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Exergy Assessment of the Hydrocracking Process with Mass and Energy Optimization: An Industrial-Scale Study

Luisa Acosta-Esalas, Sofía García-Maza, Ángel González-Delgado\*

Nanomaterials and Computer Aided Process Engineering Research Group (NIPAC), Chemical Engineering Department,

Faculty of Engineering, University of Cartagena, Av. del Consulado Calle 30 No. 48-152, Cartagena, Colombia.

agonzalezd1@unicartagena.edu.co

Hydrocracking is a key process in petroleum refining, where catalytic cracking is combined with hydrogenation to transform heavy feedstocks into lighter and commercially valuable products. This work focuses on improving the energy efficiency of a hydrocracking unit, also incorporating the reuse of wastewater streams generated within the process itself. Using the Aspen Hysys V.14 simulation tool, a detailed energy analysis was performed to identify the main sources of energy loss in the process. The results show that the overall efficiency of the process is high (98.08%), but the Hydrogen Purification stage presents the highest exergy destruction (915,717.71 MJ/h), due to the residues generated from the separation processes in the absorption and adsorption towers, where contaminants such as NH₃ and H₂S are removed from the hydrogen streams. The analysis reveals the need to improve the efficiency of this stage to increase the sustainability of the overall process. By identifying the areas of greatest energy loss, this study provides a solid basis for proposing improvements and optimizing the operation of the hydrocracking plant.

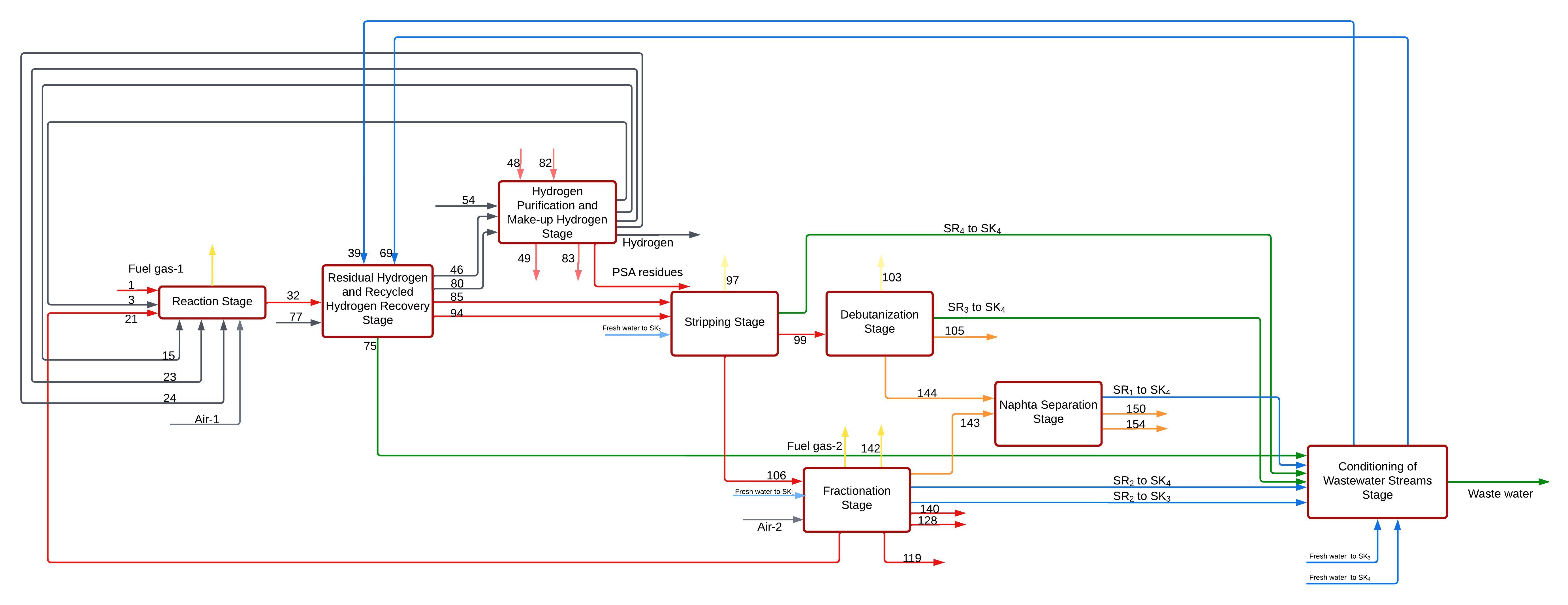
* 1. Introduction

Currently, the transportation sector is the second largest energy consumer globally, accounting for about 25% of global energy consumption, where more than 80% of energy comes from fossil fuel sources such as oil, natural gas and coal. This scenario poses a critical challenge, as the use of fossil fuels is one of the main causes of global warming and climate change (Pleyer et al., 2024). Hydrocracking, a high-pressure, high-temperature catalytic process for upgrading heavy oils into valuable fuels (gasoline, diesel, kerosene), faces energy losses through heat dissipation and pressure drops, limiting its efficiency. These losses represent an opportunity for improvement in terms of energy efficiency (Bhutani et al., 2006). In recent decades, increasing energy efficiency in industry has been a technical and scientific priority. First energy conservation measures, such as effective maintenance and awareness raising, have proven to be able to reduce up to 15 % of consumption. However, second and third level measures, which require additional investments, are necessary to make progress in reducing energy degradation. This challenge can be addressed through the concept of exergy, which assesses both the quantity and quality of energy, aligning with economic and ecological sustainability goals (Bandyopadhyay et al., 2019). On the other hand, while technologies such as hydrocracking have optimized refining processes, their implementation has posed significant environmental challenges, such as excessive water consumption and the generation of pollutants. To mitigate these impacts and make the best use of resources, it is essential to adopt a comprehensive approach that combines energy efficiency with environmental sustainability. By taking advantage of internal process flows, it is possible to reduce industrial requirements, freeing up essential resources such as water and energy, mitigating the adverse effects related to the climate crisis of the 21st century. Previous research has mainly focused on enhancing the energy efficiency of hydrocracking processes through heat integration methods, including pinch and exergy analyses. Yaylaci & Bayramoglu (2022) assessed the exergetic performance of individual equipment in a mild hydrocracking and diesel hydrotreating unit, while Goodarzvand-Chegini & GhasemiKafrudi (2017) combined pinch and exergy analysis to improve thermal efficiency in a UOP-licensed hydrocracking process. Adil (2022) extended this approach to entire refinery systems, evaluating overall exergy efficiency and loss, but without segmenting the process or considering internal resource reuse. However, none of these studies have examined water reuse strategies in conjunction with exergy analysis. In this work, a mass integration strategy was first applied to reduce freshwater consumption by reusing internal wastewater streams. A comprehensive exergy analysis was then conducted to evaluate the thermodynamic performance of the already integrated process, focusing on the identification of avoidable and unavoidable exergy losses across functional stages. The aim is to optimize internal water management through the implementation of an effluent reuse network, while also quantifying the avoidable and unavoidable exergy losses across the process.

* 1. Materials and methods

2.1. Mass/energy integrated process description

The two-stage hydrocracking process, shown in Figure 1, is a refining technology designed to convert heavy petroleum fractions into higher value products, such as diesel and kerosene, in compliance with the most stringent environmental regulations. Through an integrated system of reaction, separation and recycling, a conversion rate of close to 100% is achieved. In this process, the feed (stream 1), preheated and pressurized, is fed into a Reaction Section, where a series of reactors that operate under severe temperature (300-450°C) and pressure (85-170 bar) conditions. In these reactors, bifunctional catalysts promote both hydrogenation and cracking of hydrocarbon molecules, resulting in the production of smaller, saturated molecules. Hydrotreating catalysts, typically composed of molybdenum and nickel on alumina, remove heteroatoms (nitrogen, oxygen and sulfur), while cracking catalysts, such as zeolitics, induce the cleavage of carbon chains. Hydrogen is continuously recycled in the process. To ensure purity and efficiency, the hydrogen is recovered and purified in subsequent stages: Residual Hydrogen and Recycled Hydrogen Recovery Stage and Hydrogen Purification and Make-up Hydrogen Stage. Amine absorption processes are used to remove acidic compounds and pressure swing adsorption to remove other contaminants, thus ensuring a constant supply of high-quality hydrogen. The remaining liquid (408,813 kg/h) is directed to the Stripping Stage. The stripping process aims to remove light components and contaminants from the liquid stream, producing a sour gas stream (2,257 kg/h), sour water (4,164 kg/h) and a stream rich in naphtha and liquefied petroleum gas (LPG). In the Debutanization Stage, the LPG (3,778 kg/h) is separated from the sour water (1 kg/h), sour gas (163 kg/h) and naphtha (12,701 kg/h) streams. Finally, the Fractionation Stage yields the final products: diesel (106,585 kg/h), kerosene (60,542 kg/h) and an unconverted oil residue (194,499 kg/h). A fraction of the latter (185,385 kg/h) is recycled to the second reactor, while the rest (9,114 kg/h) goes to a Fluidized Catalytic Cracking Unit. The stream from the top of the fractionator is split into fuel gas (0.9 kg/h), recycled waters (3854 kg/h) and rich naphtha, which is separated into light (9,800 kg/h) and heavy naphtha (31,093 kg/h) and a wastewater stream (32 kg/h) in a Naphta Separation stage. The operational flexibility of the process, which allows it to adapt to different feed types and product demands, coupled with the high conversion efficiency and the use of advanced catalysts, make it a key technology in the refining industry. However, the gradual deactivation of the catalysts due to coke deposition and the formation of metallic compounds must be considered, which requires periodic regeneration or replacement. In addition, the process involves significant hydrogen and energy consumption and generates waste streams that require adequate treatment to minimize their environmental impact (Treese et al., 2015).



*Figure 1: Block diagram of the mass and energy integrated hydrocracking process of gas oils.*

The graphical targeting technique proposed by El-Halwagi et al. (2003) was applied to evaluate strategies for reducing the water footprint and optimizing internal resource consumption in the hydrocracking process. This approach identified opportunities for water reuse and recycling. Using composite curve diagrams, a recycling network was developed to enable the safe reuse of treated wastewater, ensuring appropriate mixing and preventing ammonia accumulation in receiving units (sumps). In the hydrocracking process, wastewater streams from the Naphtha Separation, Fractionation, Debutanization, Stripping, and Hydrogen Recovery stages were selected as sources (SR1 to SR5, respectively). The sinks included steam flows from the fractionation and stripping towers (SK1 and SK2), and the washing sections (SK3 and SK4) of the Hydrogen Recovery stage. Water directed to SK1 and SK2 is used for steam generation in the Industrial Services Unit, so its associated energy consumption was excluded from the exergetic analysis. For sinks SK3 and SK4, a mixture of fresh water and treated wastewater was required, ensuring that NH₃ concentration remained below established limits. Any excess water from the final source was discharged, resulting in a minimum wastewater output of 27,294.24 kg/h. Figure 1 illustrates the integrated hydrocracking process and the wastewater reuse network, including the “Conditioning of Wastewater Streams” stage, which guarantees that reused water meets the quality standards required for wash operations. The stream lines are color-coded for clarity: red lines represent hydrocarbon flows, blue lines indicate fresh water streams, gray lines correspond to hydrogen flows, light-colored lines denote light products, yellow lines indicate contaminated gas streams, pink lines represent amine solutions, and green lines correspond to wastewater with ammonia content. This integration strategy led to a 25.54% reduction in freshwater consumption and a 25.31% decrease in total wastewater generation. The subsequent energy analysis was aimed at identifying further opportunities for process optimization from a thermodynamic standpoint.

2.2. Exergy Assessment

Exergy analysis, based on the second law of thermodynamics, makes it possible to evaluate the efficiency of a process by quantifying irreversible energy losses. Exergy, defined as the maximum useful work that can be obtained from a system (Atienza et al., 2024), is calculated relative to a specific reference state (298.15 K and 1 atm in this case). By identifying the components where the greatest exergy destruction occurs, measures can be taken to improve the overall efficiency of the system. Exergy represents a fraction of the enthalpy of a stream, but enthalpy alone does not indicate the usable work potential (Kotas, 1995). As the stream temperature (T) approaches room temperature (T₀), the exergy content decreases until it disappears when both temperatures are equal. Exergy analysis uses parameters such as temperature and pressure to calculate enthalpy, entropy and recoverable energy, showing how the quality of energy degrades during its use in the process. This concept has economic implications, as it measures the quality of the energy and its ability to do work, allowing costs to be allocated (Samad et al., 2023). The exergy of a flow is composed of various forms of energy, such as kinetic, potential, physical and chemical (Rahma et al., 2024). However, in this study, the analysis has been simplified by considering only the physical and chemical exergy, since the kinetic and potential contributions are negligible in comparison:

(1)

where is the total mass exergy of the streams, MJ/h; is the chemical exergy, MJ/h; is the physical exergy, MJ/h. Equation (2) is used to determine the chemical exergy of a system, which is related to the differences in chemical composition between the system and its environment. This equation consists of two terms: the first term represents the sum of the exergy of each individual component of the system, while the second term considers the exergy associated with the mixture of these components (Dincer & Rosen, 2012).

(2)

In equation (2), represents the mass fraction of component ; is the standard chemical exergy, kJ/kg; R is the universal gas constant, kJ/kmol K; is the reference temperature, in K. Physical exergy represents the potential of a system to do work due to pressure and temperature differences between the system and its surroundings:

(3)

where and represent the molar enthalpy and molar entropy associated with the thermodynamic state of the current while and correspond to the molar enthalpy and molar entropy at the reference conditions of the environment (, ). Equation (4) describes how any work done can be expressed in terms of an energy that can be harnessed.

(4)

Industrial equipment, such as reactors and heat exchangers, require heat to be exchanged with their surroundings. Thermal exergy represents the maximum amount of useful work that can be obtained from that heat, and is calculated by equation (5):

(5)

where Q represents the heat flux transferred by the source, measured in kilojoules per hour; and correspond to the temperatures of the surroundings and the heat source, respectively, both in Kelvins. Total exergy losses are calculated by subtracting the output exergy from the input exergy, as shown in equation (6).

(6)

Equation (7) establishes the total exergy input to a system (or a process or a process step), which is the sum of the exergy associated with matter flows and the exergy supplied by industrial services (mechanical work, heating, cooling, etc.). Equation (8) specifies the latter contribution. Equation (9), on the other hand, shows how the exergy leaves the system, mainly through the products and wastes.

(7)

(8)

(9)

The irreversibility of a process is a measure of the degradation of useful energy during that process. Equation (10) quantifies this loss as the difference between the exergy entering the system and that leaving associated with the products.

(10)

Equation (11) defines exergy efficiency as the quotient between the useful exergy obtained in a process and the exergy supplied to it. This parameter makes it possible to evaluate the energy quality of a system and to identify the associated irreversible losses.

(11)

* 1. Results and discussion
     1. Exergy Analysis

This study builds upon a previously investigated hydrocracking process developed by García-Maza and González-Delgado (2024), in which a base configuration was established. Based on this configuration, a twofold integration strategy was implemented: (1) energy integration to enhance thermal efficiency, and (2) mass integration through the reuse of internal wastewater streams to reduce freshwater consumption. All simulations in the present work were carried out on this base case using Aspen HYSYS V.14. This represents the first documented evaluation in the literature of a hydrocracking process with simultaneous mass and energy integration employing an exergetic approach.

According to Figure 2, this process exhibits an outstanding overall energy efficiency of 98.08%; however, detailed analysis reveals opportunities to optimize its performance. The most energy demanding stages include Fractionation (243,536.16 MJ/h), Stripping (113,490.04 MJ/h) and Hydrogen Purification and Conditioning (99,170.06 MJ/h). It is necessary a deeper analysis oriented to the utilization of waste, whose total exergy output is registered in 1,041,156.66 MJ/h, as well as to the reduction of exergy losses.

*Figure 2: Overall exergetic performance of mass/energy integrated large-scale hydrocracking process*

3.1.1 Quantification of process irreversibilities

Percentage of exergy destroyed and exergy efficiency were determined. Exergy destruction, which is quantified at 915,717.71 MJ/h, 630,559.51 MJ/h and 281,053.41 MJ/h for the purification, reaction and stripping sections respectively, represents 45.19%, 31.12% and 13.87% of the total irreversibilities in the plant (2,026,484.64 MJ/h) as shown in Figure 3. The irreversibility of a process refers to the amount of exergy lost during the process, chemical reactions in which the entropy generated is proportional to the degree of the reaction play a relevant role. Identifying these irreversibilities is essential, as they represent additional energy consumption (Samad et al., 2023). The complete gas oil hydrocracking process was segmented into eight sections, visualized in Figure 4. A detailed analysis of the input and output flows in each section was performed. For each process stage, the exergy of wastes, exergy losses and total irreversibilities were analyzed. Hydrogen Purification and Make-up Hydrogen Conditioning Stage concentrates the largest exergy losses in the plant, with tower separation operations being the main culprit. These operations generate waste with high exergy content, such as rich amine streams and PSA waste. On the other hand, irreversibilities in compressors occupy a second place in impact, since the polytropic process involves entropy generation, mainly due to the friction of hydrogen with mechanical components. Also, the large pressure differences in each compression stage significantly increase the work required. Finally, in air coolers, the irreversibilities are associated with both the pressure drop and the heat transfer between the air and the environment. On the other hand, the exergy analysis revealed that hydrocrackers are the main source of irreversibility in the reaction section due mainly to the highly exothermic nature of the reactions occurring inside the reactors. Other sources of irreversibility in this stage and in the Fractionation stage include heat losses in the fired heater, both in the casing and in the flue gas discharge. Incomplete combustion of natural gas, due to inhomogeneous mixing of fuel and comburent, results in a loss of chemical exergy. Finally, heat exchangers contribute to exergy destruction due to temperature differences between the hot and cold streams (Tang et al., 2021).

*Figure 3: Contribution of each stage of the mass/energy integrated large-scale hydrocracking process to total exergy destruction.*

3.1.2 Exergy efficiency of the mass/energy integrated process

**(a)**

**(b)**

Figure 4: Exergetic evaluation of the mass/energy integrated gas oil hydrocracking process by stage.

The exergy efficiency, calculated according to equation (11), indicates the performance of the system in terms of utilization of the available energy. The plant as a whole presented an efficiency of 98.08%. However, the Wastewater Conditioning section had the lowest efficiency (15.58%), due to the significant exergy associated with the waste water stream and the low thermodynamic conditions of the product streams. The rest of the sections showed a more efficient behavior, with values above 90%, which is attributed to the high exergy content of the output streams, rich in value-added products. The implementation of strategies for recovery and reuse of waste streams in critical stages of the process, such as Hydrogen Purification, significantly increases the overall energy efficiency of the plant. The regeneration and reincorporation of rich amines, characterized by a high energy content, together with the recovery of valuable components in the adsorption residues, promotes the optimization of the system's energy balance. Furthermore, the energetic valorization of waste gases through their integration into the plant's thermal system contributes to minimize energy losses and to reduce steam consumption. However, a detailed analysis of the chemical composition of these gases is essential to ensure compatibility with the heat exchanger materials and to avoid corrosion problems. A detailed study of the energy requirements of the process and of the possible waste treatment alternatives will allow the selection of the most suitable option from a technical and economic point of view.

* 1. Conclusions

This study performs a detailed evaluation of the diesel hydrocracking process, focusing on optimizing water consumption and energy efficiency. The exergy analysis also identified the main sources of irreversibilities in the process, highlighting the Hydrogen Purification and Reaction stages as the most relevant in terms of exergy destruction, due to the separation processes and associated exothermic reactions. The Wastewater Treatment stage showed the lowest efficiency (15.58%), indicating a considerable loss of exergy in the waste stream. The results reflect a high overall performance of the process, with an exergy efficiency of 98.08%; however, opportunities for improvement were identified through the valorization of waste with higher exergy potential (avoidable losses) and the optimization of equipment operating conditions (unavoidable losses).

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