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Correlation Study of Safety, Health and Environmental Properties at Inherent Level: Benzene Synthesis Routes

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Selection of chemical process route at early stage is one of the major tasks during the R&D stage, which needs to be based on various criteria including economy, safety, health and environment (SHE). Various methods have been developed for inherent SHE assessment, but the question is; do the SHE properties correlate with each other at inherent level. In this paper, a study is conducted to determine the correlation between inherent SHE properties by applying six SHE assessment methods to three routes for benzene production - toluene hydrodealkylation (TDA), pyrolysis gasoline hydrogenation (pygas) and catalytic naphtha reforming. Overall, the study reveals a low correlation between safety, health and environmental criteria with an average R^2 value of 0.15. This poor correlation is contributed by fugitive emission aspect, which is included in health assessment and also due to the different assessment characteristics of SHE methods such as catastrophic vs. normal operating and chronic vs. acute scenarios. Besides, it is believed that the selection of the case study, in which all the three routes have only single sub-process, has contributed to this poor correlation.

1. Introduction

Selection of chemical process route at early stage is one of the major tasks during the research and development (R&D) stage of process design. Process screening at this stage is critical since it will have crucial influence on the performance of the later stages of the process lifecycle (Hassim and Hurme, 2010a). Various methods have been introduced for assessing different process properties at inherent level. These methods are tailored so that only that information available at early design are required .The outcomes of the assessment will give suggestion for a selection of the better chemical process route.
Among the most notable inherent safety methods are by Heikkila (1996) (Inherent Safety Index, ISI) and Palaniappan et al. (2004) (iSafe index). For inherent occupational health the earliest methods are by Johnson (2001) (Occupational Health Hazard Index, OHHI), Hellweg et al. (2005), and Hassim and Edwards (2006) (Process Route Healthiness Index, PRHI) (Hassim and Edwards, 2006). As for the inherent environmental aspect, among the methods are by Cave et al. (1997) (Environmental Hazard Index, EHI), Gunasekera and Edwards (2003) (Atmospheric Hazard Index, AHI), and Gunasekera et al. (2006) (Inherent Environmental Toxicity Hazard, IETH).
Based on the review of the methods discussed above, some properties addressed in inherent safety indexes also are evaluated in health and/or environmental indexes. Therefore the aim of this paper is to determine the correlation between the inherent properties of safety, health and environmental criteria.

2. The Existing Comparisons on Inherent SHE Indexes

Several studies have been conducted to compare different index safety, health and environmental assessment methods. Adu et al. (2007) have compared 21 SHE index methods (7 safety methods, 4 health, and 10 environmental). They concluded that there is no unique merit of one method over the other in any of the SHE aspects. The only merit that separates the methods is their simplicity which is appropriate for early design phase (Adu et al., 2007).

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Koller et al. (2001) compared compared several methods that can be used to assess the hazard potential of processes during the design stage. Index based methods such as PIIS, ISI, and Dow Fire & Explosion Index were involved in this comparison. Nine processes including eight batch processes and one continuous process were selected as a case study in this comparison. The outcomes have shown that some of the methods (for example the ISI and Dow F&E index) gave nearly similar assessment ranking for the fire, explosion and reaction hazards. However both methods gave totally different results for toxic hazards. Rahman et al. (2005) compared several inherent safety based methods between each other as well as against expert evaluations. The methods considered are the PIIS (Edwards and Lawrence, 1993), ISI (Heikkila, 1999) and i-Safe (Palaniappan et al., 2004). Methyl methacrylate (MMA) process routes were selected as a case study. It is concluded that the ISI method gave the closest results to those given by the experts both in sub-process and process route evaluations. The difference in the results between the ISI and expert values on the MMA sub-process level assessment is around 10 %, whereas both the PIIS and i-Safe gave 15 % difference in comparison to the expert values. As for process route evaluations, the differences are only 3.5 % for the ISI, 9 % for the PIIS and 10 % for the iSafe (Rahman et al., 2005).

3. Methodology

In this paper, six inherent safety, health and environmental index methods are selected for the correlation study. The methods are the Inherent Safety Index (ISI) (Heikkilä et al., 1996) and i-Safe index (Palaniappan et al., 2004) for safety, the Inherent Occupational Health Index (IOHI) (Hassim et al., 2006) and Process Route Healthiness Index (PRHI) (Hassim and Edwards, 2006) for occupational health and the Inherent Environmental Toxicity Hazard (IETH) (Gunasekera and Edwards, 2006) and Environmental Hazard Index (EHI) (Cave and Edwards, 1997) for the environmental assessment. The methods were used to calculate the S, H, and E hazards level of three routes for benzene production as case study.

In general, each index uses various set of parameters in assessing the process hazards. Also the type of index calculation, operating scenario and time scale considered differs. For example all safety and environmental methods assume a worst-case scenario, i.e. total loss of containment. Health methods are in contrast, normal operation based. Time scale refers to the length of timescale during which the adverse impacts are considered. All safety and environmental methods discuss short-term events. Meanwhile the occupational health methods presented in this paper consider both short and long-term effects (Hassim et al., 2008).

Pair-wise linear regression is used as a correlation method in this study. The analysis was conducted between the MMA process route index values to find out the correlation between the SHE index methods. This technique allows two methods with different scales to be compared through correlation (e.g. ISI vs. IOHI). The coefficient R^2 indicates the correlation between the methods compared; the higher the R^2 value, the stronger the correlation. The average R^2 values are also calculated between the SHE criteria (e.g. health vs. environment) (Hassim et al., 2008).

4. Benzene Production Process Case Study

The six inherent SHE index methods are applied to three routes of benzene production as case study. The process routes are; toluene hydrodealkylation (TDA), pyrolysis gasoline hydrogenation (pygas) and catalytic reforming of naphtha. Aspen Hysys 7.3 was used to simulate the catalytic naphtha reforming process. The other two processes were not simulated since the process data are available from the literature (Turton et al., 2008).

4.1 Toluene Hydrodealkylation (TDA)

In the TDA process, toluene reacts with hydrogen to produce benzene as a desired product, with methane and diphenyl as the by-products. In this process, the conversion of toluene is 75 % with yield of 95 % - 98 %. The reaction takes place at 630 ^{0}C and 23 bar (Turton et al., 2008). The TDA process route comprises of two non-catalytic vapor-phase reactions. The first reaction is the only main reaction which is accompanied by the side reaction as shown below (Howe et al., 2005).

Main reaction: $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$ (1)

Side reaction: $C_6H_6 \leftrightarrow C_{12}H_{10} + CH_4$ (2)

4.2 Pyrolysis Gasoline Hydrogenation (pygas)

Pyrolysis gasoline (pygas) contains a mixture of about 100 chemical compounds; therefore many hydrogenation reactions take place in the reactor. The C_6 cut represents 26.2 % of the total chemicals fed to the reactor. This is the second largest feed after benzene 46.4 %. Cyclohexene is considered to be the key component of C_6 cut (Mostoufi et al., 2005). Based on that, the hydrogenation of cyclohexene is selected to be the main reaction chosen for this case study Eq.(3).

In pyrolysis process, the C_5 cut is first removed by distillation (depentanizer) and sent via the overhead to leave the central C_6 – C_8 cut which is then purified through hydrogenation process (Yang et al., 2008).

$$C_6H_{10} + H_2 \xrightarrow{\text{Hydrogenation}} C_6H_{12} \tag{3}$$

4.3 Catalytic Reforming of Naphtha

Naphtha feed normally contains about 300 chemical compounds. However, components like n-heptane, n-octane, methylcyclohexane, toluene, ethylbenzene, and xylenes are usually present in significant concentrations. These components represent more than 63 % of naphtha cut. The other components are present in much smaller amounts. The typical composition of naphtha feed includes paraffins (40 – 70 wt %), naphthenes (20 – 50 wt. %), aromatics (2 – 20 wt. %) and olefins (0 – 2 wt. %) (Raseev, 2003).

Naphtha feed is heated up to 400 – 540 ^{0}C and then fed under pressure of 10 – 20 bar. Then the feed then passes through series of catalyst-equipped reactors and furnaces between the reactors to keep the reactions temperature at desired level (Antos and Aitani, 1997). The reactions of this process are shown in Eqs. (4), (5) and (6).

$$C_6H_{14} \xrightarrow{\text{Dehydrocyclization}} C_6H_6 + 4H_2 \tag{4}$$

$$C_7H_{16} \xrightarrow{\text{Isomerization}} C_7H_8 + 4H_2 \tag{5}$$

$$C_8H_{18} \xrightarrow{\text{Isomerization}} C_8H_{10} + 4H_2 \tag{6}$$

The product from the last reactor which is called as reformate, is then transported into a high-pressure separator to remove the light cut C_1-C_2 (Antos and Aitani, 1997). Reformate is then sent via the bottom outlet into a stabilizer for more purification by separating the C_3-C_4 cuts from reformate cut (C_5-C_{8+}) (Yang et al., 2008). The reformate is then transported into a reformate process unit for further processing to produce benzene.

5. Results and Discussion

This section discusses the S, H and E hazards calculations of the three routes for benzene synthesis using the six methods mentioned earlier. In all the methods, the scoring of the hazard parameters was done based on penalty system. The penalty is used to indicate the level of hazard and tendency for exposure based on properties data on chemical (e.g. flammability for safety, occupational exposure limit value for health and atmospheric impact hazard of a chemical for environment as well as properties of the process (e.g. operating temperature for safety, process mode for health and chemical inventory for environment). It should also be noted that the penalty system for all indexes is consistent, in that a higher score indicates a more unsafe or severe (more hazardous) situation.

5.1 Calculation of the indexes

Chapter 2 Based on the ISI assessment, both pygas hydrogenation and catalytic naphtha reforming are considered to be the least safe routes with the index value of 32. The TDA route however exhibits almost the same inherent safety level but slightly safer than the two routes with the index value of 31. The higher index values in both pygas hydrogenation and naphtha reforming processes are due to higher penalties received by pressure & corrosiveness and equipment & safety structure parameters, respectively.

For iSafe index, In contrast to the ISI, pygas is considered to be the most hazardous route with index value of 20. Both TDA and naphtha reforming routes have the same value of 18 and considered as less hazardous than pygas route. Very low process yield is among the major causes contributing to the higher total index values received by the pygas process.

In the IOHI assessment, pygas hydrogenation and naphtha reforming have the highest IOHI value of 22 and hence are considered to be the least healthy routes, whereas TDA is slightly better with 21. Both pygas and naphtha routes have highly corrosive chemical substances compared to the TDA route.
In contrary the TDA process is regarded as the most harmful route to health based on the PRHI calculation (index value of 100). This is followed by pygas and naphtha reforming with the PRHI value of 36 and 27, respectively. In TDA case, the very low value of the average occupational exposure limit (OEL_{avg}) contributes to a higher PRHI index value compared to the pygas and naphtha case studies. The OEL_{avg} represents the average toxicity level of the chemical mixtures present in the process. The lower the OEL_{avg} value, the more toxic the substances are averagely.
Based on the IETH assessment, naphtha reforming is the least environmental friendly route with the IETH value of 41. This is followed by the TDA and pygas routes with index value of 26 and 23, respectively. The pygas route has the smallest inventory of some intermediate chemicals, which is among the biggest contributors for the low index value calculated for this process.
In the EHI assessment, naphtha reforming route is the route with the greater environmental hazards (EHI value of 16) compared to the pygas and TDA routes with the index value of 5 and 1.5, respectively. Like for the IETH, chemical inventory contributes to such assessment outcomes.

5.2 Correlation of the index methods

The index values of the six methods for the benzene case study are presented in Table 1. A higher index value indicates a greater hazard. The index values were correlated by pair-wise linear regression to determine the correlation among the six index methods. Table 2 presents the correlation coefficient R^2 values. The closer the R^2 value to the value of 1, the stronger the correlation (Hassim et al., 2008).

Table 1: Values of the ISHE index methods

Process route	ISI	iSafe	IOHI	PRHI	IETH	EHI
TDA	31	18	21	100	27	2
Pygas	32	20	22	36	23	6
Naphtha reforming	32	18	22	27	41	16

Table 2: Correlation R^2 of benzene production route index values by linear regression

<table>
<tr><th>Index</th><th>iSafe</th><th>IOHI</th><th>PRHI</th><th>IETH</th><th>EHI</th></tr>
<tr><td>ISI</td><td>0.25</td><td>1</td><td>0</td><td>0.069</td><td>0.51</td></tr>
<tr><td>iSafe</td><td></td><td>0.25</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td rowspan="2">Average</td><td></td><td>0.63</td><td>0</td><td>0.035</td><td>0.26</td></tr>
<tr><td></td><td colspan="2">0.31</td><td colspan="2">0.15</td></tr>
<tr><td>IOHI</td><td></td><td></td><td>0</td><td>0.069</td><td>0.51</td></tr>
<tr><td>PRHI</td><td></td><td></td><td></td><td>0</td><td>0</td></tr>
<tr><td rowspan="2">Average</td><td></td><td></td><td></td><td>0.035</td><td>0.26</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">0.15</td></tr>
<tr><td>IETH</td><td></td><td></td><td></td><td></td><td>0.73</td></tr>
<tr><td>EHI</td><td></td><td></td><td></td><td>0.73</td><td></td></tr>
</table>

5.2.1 Correlation between Safety and Health Index Methods

As shown in Table 2, the only strongest correlation of the different indexes was shown by the ISI and IOHI indexes with R^2 of 1. This is primarily contributed by several similar type of parameters considered in these two indexes e.g. material corrosiveness. It is interesting to point out that the ISI and iSafe showed poor correlation despite both are safety indices. This poor correlation is contributed by the different parameters considered in the assessment. For instance corrosiveness, inventory, safety equipment and safety structure are included in the ISI but not in the iSafe; instead iSafe assesses other additional parameter which is process yield sub-index.
The IOHI showed an excellent correlation with ISI (R^2 = 1) and poor correlation with iSafe index (R^2 = 0.25). The reason is that the iSafe method considers the catastrophic and short-term scenario. In contrast the IOHI is based on normal operating and long term events. Besides the parameters considered by the iSafe

and the IOHI are very much different, hence contributing to such poor correlation between these two methods.
No correlation with the PRHI was shown by any index, primarily because it is the only method which considers fugitive emission aspect in the assessment. Also the PRHI has only two parameters in common with inherent safety methods which are pressure and temperature and with different penalty system.

5.2.2 Correlation between Safety and Environmental Index Methods

The ISI has a moderate correlation with the EHI (R^2 value 0.52) and very poor correlation with the IETH (R^2 value 0.07). However, no correlation was shown by the iSafe with any of the environmental methods. Overall, the correlation between safety and environmental indexes is bad with an average R^2 value of 0.15. The reason is, even though both safety and environmental methods consider the catastrophic and short-term scenario, they have no common parameters.

5.2.3 Correlation between Health and Environmental Index Methods

As with the ISI index, the IOHI correlates moderately with the EHI (R^2 = 0.51), but very poorly with the IETH (R^2 = 0.07). This can be interpreted by the fact that; environmental index methods are based on catastrophic and short-term events whereas occupational health methods are based normal, day-to-day operation and long-term exposure. The average correlation between the health and environmental indexes is poor with R^2 value of 0.15.

5.2.4 Average Correlation between Safety, Health and Environmental Criteria

As shown in Table 2, the correlation of SHE indexes in the case study is poor. The correlation between safety and health criteria is weak with an average R^2 value of 0.31. If the PRHI is excluded (since this method does not show correlation with any of the other methods), the two criteria correlate reasonably with an average R^2 value of 0.63. This shows that the PRHI does contribute to the poor correlation between health and safety criteria since the PRHI considers fugitive emissions, which is not assessed in any of the other five methods. Table 2 also shows that the correlation of the environmental criterion with both safety and health criteria is very poor with both having an average R^2 value of 0.15. This is because; the environmental methods have no common parameters with safety and health methods. Based on the results of correlation between the indexes, either the ISI or IOHI can be used as single method to assess the all the three S, H and E criteria simultaneously as they showed significant correlation (ranges from 0.51 to 1) with other health, safety or environmental index methods.

6. Conclusions

In this paper, a study was conducted to determine the correlation of SHE properties at inherent level. Six index methods were used which are the ISI and iSafe (for safety), the IOHI and PRHI (for health) and the IETH and EHI (for environment). The methods employ different approach of assessment principles i.e. index calculation (additive vs. average), operating scenario (normal vs. catastrophic) and time scale (short-term vs. long-term). Three process routes for benzene production were selected as a case study; toluene hydrodealkylation (TDA), pyrolysis gasoline hydrogenation (pygas) and catalytic naphtha reforming. Almost all methods gave different hazards ranking to the three processes, except for the ISI, IOHI and EHI which regarded TDA as the least hazardous route. From the ISI and IOHI assessment perspective, the TDA process is ranked as the least hazardous because it does not consist of corrosive chemicals unlike the other two alternative routes. The TDA process also has the smallest inventory of chemicals, hence is considered as the least hazardous route from the EHI assessment standpoint. It is important to point out that the IETH does also consider inventory in the assessment. However, the scoring scale of the impact severity used in the IETH calculation neglects the small inventories of individual chemicals, thus lowering the overall value of the IETH index. This is the reason for the TDA process to be regarded as the least environmental friendly route by the EHI calculation, but not from the IETH evaluation.
From this study, it was found that the average correlation between SHE criteria at inherent level is generally poor. The average correlation between safety & health aspects is below moderate level with R^2 of 0.31. The average correlation between safety & environmental and health & environment criteria is even worse (both with R^2 = 0.15). However it is interesting to find that the ISI correlates perfectly with the IOHI (R^2 = 1). The correlations of these two methods with the EHI also were quite good with the R^2 of 0.51. This is a much stronger correlation compared to the correlation study involving other methods. Therefore it can be concluded that either the ISI or IOHI could be used as a single method to assess all the safety, health, and environmental criteria simultaneously even though they were originally developed exclusively for safety (ISI) and health (IOHI) assessment separately.

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