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Abstract. The design inadequacy of chemical reactor has caused many major accidents in process industries. The absence of safety analysis for chemical reactor especially in the early design stage is one of the reasons for faulty designs. Inherent safety can be used to perform the safety analysis at preliminary design phases. However, the literature is deficient in reporting inherent safety assessment method for chemical reactors. Therefore, this paper introduces a new indexing method for inherently safety assessment of chemical reactors at the preliminary design stage. Chemical Reactors Inherent Safety Index (CRISI) is based on three sub-indices; chemical index, process index and reaction index. These sub-indices are estimated through scores of numerous parameters in each dimension. For the unacceptable score, the process conditions are changed according to the favorable reaction conditions. CRISI is estimated for all combination of process conditions and lowest CRISI value indicates the inherently safer design of the reactor.

1. Introduction
Chemical reactor is absolutely the heart of any process industry as the transformation of raw materials into valuable chemicals is carried out in the reactors. From the literature, it is identified that the reactor design is of critical importance because of the significant energy involvement [1]. The industrial disasters in the last century such as Flixborough and Chernobyl have revealed that the failure of chemical reactors can transform into serious consequences, such as production loss, fatalities, injuries and plant damage. Numerous reasons for Chernobyl accident involve design inadequacy, breaching of safety regulations for the construction followed by inadequate documentation for reactor operation [2]. An analysis of the reactor accidents has revealed that about 85\% accidents are caused by runaway reaction. A further study has identified that 60\% of runaway reactions occur due to inadequate reactor design, which can be improved through inherently safety concept implementation [3, 4].

The study of past incidents has identified the importance of process safety to operate a process plant. Over the last three decades, many guidelines and methodologies have been implemented to identify, analyze and manage risks from different stages of the process plant, which are demonstrated in figure 1 [5].
The former conventional safety methodologies are used after finalization of process design. Although, these studies identify the consequences and risk of the design, however, at this stage only passive, active and procedural techniques can be implemented to reduce the impact [6]. Further, the application of these strategies to modify the process after design finalization leads to extra investment in comparison to the modifications during the preliminary design stage [7].

The modifications during early design phases can be achieved by inherently safety approach. The aim of inherent safety concept is to reduce and eliminate the root cause of hazards associated with materials and operation. The key principles for inherent safety involve four major elements; as tabulated and described in table 1 [1].

### Table 1. Inherently safety elements [1]

| Principles       | Definition                                          |
|------------------|-----------------------------------------------------|
| Minimization     | Reduce the quantity of hazardous material           |
| Substitution     | Substitute the hazardous material with less hazardous material |
| Moderation       | Operate at less hazardous conditions                |
| Simplification   | Eliminates unnecessary design complexity            |

Quantification of the inherent safety principles has always been a big challenge to evaluate various options for process design. For this reason, various metrics for measurement of inherent safeness have been developed. Majority of the methods use indexing technique for inherently safer process route selection [8]. These include inherent safety index (ISI), integrated inherent safety index (I2SI) and process route index (PRI), process stream index (PSI) [8-12].

However, none of the technique is applicable to assess inherent safety level of the chemical reactor. Therefore, this paper aims to propose a new indexing method for the inherent safety assessment of the chemical reactor during the preliminary design stage. In chemical reactor inherent safety index (CRISI), different design options for the reactor are studied and analyzed to identify the inherently safer design for the reactor. This index would help to identify the more safe and cost-effective design for the reactor at the early design phase.

### 2. Methodology

There are numerous factors associated with reactor design and are grouped in three dimensions namely chemical, process, and reaction, outlined below in table 2.

### Table 2. Parameters for CRISI

| Category | Parameters                               |
|----------|------------------------------------------|
| Chemical | Auto-ignition temperature, flammability, explosiveness |
| Process  | Operating pressure, temperature          |
| Reaction | Reaction parameter, the heat of reaction, yield |
A systematic approach based on above-mentioned factors to design an inherently safer chemical reactor at the preliminary design stage is presented in figure 2.

![Diagram](image-url)

**Figure 2.** Framework for the chemical reactor inherent safety index (CRISI).

The higher the score for a parameter, the more hazardous is the scenario. At first, these factors for reactor design are analyzed and then combined to define the chemical reactor inherent safety index (CRISI). The scoring values for these factors are explained in table 3. Finally, index values for different design options of chemical reactor relatively ranked.

**Table 3. Score for CRISI**

| Score | Description      |
|-------|------------------|
| 1     | Recommended      |
| 2     | Sound engineering practice |
| 3     | Probably unsafe  |
| 4     | Minor accident   |
| 5     | Major accident   |

In next subsections, the parameters that contribute to the design and ultimately the safety of chemical reactor are explained. The scoring of all the parameters is provided in table 4.

### 2.1. Chemical Score (CS)

The overall chemical score (CS) is comprised of the scores for autoignition temperature, flammability, and explosiveness, which can be written as:

\[
CS = CS_{\text{AIT}} + CS_{\text{FM}} + CS_{\text{EX}}
\]  

(1)
2.1.1. Auto Ignition Temperature Score (C_{AIT}). Identifying the auto-ignition temperature of the fluid inside the reactor is vital to identify the safer operating condition for the reactor. Chemical mixture temperature greater than the autoignition temperature favors the fire and explosion scenarios and vice versa. The score in table 4 is based on the comparison of reactor temperature and autoignition temperature.

2.1.2. Flammability Score (C_{FM}). Flammability indicates the capability of the material to ignite, which can lead to either major fire or explosion scenario. The score for flammability in table 4 is adapted and modified from ISI [9].

2.1.3. Explosiveness Score (C_{EX}). The calculation of explosiveness is based on the difference between lower flammability limit (LFL) and upper flammability limit (UFL) of a mixture. Like flammability, the explosiveness score is adapted from ISI and can be used to indicate the level of explosiveness in the chemical reactor, available in table 4 [9].

2.2. Process Score (PS)
The operating conditions of the reactor are the contributing factors for the process score. Process Score can be obtained through:

\[ PS = PS_P + PS_T \quad (2) \]

2.2.1. Pressure Score (PS_{P}). The pressure of the reactor is one of the vital factors to define the safety level of the vessel. Operation with a high pressure will increase the chances to leak. The score for pressure is adapted from ISI method and furnished in table 4 [9].

2.2.2. Temperature Score (PS_{T}). The runaway of a chemical reaction can be controlled if the maximum temperature of synthesis reaction (MTSR) is lower than the maximum allowable temperature (MAT) [13]. The MSTR is a function of adiabatic temperature difference and conversion, given below:

\[ MSTR = \Delta T_{ad} \times (1 - \varepsilon) \quad (3) \]

2.3. Reaction Score (RS)
The reaction characteristics also contribute to defining the safety level of the chemical reactor. The reaction score is a function of yield from the reaction, heat involved and reaction parameter and can be written as:

\[ RS = RS_{RP} + RS_{HR} + RS_{Y} \quad (4) \]

2.3.1. Reaction Parameter Score (RS_{RP}). Reaction parameter (B) can be used to estimate the tendency of a runaway reaction in a chemical reactor [14] and can be estimated by using equation (5). Here, E is activation energy, \( \Delta T_{ad} \) is adiabatic temperature rise, R is gas constant and T is reaction temperature. If, \( B \leq 5 \), the reactor operation is considered as safe. Meanwhile, if \( B > 5 \), the reactor is operating under severe conditions and the process temperature needs to be modified [14].

\[ B = \frac{E\Delta T_{ad}}{RT^2} \quad (5) \]

2.3.2. Heat of Reaction Score (RS_{HR}). The heat of reaction indicates the energy involved in the reaction. If this energy is being released by the reaction, the reaction is exothermic and the scenario is more hazardous. This liberated heat results in a higher temperature in the reactor leading to runaway conditions. The scoring is comprised of heats of the main reaction (HR_{MR}) and the side reaction (HR_{SR}). The same scoring is used for the main and side reactions, which is provided in table 4.
MR SR HR = HR\textsuperscript{MR} + HR\textsuperscript{SR} \hspace{1cm} (6)

2.3.3. Yield Score (RS\textsubscript{Y}). Although, a higher yield is required from the reactor, however, the higher yield can be translated as the higher residence time for the mixture inside the reactor. As the residence time is increased, there are chances that the temperature of the reactor becomes high such that the runaway reaction occurs. Reactor with higher yield can have the higher score i.e., operating under severe scenario and vice versa. Scoring of reactor yield is provided in table 4.

2.4. Evaluation of Scores
The score for each category is obtained from equations (1), (2) and (4) and these scores define the safety level of the reactor. The safety criteria are defined as if the category score for the reactor design is more than the half of the maximum category score, the design is unsafe. However, if the score is less than the half of maximum category score, the design is safe. For example, the maximum score for the chemical category is 15, and for a design, if the chemical score is 8, the design is unsafe.

2.5. Estimation of the chemical reactor inherent safety index (CRISI)
The score values are used to define the indexing value for each category, and can be estimated through:

\[ CI = \frac{\text{CS}}{15}, \quad PI = \frac{\text{PS}}{10}, \quad RI = \frac{\text{RS}}{15} \hspace{1cm} (7),(8),(9) \]

| Score | Chemical | Process | Reaction |
|-------|----------|---------|----------|
| 1     | Auto-ignition temperature | Reactor temperature < Auto ignition temperature | Non-flammable | Non explosive | 0.5-5 | Maximum allowable temperature > Maximum temperature of synthesis reaction (MTSR) | B ≤ 5 | Thermally neutral < 200 | 0-39 |
| 2     |  | - | Combustible (flash point > 55°C) | 0-20 | 6-25 | - | - | Mildly exothermic < 600 | 40-59 |
| 3     |  | - | Flammable (flash point < 55°C) | 21-45 | 26-50 | - | - | Moderately exothermic < 1200 | 60-79 |
| 4     |  | - | Easily flammable (flash point < 21°C) | 46-70 | 51-200 | - | - | Strongly exothermic <3000 | 80-89 |
| 5     | Reactor temperature > Auto ignition temperature | Very flammable (flash point < 0°C & boiling point < 35°C) | 71-100 | 201-1000 | Maximum allowable temperature < Maximum temperature of synthesis reaction (MTSR) | B > 5 | Extremely exothermic >3000 | 90-100 |

Table 4. Scoring description for parameters
The overall value of CRISI can be determined by the summation of the chemical index, process index, and reaction index, as follows:

\[ \text{CRISI} = \text{CI} + \text{PI} + \text{RI} \]  

(10)

Chemical reactor design with lower CRISI value is preferable in terms of safety in comparison and vice versa.

3. Results and Discussions

The design of methanol synthesis reactor is used to demonstrate the capability of CRISI for chemical reactor safety assessment at the preliminary design stage. Two different design options are considered for the reactor, which is tabulated in Table 5.

| Parameter                     | Design 1 | Design 2 |
|-------------------------------|----------|----------|
| Operating Pressure (bar)      | 72.1     | 50.0     |
| Operating temperature (°C)    | 249.3    | 217.7    |

The simulation of methanol process is available in figure 3 [15]. Industrially the methanol is manufactured through catalytic reaction of synthesis gas. Extra heat is removed through cooling and the methanol is separated from the mixture using phase separation method. The remaining mixture is recycled to increase the process efficiency.

CRISI concept has been applied to the methanol synthesis reactor. The process information for the design option 1 is obtained from process simulation software and transferred to MS Excel program through VBA coding. The components data is collected from literature and nested to the spreadsheet tool through user input. The reactor scores for all three categories are estimated as per equations (1), (2) and (4), presented in Table 6. By analyzing the scores, it is identified that chemical score is acceptable, while process and reaction scores are unacceptable. To minimize these scores, the process conditions for the reactors are moderated as per the study of favorable conditions for the methanol synthesis reaction and provided as design 2 in Table 5. The calculations of chemical, process and reaction scores are performed again, outlined in Table 6. Study of these scores has revealed that chemical score is not changed, however, it is acceptable. For process score, it is slightly moderated, and now acceptable. Whereas, the reaction score has not changed. However, the reaction chemistry does not allow to further moderate the process conditions. For the initial and final score values, the CRISI has been estimated.
using equations (7) to (10), a slight change in the index value is observed. From the score and index values, design 2 is considered as the best design option for the methanol synthesis reactor.

Table 6. Parameters scores and CRISI for methanol synthesis reactor

| Parameter                      | Score Value | Design 1 | Design 2 |
|--------------------------------|-------------|----------|----------|
| Chemical Aspect                |             |          |          |
| Auto ignition temperature      | 1 or 5      | 1        | 1        |
| Flammability                   | 1 - 5       | 2        | 2        |
| Explosiveness                  | 1 - 5       | 4        | 4        |
| Chemical Score                 | 7           | 7        |          |
| Chemical Index                 | 0.467       | 0.467    |          |
| Process Aspect                 |             |          |          |
| Pressure                       | 1 - 5       | 4        | 3        |
| MSTR                           | 1 or 5      | 5        | 5        |
| Process Score                  | 9           | 8        |          |
| Process Index                  | 0.900       | 0.800    |          |
| Reaction Aspect                |             |          |          |
| Yield                          | 1 - 5       | 1        | 1        |
| Heat of Reaction               | 1 - 5       | 4        | 4        |
| Reaction Parameter             | 1 or 5      | 5        | 5        |
| Reaction Score                 | 10          | 10       |          |
| Reaction Index                 | 0.667       | 0.667    |          |
| Chemical Reactor Inherent safety Index (CRISI) | 2.033 | 1.933 |

Additionally, the effect of the moderation has been investigated in the process to reveal the advantages of inherent safety concept to design the chemical processes. The safety criteria in this work is the lower value of CRISI, which is achieved through moderation of process conditions. Additionally, the moderated conditions have improved the process efficiency. The process efficiency can be defined as improved with lesser duty requirements and increased product amount to process same amount of feed. For the methanol process, the moderated conditions have affected the reactions in terms of conversion, and an increment of about 53% in the amount of methanol produced is observed. Further, the moderated conditions have reduced the load on all heat exchangers as well as the compressor. For overall process, the duty requirements are improved by 0.7 %. Conclusively, the inherent safety has improved the safety level along with process efficiency, demonstrated in figure 4.

Figure 4. CRISI effect on the methanol process.

For future work, more case studies can be executed for improvement of the suggested methodology by the inclusion of additional influential parameters to define the safety of chemical reactors. Moreover, the type of the chemical reactor can be integrated to design an inherently safer chemical reactor from the very early design stages.
4. Conclusion
A new indexing method to assess the inherent safety level of a chemical reactor in the preliminary design stage is presented in this paper. Chemical reactor inherently safety index (CRISI) evaluates different design options of the chemical reactor by considering the chemical, process and reaction aspects. The score values of each category are converted to index, values and a combined index through relative ranking can identify an inherently safer design for the reactor. High CRISI value identifies the design as unsafe design and inherent safety guide words can be used to modify the design. As a future direction, the type of chemical reactor can be integrated with the aforementioned characteristics.

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