to higher degree of freedom in altering the design with minimal cost incurred.

2. Inherent SHE Analysis During Process Research and Development (R&D) Stage

There are different methods developed for inherent SHE evaluation during process R&D. For inherent safety, the earliest method is known as Prototype Index of Inherent Safety (PIIS) which was developed by Edwards and Lawrence (1993). PIIS is the simplest method applicable to inherent safety analysis during earliest design stage. Later, several improved methods were proposed to more comprehensively quantify the inherent safety hazard, such as Inherent Safety Index (ISI) (Heikkila, 1999), i-Safe (Palaniappan et al., 2002), etc. However with the efforts in enhancing inherent safety analysis, the application of the developed tools in industries is still limited. According to Khan and Amyotte (2002), the main hurdles could be attributed to the lack of awareness about applying inherent safety and lack of understanding or knowledge about the analysis tool. Hence, the continual pursuing for the inherent safety analysis is still important to ensure high application in industries.

The available inherent health analysis during the stage of process R&D design is very scarce. This could possibly be due to relatively less emphasis given to the chronic (or long term) health impact. This occupational health hazard could potentially be developed through the routine industrial activities that involve the handling and exposure to hazardous chemicals. The earliest methods developed are known as Occupational Health Hazard Index (OHHI) by Johnson (2001) and Process Route Healthiness Index (PRHI) by Hassim and Edwards (2006). As improvement to OHHI and PRHI, Inherent Occupational Health Index (IOHI) was then introduced by Hassim and Hurme (2010). IOHI is an index-based method whereby the hazard is evaluated based on the process and the healthiness properties of the chemicals. Unlike OHHI and PRHI, the method of IOHI only requires the data (such as pressure, temperature, chemical exposure limit, etc.) which are easily available during early design stage. Therefore, it can effectively be adopted for hazard assessment during early design stage analysis.

Inherent environmental analysis focuses on the toxicity impact from the release of chemical to environment due to either catastrophic failure or normal emission during operation. Inherent Environmental Toxicity Hazard (IETH) was developed by Gunasekera and Edwards (2006) to perform comprehensive evaluation of environmental impacts in terms of aquatic, terrestrial and atmospheric hazard. In order to assess the impact, the chemical substances are assumed to be in steady state distribution in multimedia world, which comprises of the compartments of air, soil, water, biota, suspended sediment and sediment. The environmental impact can be evaluated based on its toxicity that could kill the animals in different environmental compartment.

Besides the individual aspect evaluation method, there are existing works which evaluate the inherent safety, health and environment altogether, such as EHS method (Koller et al., 1999), INSET toolkit from INSIDE Project (2001), etc. Those methods consider comprehensive aspects of inherent SHE but however, they are not mainly focusing on R&D stage. Those methods also involve a number of tools and user interfaces which requires large quantity of data for completion of evaluation. This makes the inherent SHE evaluation becomes more complicated. Therefore, a simple yet effective inherent SHE hazard evaluation approach for application in process R&D stage is important to facilitate the hazard analysis in chemical industries. Besides, a systematic and reliable assessment framework based on inherent approach is also crucial for effective process design (Tugnoli et al., 2009). In this study, a systematic multiple criteria decision making approach using fuzzy optimization was presented. Similar approach employed by Liew et al. (2012) in the process synthesis of methyl methacrylate (MMA) has indicated that such technique is reliable for screening of reaction pathway. Using the mentioned method, the criteria of inherent SHE can be integrated holistically into the pathway assessment.

3. Biodiesel Production Through Transesterification Process

For production of biodiesel, transesterification process is the most common production method out of others, such as direct use and blending, micro-emulsions and thermal cracking (pyrolysis) (Leung et al., 2009). Transesterification process can effectively convert the oils to biodiesel by reacting the triglycerides with straight chain aliphatic alcohols (e.g. methanol or ethanol). From the reaction, biodiesel (or esters of fatty acids) and glycerol (trihydric alcohol) are produced. The conventional feedstock for biodiesel production is supplied from food crop, but it significantly induces high cost to biodiesel product due to food competition for human and animal consumption. Non-food crop such as waste vegetable oil was suggested to be used in biodiesel production in order to reduce the production cost. The conventional transesterification is taken place by using base catalysis (such as sodium hydroxide, NaOH or potassium hydroxide, KOH). Base-catalyzed transesterification generates high product yield and short reaction time (e.g. 95 % yield achieved in 90 min when using soybean oil). However, it is not suitable to react with oil feedstock with high free fatty acids (>2.5 wt%) (Leung et al., 2009). Later, the pre-treatment process through acid esterification was introduced to convert the small amount of free fatty acids into biodiesel, which is then followed by base-catalyzed transesterification for the primary biodiesel production. The processes, such as acid catalyzed and enzymatic transesterification, were developed to overcome the issue of high free fatty acids content in oil feedstock. Nonetheless, those processes are having the shortfalls of slow reaction rates that limit the production rate. Supercritical transesterification was latest proposed to overcome the problem of slow reaction rate and the presence of free fatty acids. Using this method, both oil feedstock and free fatty acids can be completely converted to biodiesel under the operational condition with extreme pressure and temperature (that close to supercritical condition).

4. Case study

This study performs screening on biodiesel production pathway which is applicable to the design stage of process R&D. Considering different types of feedstock and transesterification process, eight independent production pathways are formed. Every pathway is subject to separate assessment of inherent SHE. In order to generalize the scores from those independent analyses, fuzzy optimization is applied to normalize all the indices into single comparable figure. Each category of inherent SHE is given equal consideration without over-emphasizing on certain aspect. The overall process model is illustrated in Figure 1, which indicates the pathways with the differences in the type of feedstock (fresh and waste vegetable oil); and transesterification process (base-catalyzed, acid-catalyzed, acid-catalyzed esterification followed by base-catalyzed, supercritical and enzymatic transesterification). In order to ease the classification of the production pathway (PP), those eight pathways are named according to Table 1. All those pathways form the differences of the intrinsic SHE hazards posed by the chemicals used and process conditions. Since the required data are focussed on chemical properties and process conditions only, therefore during the design stage of process R&D, the available information is sufficed to perform inherent SHE hazard assessment. The assessment methods for inherent SHE in this case study are based on PIIS, IOHI and IETH respectively. Those methods focus on the inherent SHE hazards detected during process R&D stage and hence only the fundamental data such as chemical properties and laboratory experiments are required. For inherent safety evaluation, PIIS is an index-based method whereby the total score is resulted by the summation of the scorings for parameters of inventory, flammability, toxicity, explosiveness; while process hazards consider the parameters such as temperature, pressure and reaction yield. For inherent health analysis, IOHI is also an index-based method which considers the physical and process hazards i.e. process mode, pressure, temperature, material phase, volatility, corrosiveness; and health hazards based on exposure limit data and R-phase. Similar as PIIS, the final score of IOHI is resulted by the summation of scorings of all hazard aspects involved. Lastly for inherent environmental analysis, IEHI calculates the scaled toxicity impact scorings for atmospheric, aquatic and terrestrial environment respectively. IEHI requires some general data of chemical properties (e.g. lethal concentration/dose, aqueous solubility, etc.) and inventory for purpose of estimating the worst impacts that could have killed the animals.

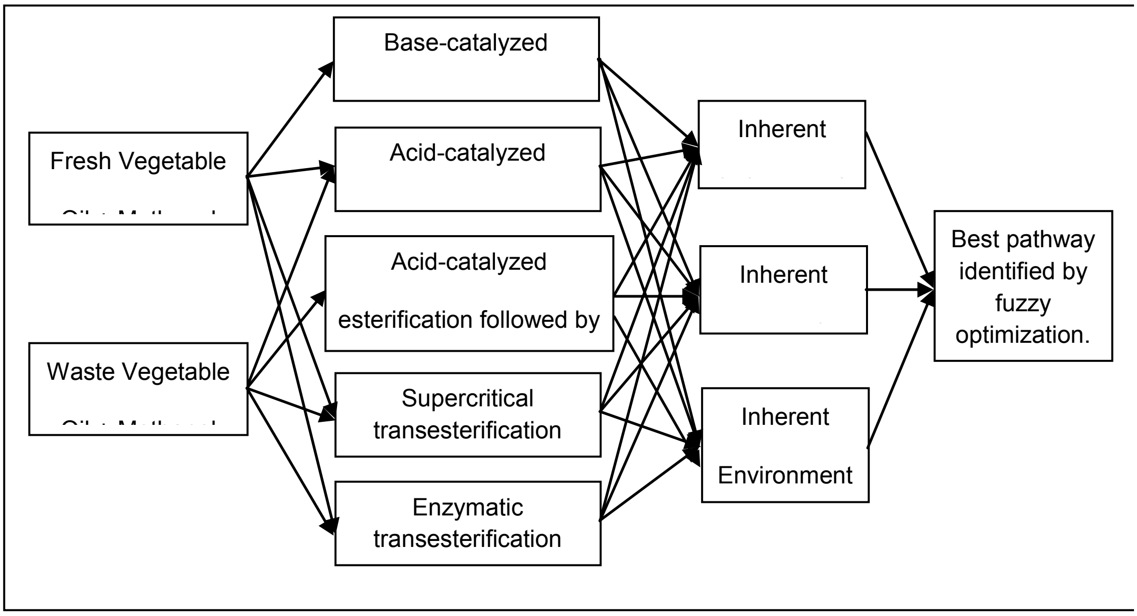

Figure 1: Overall process model for biodiesel production pathway screening

Table 1: Classification of biodiesel production pathway

Classification	Production Pathway Description
PP1	Base-catalyzed transesterification using fresh vegetable oil
PP2	Acid-catalyzed transesterification using waste vegetable oil
PP3	Acid-catalyzed esterification followed by base-catalyzed transesterification using waste vegetable oil.
PP4	Supercritical transesterification using waste vegetable oil.
PP5	Enzymatic transesterification using waste vegetable oil.
PP6	Acid-catalyzed transesterification using fresh vegetable oil.
PP7	Supercritical transesterification using fresh vegetable oil.
PP8	Enzymatic transesterification using fresh vegetable oil.

To illustrate the proposed approach, the biodiesel production with capacity of 800,000 tonnes per year is considered. This capacity is referred to the currently largest biodiesel plant built by Neste Oil company in Singapore. Besides, yearly operating hours of 8,150 hours, reactor residence time of 2 hours, and chemicals storage duration of 14 days are also assumed. By using those mentioned figures, the total inventory of the chemicals (feedstock, product and by-product) can be calculated as the volume available in storage tank and reactor. For the optimization with multiple objectives, fuzzy optimization introduces the degree of satisfaction (λ) to trade off the difference of satisfaction amongst the category X. X is the individual hazard index for inherent S, H and E which is calculated based on PIIS, IOHI and IETH. Lower value of individual index X indicates lower impact. Fuzzy optimization resolves the issue of difference range that might appear to the X by normalizing it to a single index. The λ_i is the final index that represents the mutual impact of inherent SHE for every production pathway. Prior to calculating λ_i, the upper (S^U, H^U, E^U) and lower (S^L, H^L, E^L) fuzzy limits are defined based on the maximum and minimum value of the index data. The λ_i for pathway *i* can then be determined via Eq. (1) which assumes linear relationship between the X and the upper-lower bound. In this case, the possible range of λ_i is 0 to 1 whereby the higher λ_i value denotes better impact to inherent SHE.

$$\lambda_i \leq \frac{X_i^U - X_i}{X_i^U - X_i^L} \tag{1}$$

where,

X : Category of hazard, X ϵ inherent S, H and E.

i : Production pathway (PP), *i* ϵ PP1, PP2, ..., PP8

Superscript U : Upper value of parameter X
Superscript L : Lower value of parameter X

To determine the most sustainable pathway, the optimization objective is set as below:

Maximize λ_i (2)

5. Results and discussions

Based on the chosen analysis tools of PIIS, IOHI and IETH, individual assessment of inherent SHE was conducted by referring to the reaction chemistry, process condition and properties of the chemicals involved. The hazard impacts for inherent SHE were quantified individually and tabulated in Table 2. For every individual assessment, pathway with higher score denotes the presence of higher level of hazard when in comparison with other pathways. For the conventional single objective approach, the best pathway could be easily identified through the scores. However to solve the multiple objectives problem, the direct methods (e.g. summation of scores, etc.) always cannot produce a conclusive result because the scores from different assessment tools could appear in different scaling or weight. Besides, different pathways could indicate best performance based on specific criteria of assessment and therefore, equal consideration to every objective should be given. For this case study with multiple objectives involved, the pathway which exhibits the best performance in all three criteria of inherent SHE would be chosen via fuzzy optimization. From the result of inherent SHE assessment during process R&D stage, the biodiesel production pathway with highest sustainability could be determined. By applying multiple objectives optimization approach, all hazard impacts within a pathway can be considered simultaneously using λ as trade-off to all the objectives. Referring to Eq (2), the best pathway can be identified with highest value of λ, which indicates highest compliance to all the factors.

From the fuzzy optimization result as tabulated in Table 3, production pathway of enzymatic transesterification using fresh vegetable oil (PP8) is shown as the best production pathway with highest λ value of 0.8936. It is noted that the pathway of PP8 adapts less hazardous chemicals and process conditions, which leads to the most satisfied performance in inherent SHE. Next, the pathway with second highest λ of 0.6667 is noted as base-catalyzed transesterification using fresh vegetable oil (PP1). PP1 applies moderately mild operating conditions and catalyst (sodium hydroxide, NaOH) that manifest lower hazards in SHE. PP1 is also the most conventional production pathway that has been commercialized using the feedstock of fresh vegetable oil. The biodiesel generated through PP8 and PP1 is known as first generation biodiesel because it utilizes food crop as feedstock. Using feedstock of food crop has become as less economically effective option because it inflicts food competition with human and animal feed. As solution to the food issues, non-food crops (e.g. waste vegetable oil, etc.) are introduced as a more sustainable feedstock for biodiesel production. Nonetheless, the result from this study indicates that the hazards in inherent SHE when using waste vegetable oil is generally higher than fresh vegetable oil. This could probably be due to the presence of free fatty acids in waste vegetable oil that brings significant toxicity impact to the atmospheric and aquatic environment. Apart from that, the poorest performance pathways are identified as the acid-catalyzed esterification followed by base-catalyzed transesterification using waste vegetable oil (PP3), supercritical transesterification using waste vegetable oil (PP6) and fresh vegetable oil (PP7) which indicate λ value as zero. This denotes the non-compliance to inherent SHE and it is highly recommended that those pathways only be applied with the implementation of all necessary hazard mitigation actions. Finally, it is concluded that the proposed systematic approach of biodiesel production pathway screening using fuzzy optimization is effective in identifying the pathway which is sustainable in inherent SHE. This pathway screening approach should be applied in earlier plant design stage due to the highest benefits of generating the pathway with minimal SHE hazard.

Table 2: Biodiesel production pathway scoring based on inherent SHE

Category	PP1	PP2	PP3	PP4	PP5	PP6	PP7	PP8
Safety (PIIS)	25	25	25	33	21	25	33	21
Health (IOHI)	11	14	14	16	11	14	16	11
Environment (IETH)	32.22	60.49	61.52	46.45	49.75	45.21	28.74	32.22

Table 3: *Biodiesel production pathway screening result from fuzzy optimization*

Category	PP1	PP2	PP3	PP4	PP5	PP6	PP7	PP8
Safety (PIIS)	0.67	0.67	0.67	0.00	1.00	0.67	0.00	1.00
Health (IOHI)	1.00	0.40	0.40	0.00	1.00	0.40	0.00	1.00
Environment (IETH)	0.89	0.03	0.00	0.46	0.36	0.50	1.00	0.89
Lambda, λ_i	0.6667	0.0315	0.0000	0.0000	0.3592	0.4000	0.0000	0.8936

6. Conclusions

In this study, biodiesel production pathway screening was conducted based on inherent SHE during process R&D stage. Eight potential biodiesel production pathways which differed in the type of transesterification process and feedstock were identified. Fuzzy optimization was applied as the multiple objectives optimization approach to determine the most sustainable production pathway. Based on the optimized result, the pathway of enzymatic transesterification using fresh vegetable oil shows the best performance in inherent SHE. It is followed by the pathway of base-catalyzed transesterification using fresh vegetable oil which is most conventional biodiesel production method. Application of fuzzy optimization is effective in synthesizing the most sustainable production pathway for the preservation and protection of human and environment.

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