CHEMICAL ENGINEERING TRANSACTIONS

VOL. 117, 2025

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Fabrizio Bezzo, Flavio Manenti, Gabriele Pannocchia, Almerinda di Benedetto

ISBN 979-12-81206-17-5; **ISSN** 2283-9216

DOI: 10.3303/CET25117098

Inherent Safety Assessment of a Mass/Energy Integrated Large-Scale Gas Oil Hydrocracking Process

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In this study, an inherent safety analysis of the mass/energy integrated large-scale gas oil hydrocracking process was carried out using the Inherent Safety Index (I_{SI}) methodology using Computer Aided Process Engineering (CAPE) tools and Aspen Hysys V.14 simulator. This industrial process was designed to produce high value-added fuels, such as naphtha, kerosene, gasoil and liquefied petroleum gas, using Medium Vacuum Gas Oil (MVGO), Light Cycle Gas Oil (LCGO) and Heavy Coke Gas Oil (HKGO) as fresh feed. The I_{SI} assessment identified risks inherent in the process and proposed areas for improvement. The analysis was based on industry data obtained from mass and energy balances and operating conditions. The ISI integrates the Inherent Chemical Safety Index (I_{CS}) and the Inherent Process Safety Index (I_{PS}), which, in this case, yielded scores of 28 and 19, respectively, with an overall value of 47. The results indicated that the greatest risks are associated with the handling of compounds such as hydrogen, methane and benzene, whose toxic and flammable properties increase the operational hazard, and with the exothermicity of hydrotreating and hydrocracking reactions. Finally, it was concluded that the risks identified exceed the limits recommended by the regulations, which highlights the need to optimize process safety.

1. Introduction

The chemical industry has been a fundamental pillar for the development of con-temporary society, providing essential products and processes for numerous economic activities. However, since 2000, more than 700 serious accidents have been recorded in this sector according to the Major Accident Reporting System (eMARS) (Chebila, 2021), generating significant damage to public health, the economy and the social fabric. These events have provoked a deep reflection and the development of research focused on improving the safety of chemical processes. In particular, refineries and petrochemical plants have been the scene of multiple incidents derived from failures in safety barriers, deviations in operating parameters and exposure to hazardous materials (Zainal et al., 2018). These facilities handle flammable hydrocarbons and operate under extreme conditions, which increase the risk of explosions, fires, and accidental releases of toxic substances (Qi et al., 2022).

Hydrocracking, a catalytic process employed to convert heavy hydrocarbons into lighter and more valuable products such as diesel, kerosene, naphtha and liquified petroleum gas, is carried out under high pressure and temperature conditions, using hydrogen in excess to control its highly exothermic nature. Given their operational dynamism, hydrocracking plants face challenges related to safe material handling and compliance with strict product specifications (García-Maza & González-Delgado, 2024). Ensuring safety in this type of process requires risk mitigation strategies that include inherent, passive, active, and procedural approaches, with inherent safety being the most effective approach to minimize risks at their source (Ade et al., 2018). In the present work, the Inherent Safety Index (ISI) developed by Heikkilä (1999), widely recognized in the literature as an integral tool for designing safer chemical processes, is used. This index evaluates both chemical and process aspects by means of two sub-indices: the chemical one, which considers parameters such as reactivity, flammability, toxicity and corrosiveness; and the process one, which includes inventories, temperatures, pressures and equipment characteristics. Through the ISI methodology, it is possible to identify streams with

Paper Received: 25 December 2024; Revised: 10 February 2025; Accepted: 26 May 2025
Please cite this article as: Acosta-Esalas L., Garcia-Maza S., Gonzalez-Delgado A.D., 2025, Inherent Safety Assessment of a Mass/energy Integrated Large-scale Gasoil Hydrocracking Process, Chemical Engineering Transactions, 117, 583-588 DOI:10.3303/CET25117098

unfavorable safety levels, making it possible to prioritize mitigation strategies from a perspective based on process engineering (Janošovský et al., 2022).

Most existing studies on inherent safety focus on polymerization or conventional petrochemical operations, without addressing the unique challenges posed by highly exothermic, high-pressure catalytic processes such as hydrocracking. This work contributes to filling this gap by presenting a detailed case study of a gas oil hydrocracking process, where the ISI is applied systematically to evaluate and compare the safety performance of different process streams and equipment. The novelty of this study lies in the integration of the Inherent Safety Index (ISI) with advanced Computer-Aided Process Engineering (CAPE) tools to support process-level decision making. This combined approach enables the early identification of critical risk points during the design and optimization phases, facilitating the development of inherently safer process alternatives. In particular, the application of this methodology to the gas oil hydrocracking process provides a comprehensive evaluation of operational conditions, equipment vulnerabilities, and substance-related hazards. Beyond accident prevention, this study reinforces the role of inherent safety as a foundational principle for achieving sustainable, resilient, and efficient design in the petrochemical industry.

2. Materials and methods

2.1 Process description

Hydrocracking is a secondary refining process that utilizes residues from other units that could not be processed earlier. The process begins by heating a mixture of oils—Medium Vacuum Gas Oil (MVGO), Heavy Gas Oil (HKGO), and Light Cycle Gas Oil (LCGO)—to 234°F using a series of heat exchangers. The preheated mixture then flows to a furnace before entering the first hydrocracking reactor, where it reaches 715°F and a pressure of 2379 psig. In this reactor, the feedstock reacts with recirculated hydrogen (76,881 lb/h) at 150°F and 2419 psig. The process also produces unconverted oil (UCO), which is drawn from the bottom of the fractionation tower. A portion (20,092 lb/h) is sent to the fluidized catalytic cracking (FCC) process, while the remainder (408,695 lb/h) is recirculated back into the system. This recirculated oil enters the second hydrocracking reactor at 720°F and 2244 psig, where it reacts with two additional recirculated hydrogen streams at 150°F and 245°F, both at 2419 psig (García-Maza & González-Delgado, 2024). The process diagram is shown in Figure 1.

The reactor effluent passes through multiple separation stages operating under extreme temperature and pressure conditions. These stages have two main objectives: to recover the hydrogen used in the reactions and to produce high quality fuels (light/heavy naphtha, liquefied petroleum gas, diesel, kerosene and light gas oils). The process is designed to be energy efficient, reusing the heat generated in certain parts of the process to reduce fuel consumption and the need for industrial services. In addition, the process integrates the management of internally generated wastewater. This water is mixed with fresh water to reduce the load of contaminants such as ammonia, and then used as wash water or sent to other areas of the process to generate steam. This integrated approach minimizes resource consumption and promotes process sustainability.

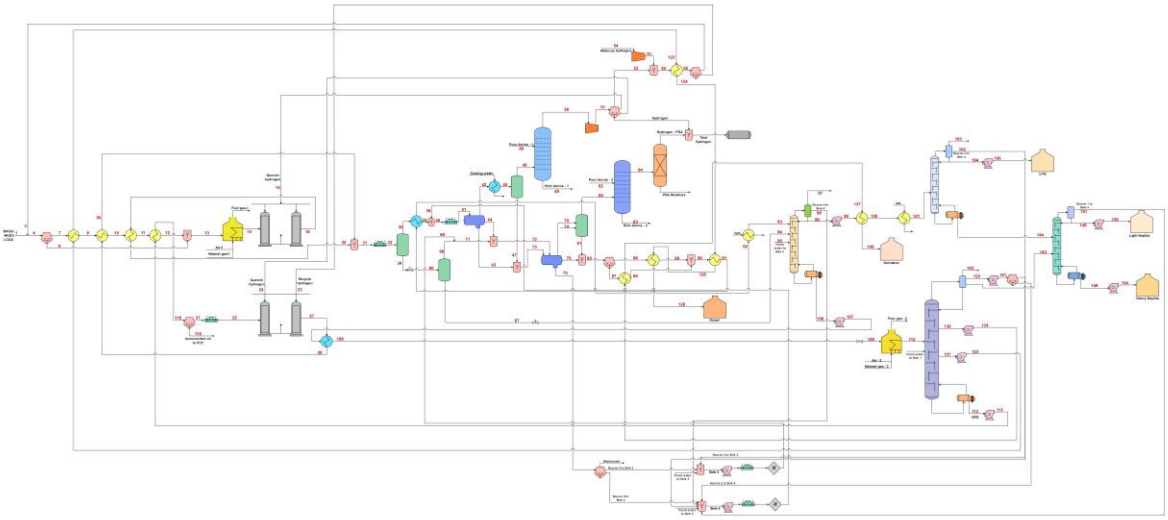

Figure 1: Process flow diagram of mass/integrated hydrocracking process

2.2 Inherent process safety assessment

Heikkilä (1999) developed the Inherent Safety Index (ISI) to simplify the quantitative assessment of inherent risks in process design. Accurate quantification of inherent safety has a direct correlation with the level of design detail. As one progresses through the design stages, a deeper understanding of the underlying chemical process system allows for a more rigorous and detailed assessment of inherent risks. The applicability of the ISI aligns optimally with the early stages of process design, given its congruence with other safety indices and its ability to assess the level of inherent safety from a still limited process data set. The total inherent safety index (I_{SI}), determined by equation (1), results from the weighting of the chemical (I_{CS}) and process (I_{PS}) inherent safety sub-indices.

$$I_{SI} = I_{CS} + I_{PS} \tag{1}$$

The I_{CS}, according to equation (2), is calculated from the sum of several dimensionless sub-indices representing the hazardous characteristics of all chemicals involved (reactants and products), such as reactivity, chemical interaction, toxicity, flammability, explosiveness and corrosiveness (Heikkila, 1999).

$$I_{CS} = N_{RM,max} + N_{RS,max} + N_{Int,max} + (N_{Fl,max} + N_{Ex,máx} + N_{Tox,max}) + N_{Cor,max} \tag{2}$$

These indices are $N_{RM,max}$ (Main reaction heat), $N_{RS,max}$ (Secondary reaction heat), $N_{Int,max}$ (Chemical Interaction), $(N_{Fl,max} + N_{Ex,máx} + N_{Tox,max})$ is the maximum sum of subscripts for hazardous substances y $N_{Cor,max}$ (Corrosivity). Scoring criteria are qualitative and drawn from industrial standards and safety data sources such as Occupational Safety and Health Administration (OSHA) and American Conference of Governmental Industrial Hygienists (ACGIH). When assigning values, a conservative "worst-case scenario" approach is adopted. Tables 1 and 2 summarize the criteria used for assigning scores. This approach allows a structured but flexible evaluation tailored to process design data availability.

Table 1: Contributing Factors to the Chemical Inherent Safety Index (I_{CS})

Sub-Index for Reactions Hazards		Score range
Main reaction heat	$N_{RM,max}$	0-4
Secondary reaction heat	$N_{RS,max}$	0-4
Chemical Interaction	$N_{Int,max}$	0-4
Hazardous Substances Sub-Indexes		**Score range**
Flammability	$N_{Fl,max}$	0-4
Explosivity	$N_{Ex,máx}$	0-4
Toxicity	$N_{Tox,max}$	0-6
Corrosivity	$N_{Cor,max}$	0-2

Similarly, the process inherent safety index (I_{PS}), calculated by equation (3), is obtained from the quantification and normalization of critical variables of the process itself, such as inventory, operating temperature and pressure, equipment safety and robustness of the process structure. These parameters, expressed in terms of dimensionless indexes (N_{Inv}, $N_{T,max}$, $N_{P.max}$, $N_{Eq,max}$, $N_{ST,max}$) are weighted according to the methodology of Heikkila (1999), whose ranges are detailed in Table 2.

$$I_{PS} = N_{Inv} + N_{T,max} + N_{P.max} + N_{Eq,max} + N_{ST,max} \tag{3}$$

Table 2: Contributing Factors to the Process Inherent Safety Index (I_{PS})

Operational Process Sub-indexes		Score range
Process inventory	N_{Inv}	0-6
Process temperature	$N_{T,max}$	0-4
Process pressure	$N_{P.max}$	0-4
System Component Sub-Indexes		**Score range**
Equipment	$N_{Eq,max}$	0-4
Process structure	$N_{ST,max}$	0-5

3. Results and discussion

3.1 Chemical inherent safety analysis of the mass/energy integrated hydrocracking process

This assessment examined an industrial gas oil hydrocracking process, focusing on the most critical scenarios. The process involves two key reactions: hydrotreating (removing impurities with hydrogen) and hydrocracking (breaking down large molecules). Both reactions are highly exothermic, requiring substantial hydrogen. It should be noted that the feedstock used in this process consists of complex hydrocarbon mixtures (oil heavy fractions). In this context, the reactions identified in this study are representative of a typical conventional process. Consequently, a description of the main chemicals' substances involved is included, although there may be others in smaller proportions that have not been considered in this evaluation. The analysis identified the hydrogenation of pyrrole to isobutane and ammonia as the most exothermic primary reaction, with a significant heat of reaction of -7,138.56 J/g. Similarly, the hydrogenation of phenol to benzene and water was determined to be the most critical secondary reaction, also exhibiting high exothermicity with an energy release of -11,360.72 J/g. Therefore, these indicators have a 4 score. Table 3 summarizes the properties related to toxicity, flammability, and explosiveness for the most hazardous substances involved in the process.

Table 3: Inherent safety parameters

Chemical Substance	Explosiveness (UEL-LEL) %vol	Toxic Exposure TLV (ppm)	Flammability Flash Point (°C)
Hydrogen, H_2	72	--	--
Methane, CH_4	10	1000	-185.2
Benzene, $\mathrm{C_6H_6}$	6.6.	0.02	-11

The Chemical Inherent Safety Index (I_{CS}) is determined based on the hazard classification derived from the chemical interaction matrix developed by the United States Environmental Protection Agency (EPA) (Ten et al., 2015). This approach considers the most critical interaction among the substances present in the process, enabling the evaluation of the inherent risk associated with chemical hazards.

The most hazardous substances identified in the hydrocracking process are hydrogen ($\mathrm{H_2}$), methane ($\mathrm{CH_4}$), benzene ($\mathrm{C_6H_6}$ These compounds present high flammability, explosiveness, and toxicity risks. Hydrogen, essential for hydrocracking and hydrotreating reactions, is found throughout the plant in make-up, recovery, and conditioning sections. It forms explosive mixtures with air within a wide concentration range (4–75%), posing a major hazard in the event of leaks. Methane, present in fuel gas and off-gas streams from distillation towers, is extremely flammable (flash point: –185.2 °C) and also acts as a potent greenhouse gas. Benzene, contained in the feedstock, is a known carcinogen with a very low occupational exposure limit (TLV = 0.02 ppm), indicating high toxicity even at trace levels. Given these characteristics, maximum subindex values were assigned for explosiveness ($N_{Ex,máx} = 4$), flammability ($N_{Fl,max} = 4$) and toxicity ($N_{Tox,max} = 6$) to accurately reflect the significant impact of these hazards on the inherent safety profile of the process. Although hydrogen inventory cannot be reduced due to its essential role, mitigation strategies should focus on early leak detection, fast isolation systems, and effective ventilation. For benzene and acid gases, closed transfer systems, gas scrubbing, and vapor recovery are necessary to minimize exposure. Combustible gases like methane must be safely handled through burner control optimization, pressure relief systems, and appropriate treatment of vent streams.

In addition to the previously discussed substances, the hydrocracking process handles large volumes of flammable materials such as naphtha, kerosene, and diesel, which can form explosive mixtures when in contact with air and exposed to ignition sources. The presence of hydrochloric acid (HCl) poses additional risks due to its violent reactions with metals and bases, releasing hydrogen gas and heat. Ammonia, present in the process, particularly in sour water streams, can also react exothermically with HCl, forming ammonium chloride and releasing heat. Considering the severity of these interactions, the maximum score of 4 was assigned to the chemical interaction subindex ($N_{Int,max}$).

A materials compatibility evaluation determined that while stainless steel is adequate for most equipment, the reactor requires specialized alloys due to the presence of highly corrosive compounds and extreme operating conditions. The reactor shell was specified in 2¼Cr–1Mo alloy steel, known for its mechanical strength but limited resistance to hydrogen-induced corrosion. To improve protection, the internal cladding was constructed with Alloy 347 stainless steel, an austenitic Cr-Ni steel stabilized with niobium, offering enhanced resistance to corrosion, high temperatures, and hydrogen attack. Accordingly, a score of 2 was assigned to the corrosion subindex ($N_{Cor,max}$). The scores assigned to each chemical safety subindex are summarized in Figure 2.

To mitigate these hazards, it is recommended to implement physical segregation of reactive chemicals, inert gas blanketing in storage and separation units, and real-time monitoring of corrosive and reactive compounds. These measures can help prevent uncontrolled reactions and ensure material integrity under severe operating conditions.

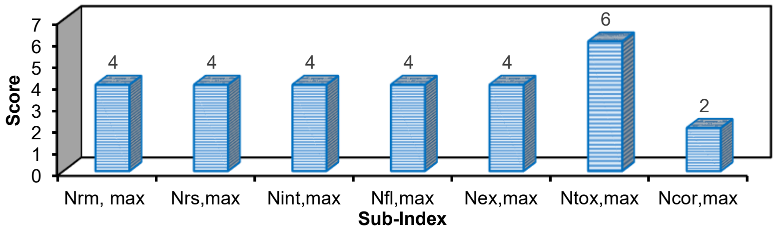

Figure 2: Impact of chemical process on the Inherent Safety Index (ISI).

3.2 Chemical inherent safety analysis of the mass/energy integrated hydrocracking process

Figure 3 presents the process safety subindexes for the large-scale hydrocracking process. Inventory was calculated by summing the mass flows over a 1-hour residence time for both ISBL and OSBL areas. ISBL inventory reached 332,269.11 kg/h (score: 4), and OSBL storage accounted for 224,396.23 kg/h (score: 2). As a conservative measure, the inventory subindex (N_{Inv}) was assigned the maximum score of 4.

Risks due to operating conditions were also significant. The highest temperature (467.51 °C) was observed in the bottom stream of the first fractionation tower, while the maximum pressure (166.78 bar) occurred in the hydrogen make-up and recycle gas system. Due to these elevated values, the temperature and pressure subindexes were each assigned a score of 3. On the other hand, fired heaters associated with the reaction and separation stages were identified as the most hazardous equipment, justifying a score of 4 for the equipment risk subindex. Lastly, the safe process structure subindex was rated 5, considering the historical record of major accidents in hydrocracking units at crude oil refineries.

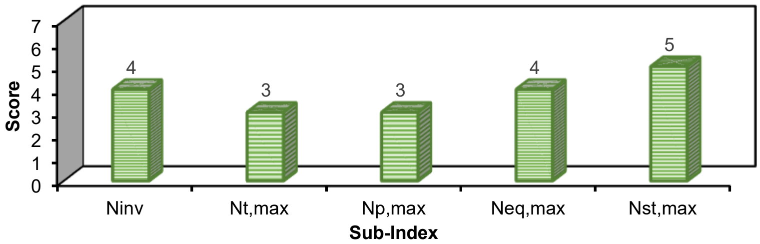

Figure 3: Impact of process safety indices on the Inherent Safety Index (ISI).

3.3 Total inherent safety index (ISI)

Figure 4 shows that the inherent safety index (ISI) for the mass/energy-integrated gas oil hydrocracking process reached a total value of 47, reflecting significant risks beyond the neutral operational benchmark. This outcome is primarily attributed to the chemical subindex (28), influenced by the presence of flammable and toxic substances and the highly exothermic nature of the reactions. The process subindex (19) indicates risks from elevated temperatures, high pressures, and critical equipment like fired heaters and high-pressure reactors, which operate under substantial thermal and mechanical stress. These elements were identified as critical points requiring risk mitigation through enhanced heat control, inert gas blanketing, segregation of reactive substances, and corrosion monitoring. In comparison with other processes assessed using the same ISI methodology, the hydrocracking process presents a more complex and hazardous profile. The PVC suspension polymerization process primarily addresses toxicity and flammability associated with vinyl chloride monomer, under moderate operating conditions and simpler process configurations (González-Delgado et al., 2023). Biodiesel production, although involving flammable solvents like methanol and hexane, operates at lower pressures and presents reduced systemic risk (González-Delgado et al., 2021). The hydrodealkylation (HDA) process shares certain operational characteristics with hydrocracking, such as the presence of aromatic hydrocarbons and high temperatures, but is generally less integrated and involves fewer critical interactions between hazardous substances (Ahmad et al., 2017).

The novelty of this work lies in the application of the ISI methodology to a hydrocracking process that integrates both mass and energy systems, increasing its complexity and the potential for cascading failures. Unlike previous studies, this analysis addresses a fully industrial configuration with interconnected units and closed recirculation of hydrogen, providing a more realistic and comprehensive perspective on inherent safety in complex refining operations.

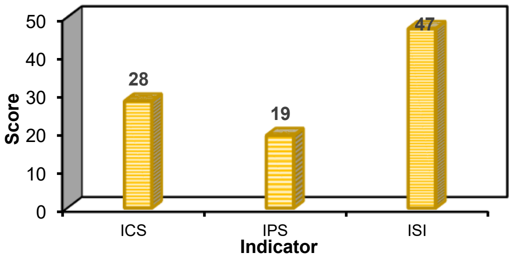

Figure 4: Impact of chemical and process safety indices on the Inherent Safety Index (ISI).

4. Conclusions

This study assessed the inherent safety of a large-scale gas oil hydrocracking process using the ISI methodology integrated with CAPE tools. The main objective was to identify critical hazards and evaluate the overall safety profile of the process. The analysis revealed a total ISI score of 47, significantly above the neutral threshold, indicating a high-risk process. The chemical safety index (I_{CS} = 28) was the dominant contributor, due to the use of hydrogen, methane, and benzene, along with highly exothermic reactions. Process-related risks (I_{PS} = 19) were attributed to extreme pressures and temperatures and high-risk equipment. Compared to other petrochemical processes evaluated in the literature, hydrocracking shows elevated risk levels, reinforcing the need for advanced mitigation strategies. These findings support the integration of ISI analysis in early design and optimization stages to improve safety performance in complex refining operations.

Acknowledgments

The authors would like to acknowledge the support of the Universidad de Cartagena, via project with Resolution 01880 of 2022 and Commitment Act No. 027 of 2022.

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