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Evaluation of Algae-Based Biodiesel Production Topologies via Inherent Safety Index (ISI)

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Abstract: Increasing energy needs have led to soaring fossil fuel consumption, which has caused several environmental problems. These environmental aspects along with the energy demand have motivated the search for new energy systems. In this context, biofuels such as biodiesel have been developing into a substitute for conventional fuels. Microalgae are considered a promising option for biodiesel production due to their high lipid content. Therefore, it is important to analyze the technical aspects of the biodiesel production system. In this work, the inherent safety analysis of three emerging topologies for biodiesel production from microalgae was performed using the inherent safety index (ISI) methodology. Selected topologies include biodiesel production via lipid extraction and transesterification, in-situ transesterification, and hydrothermal liquefaction (HTL). The results revealed that the processes are inherently unsafe achieving total inherent safety index scores of 30, 29, and 36. The main risks in the cases were associated with the chemical safety index. Operating conditions represented no risk for topologies 1 and 2, while for topology 3 pressure and temperature were identified as critical variables. In general, topology 2 showed better performance from a safety perspective.

Keywords: microalgae; biodiesel; inherent safety; transesterification; hydrothermal liquefaction; lipids

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1. Introduction

Increased energy needs worldwide have soared the consumption of fossil fuels such as coal, oil, and gas, leading to a series of environmental problems including atmospheric pollution and global warming [1]. Biomasses are received attention as a potential source of biofuels in order to trade-off energy demands without affecting impacting the environment through viable and profitable ways [2–4]. Nowadays, biodiesel is an attractive biofuel, which is a liquid fuel consisting of mono-alkyl esters (methyl or ethyl) of long-chain fatty acids [5]. Biodiesel has similar properties to petroleum-derived diesel and can be used directly in compression ignition engines without modification [6].

Biodiesel is derived from lipid sources such as oil crops, waste oils, microalgae, and animal fats [7]. Generally, oils used in biodiesel production are composed of triglycerides that can be converted into biofuels through three main methods: thermal cracking, microemulsion, and transesterification [8]. Microalgae are considered a promising option for biodiesel production due to their high lipid content [9], fast growth rate, and high oil production [10]. Other advantages of microalgae as the feedstock for third generation biofuel production include easy-to-operate cultivation conditions, worldwide distribution inhabiting freshwater and saltwater ecosystems, and the possibility of being harvested throughout the year [11,12]. Over the last 20 years, several strains of algae and cyanobacteria have been isolated and studied for their capacity to produce biofuels; however, strains possess an inherent capacity for synthesizing and storing suitable levels of lipids and carbohydrates. Strains from the genera *Spirulina* (Arthorspira) [13], *Botryococcus* [14,15], *Chlamydomonas* [16,17], *Chlorella* [18–27], *Nannochloropsis* [28–32], *Scenedesmus* [28,33–35], and *Tetraselmis* [36–38].

Biodiesel from microalgae requires the extraction and conversion of the lipid fraction into low atomic weight compounds, methyl esters of biodegradable fatty acids [39]. Different conversion techniques to obtain biofuels from microalgae have been developed including solvent extraction followed by transesterification, fermentation to alcohols, thermal conversion pathways, and hydrothermal liquefaction (HTL) [40]. Transesterification represents the most common and commercially used method to produce biodiesel [8].

Other studies concern strain selection and the development of cultivation methods [41]. Process technical aspects such as economic profitability, energy efficiency, and environmental performance have also been studied by several authors. Ranganathan and Savithri [42] performed the techno-economic analysis of microalgae-based liquid fuels production from wastewater; the cash flow analysis revealed that the minimum selling price of hydrocarbons is $4.3/GGE Tejada Carbajal et al. [2] carried out the techno-economic analysis of five microalgae biorefinery scenarios for biodiesel production and glycerol valorization. The results showed that the biorefinery approach with glycerol valorization reached higher economic performance with an internal rate of return of 19.8%. On the other hand, Peralta-Ruiz et al. [43] evaluated various technologies for microalgae oil extraction from the exergetic viewpoint. The authors identified that hexane-based oil extraction is the most alternative route for large-scale biodiesel production with an exergy efficiency of 51%. Furthermore, Pardo-Cárdenas et al. [44] analyzed the life cycle of three biodiesel production cases from microalgae. The results indicated a 156% reduction in greenhouse gas emissions for the hexane-based oil extraction process.

In this work, the inherent safety analysis of three emerging topologies for biodiesel production from microalgae is proposed to measure process safety metrics, propose improvements for optimal performance, and select the safest route for industrial-scale biodiesel production. The topologies considered include the conventional method of lipid extraction and transesterification, in-situ transesterification (extraction and transesterification in one step), and hydrothermal liquefaction. The novelty of this project lies in the extension of a laboratory-scale process and the safety evaluation for large-scale applications.

2. Materials and Methods

In this study, the inherent safety of three emerging microalgae-based biodiesel production topologies is evaluated: lipid extraction and transesterification method, in-situ transesterification, and hydrothermal liquefaction. The processes were designed based on information reported in the literature including operational conditions, reactions conversion, and mass and energy balances, among others. The technical data obtained from the process synthesis were used to perform the modeling of topologies studied. Modeling provided the extended mass and energy balances required to perform the safety analysis. Finally, the safety analysis allowed determining the process performance from the process safety perspective, identifying improvement opportunities, and selecting the safest design. Figure 1 shows the methodology by stages applied in this work.

2.1. Process Description

2.1.1. Topology 1. Conventional Method (Lipid Extraction and Transesterification)

The process diagram for biodiesel production from microalgae by the conventional method of lipid extraction and transesterification is depicted in Figure 2. Microalgae (1000 kg/h) are cultivated in the first stage along with a nutrient concentration of 90%. Next, the microalgae are harvested by centrifugation and subjected to drying to remove excess moisture [45]. Microalgae with 5% moisture are sent to the next stage where lipids are extracted; the extraction is carried out using hexane as a solvent in a lipid:hexane ratio equal to 1:20 [43]. Hexane is an interesting alternative that provides high efficiency in lipid extraction [46]. Next, the mainstream is sent to the hexane recovery unit, while the carbohydrate- and protein-rich phase (microalgae cake) is discarded from the process. Approximately 97% of the hexane is recovered for further recycling through [47]. Then, the transesterification reaction takes place by adding methanol in methanol:lipid molar ratio 12:1 [48] and sulfuric acid as a catalyst in a catalyst:lipid molar ratio at 1:1 [49]. The catalyst was selected taking into account the content of free fatty acids in the lipid-rich phase (<1%) since soap formation could be favored when using a basic catalyst [50]. The mainstream rich in biodiesel (methyl esters) and glycerol is sent to the neutralization stage to remove the acid catalyst by calcium oxide addition.

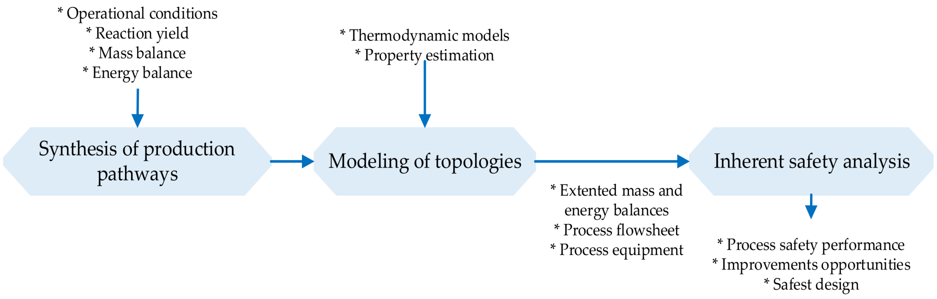

Figure 1. Schematic representation of the methodology.

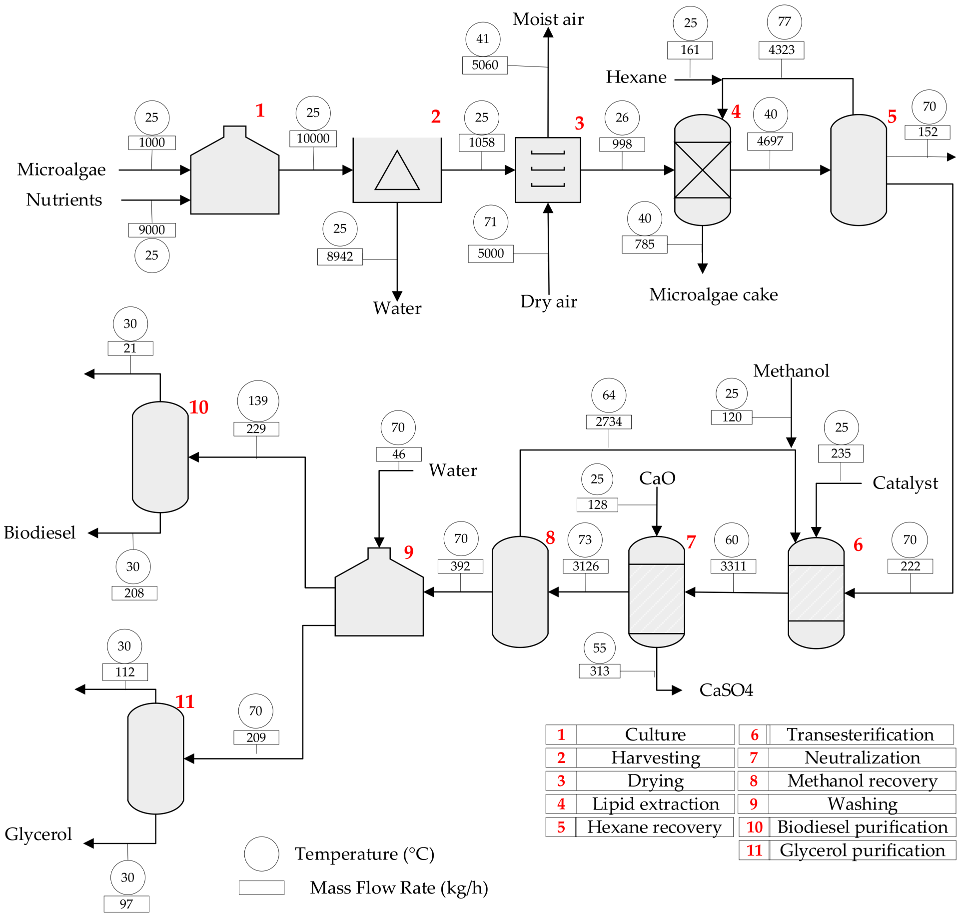

Figure 2. Process diagram for biodiesel production from microalgae via lipid extraction and transesterification.

The neutralized stream undergoes a methanol recovery of up to 87% and the resulting stream is recirculated to the transesterification unit. In the washing stage, water is added at a temperature of 70 °C to isolate the biodiesel from the glycerol. Two streams are obtained from the washing step, a hydrophilic stream containing the glycerol and a hydrophobic stream containing the biodiesel and small traces of water. The hydrophilic stream is sent to a distillation process to purify the glycerol and obtain it as a by-product. The biodiesel-rich stream goes to a flash separator where all impurities are removed, and the biodiesel leaves the process at a rate of 208 kg/h.

The transesterification reactions are shown in Equations (1)–(12) and the neutralization reaction is presented in Equation (13).

$$C_{18}H_{34}O_2 + CH_4O \rightarrow C_{19}H_{36}O_2 + H_2O \tag{1}$$

$$C_{14}H_{28}O_2 + CH_4O \rightarrow C_{15}H_{30}O_2 + H_2O \tag{2}$$

$$C_{16}H_{32}O_2 + CH_4O \rightarrow C_{17}H_{34}O_2 + H_2O \tag{3}$$

$$C_{18}H_{32}O_2 + CH_4O \rightarrow C_{19}H_{34}O_2 + H_2O \tag{4}$$

$$C_{18}H_{30}O_2 + CH_4O \rightarrow C_{19}H_{32}O_2 + H_2O \tag{5}$$

$$C_{18}H_{36}O_2 + CH_4O \rightarrow C_{19}H_{38}O_2 + H_2O \tag{6}$$

$$C_{57}H_{104}O_6 + 3\ CH_4O \rightarrow 3\ C_{19}H_{36}O_2 + C_3H_8O_3 \tag{7}$$

$$C_{45}H_{86}O_6 + 3\ CH_4O \rightarrow 3\ C_{15}H_{30}O_2 + C_3H_8O_3 \tag{8}$$

$$C_{51}H_{98}O_6 + 3\ CH_4O \rightarrow 3\ C_{17}H_{34}O_2 + C_3H_8O_3 \tag{9}$$

$$C_{57}H_{98}O_6 + 3\ CH_4O \rightarrow 3\ C_{19}H_{34}O_2 + C_3H_8O_3 \tag{10}$$

$$C_{57}H_{92}O_6 + 3\ CH_4O \rightarrow 3\ C_{15}H_{32}O_2 + C_3H_8O_3 \tag{11}$$

$$C_{57}H_{110}O_6 + 3\ CH_4O \rightarrow 3\ C_{19}H_{38}O_2 + C_3H_8O_3 \tag{12}$$

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O \tag{13}$$

2.1.2. Topology 2. In-Situ Transesterification

The production of biodiesel from microalgae by in situ transesterification method is shown in Figure 3. Microalgae (1000 kg/h) and nutrients (9000 kg/h) are fed into the system in the first stage where the biomass is cultivated. Then, microalgae are harvested by centrifugation and sent to a drying process to remove excess moisture. The dry biomass goes to the next step, where the lipid extraction and transesterification are carried out using methanol and sulfuric acid as a catalyst in a molar ratio of methanol: lipids and catalyzer: lipids equal to 12:1 [48] and 1:1 [49], respectively. From this unit, the carbohydrate and protein-rich phase is discarded, while the biodiesel and the glycerol-rich stream is sent to the neutralization stage. In the neutralization step, calcium oxide is added to neutralize the catalyst; calcium sulfate and water leave this unite as waste.

The neutralized stream is subjected to a distillation process to recover the methanol and sent it back to the process. In the washing stage, water is added to remove the glycerol, allowing the biodiesel separation. The biodiesel-rich stream is sent to a flash separation unit where all impurities are removed; while the stream containing the glycerol is subjected to a distillation process to purify the glycerol. Biodiesel is obtained as the main product at a rate of 223 kg/h, while glycerol is produced as a by-product at a rate of 127.25 kg/h. The transesterification reactions are shown in Equations (1)–(12), the neutralization reaction is presented in Equation (13).

Applications of “in situ“ technology allow the elimination of certain stages, thus reducing installation and maintenance costs of equipment and energy consumption [51].

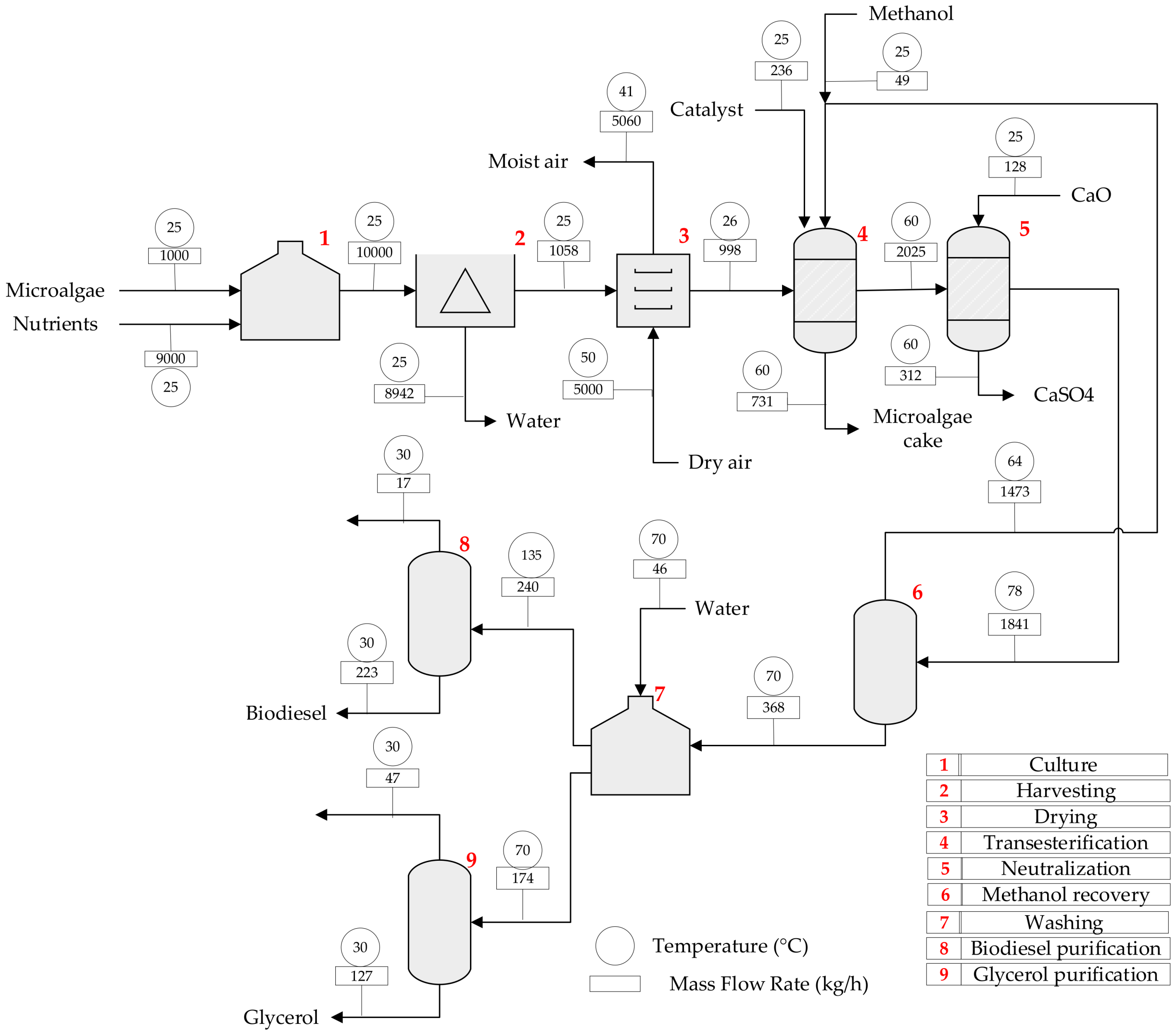

Figure 3. Process diagram for biodiesel production from microalgae via in situ transesterification.

2.1.3. Topology 3. Hydrothermal Liquefaction (HTL)

Microalgae (1000 kg/h) are fed into the cultivation stage combined with 9000 kg/h of nutrients and subsequently harvested by centrifugation (see Figure 4). The harvested biomass is sent to the next stage where the hydrothermal liquefaction reaction is performed at 200 bar and 350 °C [42]. Under these conditions, the macromolecules found within the algal biomass (including lipids, proteins, and carbohydrates) suffer depolymerization reactions (fragmentation, hydrolysis, dehydration, deoxygenation, aromatization, and repolymerization) [52], which leads to a three-phase product stream: liquid, solid and gaseous. Then, the mainstream from the HTL reactor enters the solids separation unit where ashes and carbon (CHAR) are separated and discarded. The liquid, gas, and organic phases are then separated, and the bio-crude is obtained. Bio-crude derived from thermochemical biomass conversion is a heavy organic liquid with a relatively high oxygen content, which is transformed into a conventional hydrocarbon fuel by hydrogen treatment in the hydrotreating stage [53]. In the hydrotreating unit, reactions occur at 400 °C and 100 bar [42], and hydrogen consumption is 13% of the bio-crude mass flow [54]. The hydrocarbon mixture subsequently undergoes the cracking and oligomerization stage where it is fractionated into three boiling points: C4 minus (off-gas) range, naphtha range, and heavy oil range. The latter is subjected to a distillation process to obtain pure diesel-like biofuel (160.9 kg/h).

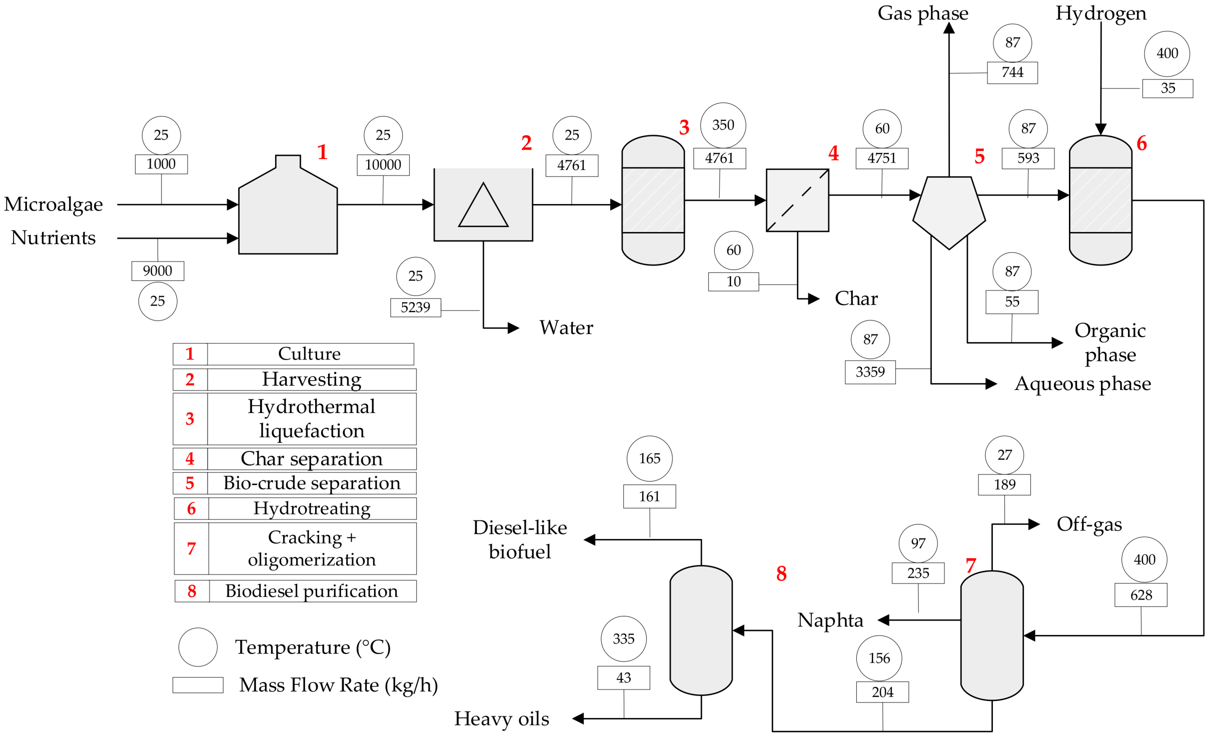

Figure 4. Process diagram for biodiesel production from microalgae via hydrothermal liquefaction (HTL).

2.2. Inherent Safety Analysis

The inherent safety of the three pathways for biodiesel production from microalgae was evaluated following the inherent safety index (ISI) methodology proposed by Heikkilä [55]. The ISI technique is used to measure the inherent safety of chemical processes at the conceptual design stage to avoid and eliminate hazards [56]. The total inherent safety index I_{TI} includes two terms: chemical safety index I_{CI} and process safety index I_{PI} as shown in Equation (14).

$$I_{TI} = I_{CI} + I_{PI} \tag{14}$$

The first term is determined from the contribution of parameters such as reactions heat, toxicity, explosiveness, flammability, corrosiveness, and chemical interaction of the substances involved in the process. The second term is calculated from process parameters such as temperature, pressure, inventory, safety equipment, and safe process structure. Figure 5 depicts the criteria to evaluate I_{CI} and I_{PI}.

The chemical safety index and the process safety index are determined as shown in Equations (15) and (16), considering the sum of the subindices related to the criteria mentioned in Figure 5.

$$I_{CI} = I_{RM,max} + I_{RS,max} + I_{INT,max} + (I_{fl} + I_{ex} + I_{tox})_{max} + I_{COR,max} \tag{15}$$

$$I_{PI} = I_{I} + I_{T,max} + I_{P,max} + I_{EQ,max} + I_{ST,max} \tag{16}$$

where I_{rmmax} and I_{rsmax} are the main and side chemical reaction subindices, respectively, I_{intmax} is the chemical interaction subindex, $(I_{fl} + I_{ex} + I_{tox})_{max}$ is the dangerous substance subindex and I_{cormax} represents the corrosiveness subindex. I_{I} is the inventory subindex, I_{Tmax} and I_{pmax} are the subindices for process temperature and pressure, I_{EQmax} is the subindex for equipment risk and I_{STmax} is the subindex for process safe structure.

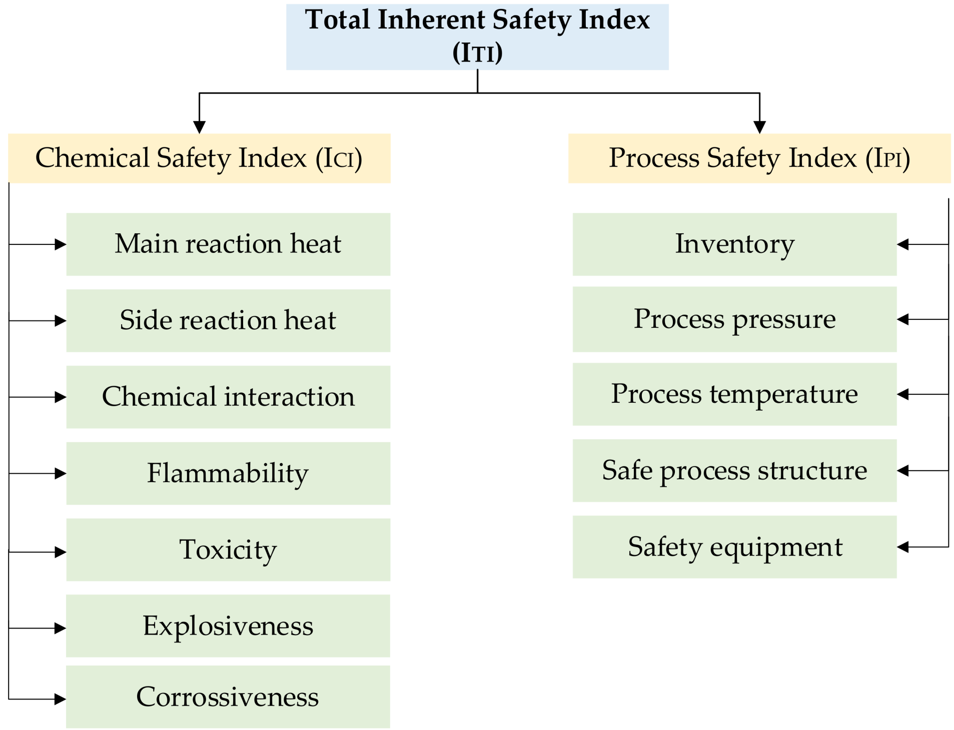

Figure 5. Criteria used to calculate I_{CI} and I_{PI}.

The calculations under the ISI methodology are performed considering the worst-case scenario. The chemical reactivity subindex is determined for the main and side reactions according to the released reaction heat (ΔH_r). Equation (17) shows the expression to calculate the heat of reaction, where H_{fprod} and H_{freac} are the standard enthalpy of formation for products and reactants, respectively.

$$\Delta H_r = \Sigma H_{fprod} - \Sigma H_{freac} \tag{17}$$

The chemical interaction sub-index evaluates undesirable reactions between chemicals and materials in the plant area. These reactions are not expected to take place inside the reactor, therefore, are not considered within the chemical reactivity subindex. The dangerous substance subindex is assessed according to the flammability (flashpoint), explosivity (Lower and Upper explosive limit), and toxicity (Threshold limit value—TLV). The corrosiveness subindex is determined based on the construction material required for the equipment depending on the corrosive substances. The values assigned for the chemical safety sub-index are determined using specific weights, as shown in Table 1.

Table 1. The score for chemical safety subindices.

I_{CI}	Symbol	Score
Mean heat of reaction	I_{RM}	0–4
Side heat of reaction	I_{RS}	0–4
Chemical interaction	I_{INT}	0–4
Flammability	I_{fl}	0–4
Explosiveness	I_{ex}	0–4
Toxicity	I_{tox}	0–6
Corrosiveness	I_{COR}	0–2

The inventory subindex is measured by the mass flows in the equipment of inside battery limits area (ISBL) during a retention time of 1 h. The temperature and pressure subindices consider the maximum temperature and pressure registered in the process. Finally, the safety equipment subindex evaluates the most unsafe equipment within the operation, while the safe process structure subindex considers the risks of an operation from an engineering standpoint. The assignment of values for process safety sub-indexes is based on specific weights, as shown in Table 2.

Table 2. The score for process safety subindices.

I_{PI}	Symbol	Score
Inventory	I_I	0–5
Process temperature	I_T	0–4
Process pressure	I_P	0–4
Equipment safety	I_{EQ}	0–4 (ISBL); 0–3 (OSBL)
Safe process structure	I_{ST}	0–5

3. Results and Discussion

The inherent safety analysis for the three microalgae-based biodiesel production topologies included the assumption of the worst-case scenario for the subindices assessment. The first step was the evaluation of hazards regarding chemical reactions. For biodiesel production by conventional and in situ transesterification methods, the main reactions occur in the transesterification stage where triglycerides and fatty acids are converted into alkyl esters (biodiesel) and glycerol [57]. The conversion of palmitic acid and methanol to methyl palmitate and water (see Equation (3)) was identified as the most exothermic reaction, showing a heat of reaction equal to 10,298.62 J/g. Regarding the biodiesel production via HTL, the main reactions of depolymerization (fragmentation, hydrolysis, dehydration, deoxygenation, aromatization, and repolymerization) take place in the hydrothermal liquefaction stage, which showed an exothermic behavior. A score of four is assigned for the chemical reactivity (main reaction) subindex for the three cases.

For the $I_{RS,max}$ metric, the side reactions for the first (conventional) and second (in situ transesterification) topologies were identified in the neutralization stage where the acid catalyst is neutralized by adding CaO (see Equation (13)). The reaction shows exothermic behavior releasing heat of -6768 j/g; hence, a score of two is assigned for both topologies. The side reactions for the third topology (HTL) correspond to hydrotreating the HTL stream to produce hydrocarbon fuels, which also showed to be exothermic.

The most dangerous substances are presented in Table 3 for each process. Properties related to toxicity, explosiveness, and flammability were checked in the safety data sheets. Hexane, methanol, piperidine, and carbon monoxide showed to be the most dangerous substances given that these are highly flammable and toxic, which led to a score of 8, 7, 8, 8, and 8, respectively. Other substances such as toluene, methylcyclohexane, heptane, methyl hexane, pentane, formic acid, acetone, ethanol, and ethylbenzene were also shown to be highly dangerous (score = 7) for topology 3. Moreover, the analysis of each property enabled the identification of the most dangerous undesired chemical interaction. For topology 1 and 2, the most dangerous interactions included the explosive mixture that vapors of substances such as hexane, methanol, and glycerol can form with air and the strongly violent reaction that occurs when sulfuric acid and water are mixed; therefore, a score of four was assigned for $I_{int,max}$. For topology 3 the possible heating of highly flammable substances (methanol, glycerol, 1-ethyl-2-pyrrolidinone, ethylbenzene, cresol, hexadecenoic acid, naphthalene, ethanol, acetone, formic acid, ammonium, acetic acid, methyl-butane, pentane, methyl pentane, hexane, methyl hexane, heptane, methyl hexane, piperidine, toluene, methyl heptane, octane, xylene, and carbon monoxide), whose vapors form an explosive mixture with air is considered the most hazardous interaction, assigning a score of four also for this subindex.

Table 3. Safety parameters for dangerous substances.

	Topology 1	**Topology 2**	**Topology 3**		
Substances	**Hexane**	**Methanol**	**Hexane**	**Piperidine**	**CO**
Flash point (°C)	−22	9.7	−22	4	Flammable
I_{fl}	4	3	4	3	2
UEL-LEL (v/v%)	7.1	38.5	7.1	9	62
I_{ex}	1	2	1	1	3
TLV (ppm)	50	200	50	1	50
I_{tox}	3	2	3	4	3
$I_{(fl+ex+tox)max}$	8	7	8	8	8

Furthermore, the material of construction for the equipment was evaluated according to the substance requirements. It was found that the majority of the substances involved in the processes were corrosive; thus, stainless steel was required as the construction material. However, a special alloy is needed in the transesterification and neutralization stages in topologies 1 and 2 due to the handling of sulfuric acid, which is a highly aggressive chemical for metals. Hastelloy c-200 was selected for these units since it is a nickel, chromium, and molybdenum-based alloy highly resistant to corrosion. Hastelloy c-200 was also required in the HTL, char separation, and bio-crude separation stages of topology 3, given the presence of highly corrosive substances and extreme conditions that affect the metals. Consequently, a score of two was assigned to $I_{cor,\ max}$ metric. Tables 4–6 presents the stages used in the biodiesel production from microalgae by the conventional method, in-situ transesterification, and HTL, respectively.

Table 4. Description of the main unit used for biodiesel production from microalgae via conventional.

Unit	Type of Unit	Temperature (°C)	Pressure (bar)	Inventory (t)	Material
Culture	Tank	25	1.013	10.00	Stainless steel
Harvesting	Centrifuge	25	1.013	10.00	Stainless steel
Drying	Dryer	71.38	1.013	6.06	Stainless steel
Lipid extraction	Column	40	1.013	5.48	Stainless steel
Hexane recovery	Distillation column	94.64	1.013	4.70	Stainless steel
Transesterification	Reactor	60	1.013	3.31	Hastelloy-c 200
Neutralization	Reactor	55	1.013	3.31	Hastelloy-c 200
Methanol recovery	Distillation column	81.24	1.013	3.13	Stainless steel
Washing	Tank	70	1.013	0.44	Stainless steel
Biodiesel purification	Flash separator	138.61	0.10	0.21	Stainless steel
Glycerol purification	Distillation column	100.70	1.013	0.23	Stainless steel

Table 5. Description of the main unit used for biodiesel production from microalgae via in situ.

Unit	Type of Unit	Temperature (°C)	Pressure (bar)	Inventory (t)	Material
Culture	Tank	25	1.013	10.00	Stainless steel
Harvesting	Centrifuge	25	1.013	10.00	Stainless steel
Drying	Dryer	71.38	1.013	1.06	Stainless steel
Transesterification	Reactor	60	1.013	2.75	Hastelloy-c 200
Neutralization	Reactor	55	1.013	2.15	Hastelloy-c 200
Methanol recovery	Distillation column	99.53	1.013	1.84	Stainless steel
Washing	Tank	70	1.013	0.41	Stainless steel
Biodiesel purification	Flash separator	134.87	0.10	0.24	Stainless steel
Glycerol purification	Distillation column	100.04	1.013	0.17	Stainless steel

Regarding the inherent safety analysis for process attributed the total inventory estimated at 41.08 t for topology 1, 28.63 t for topology 2, and 35.73 t for topology 3. It was found that the process by the conventional method handles a higher amount of mass, however, the score assigned for the inventory sub-index was 2 for all three cases. The maximum temperature for topologies 1 and 2 were registered in the biodiesel purification stage (138.6 °C and 134.87 °C); therefore, a score of one is assigned for $I_{t,max}$ for both processes. The pressure for cases 1 and 2 were kept at safe conditions (0.5–5 bar). For topology 3, the maximum temperature is reached in the hydrotreating stage (400 °C); hence, a score of three was assigned to the temperature subindex. The maximum pressure was observed in the hydrothermal liquefaction reactor (200 bar), and consequently, a score of four is assigned for this subindex.

Table 6. Description of the main unit used for biodiesel production from microalgae via HTL.

Unit	Type of Unit	Temperature (°C)	Pressure (bar)	Inventory (t)	Material
Culture	Tank	25	1.013	10.00	Stainless steel
Harvesting	Centrifuge	25	1.013	10.00	Stainless steel
HTL	Reactor	350	200	4.76	Hastelloy-c 200
Char separation	Separator	60	0.9	4.76	Hastelloy-c 200
Bio-crude separation	Separator	87.22	0.9	4.75	Hastelloy-c 200
Hydrotreating	Reactor	400	100	0.63	Hastelloy-c 200
Fractioning	Tank	155.60	1.013	0.63	Stainless steel
Biodiesel purification	Flash separator	165.09	1.43	0.20	Stainless steel

Another important parameter associated with inherent process safety is equipment safety. According to the equipment characteristics reported in Tables 2–4, it was indicated that the riskiest equipment in the three cases are the reactors where the transesterification, neutralization (topology 1 and 2), hydrothermal liquefaction, and hydrotreating (topology 3) reactions are carried out. Consequently, a score of three is assigned for the subindex $I_{EQ,max}$ Finally, the safe structure subindex is established according to historical data, report heuristics, and engineering experience [58]. For the cases studied there is no historical information showing process safety aspects, therefore, a neutral position is assumed and a score of two is assigned for this subindex. This value refers to novel processes or emerging large-scale topologies such as the case of biodiesel production from microalgae.

Figure 6 shows the results for the safety subindices evaluated for the three topologies of biodiesel production from microalgae. The chemical safety index for topology 1 and 3 was 22, values slightly higher than topology 1 with I_{CI} of 21. The contribution of the chemical reactivity, chemical interaction, and corrosiveness subindices is equal for the three topologies since the reactions performed are highly exothermic and the substances involved are corrosive and tend to form fire and explosion. However, the dangerous substance subindex contribution is lower for topology 2 since no flammable solvents are used compared to the conventional method and no highly flammable hydrocarbons are obtained as in topology 3.

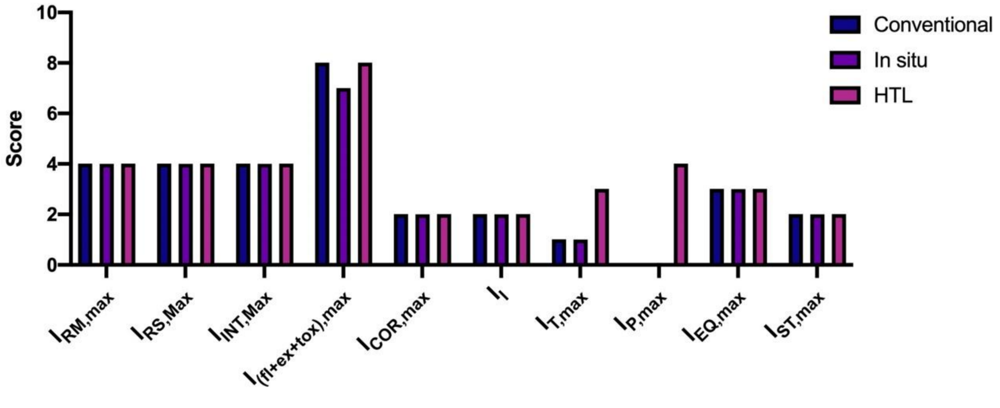

Figure 6. Subindices for chemical and process safety indices.

Regarding the process safety index, a score of 8 was achieved for topologies 1 and 2 and a score of 14 for the third topology. The findings revealed that inventory does not represent a risk or stress factor for the case studies since inventories under 50 t/h are handled. Temperature and pressure were no critical factors for the topology 1 and 2 safety because of the operation under relatively low temperatures and pressure at atmospheric conditions. For biodiesel production via HTL, the operating conditions of pressure and temperature represent a high safety risk. The high temperatures and pressures required in the hydrothermal liquefaction and hydrotreating stages represent critical variables for the process.

The most unsafe equipment for the three processes were the reactors owing to their exothermic reactions and operating conditions reached in these stages. Therefore, constant monitoring of the reactors is fundamental to avoid incidents. The safe process structure subindex contribution on the safe process index was two for the three cases since there is no information related to the behavior of the set of equipment and operations that integrate these systems.

As shown in Figure 7, was calculated a total inherent safety index of 30, 29, and 36 for the three processes. According to Heikkilä [55], inherently safe processes show an below 24 and inherently unsafe processes reach an I_{TI} above 24. The results reflect that the three topologies exhibit an inherently risky performance. The main risks are associated with the chemical factor due to the dangerous substances and the reaction type taking place. The factor associated with operating conditions represented no risk for topology 1 and 2; however, the high pressures and temperatures required for processing stages in the third topology strongly affect the process safety. It was also found that among the three pathways studied, the biodiesel production by in situ transesterification method presents an inherently safer performance compared to the other two methods. This result is attributed to the lipid extraction and transesterification carried out in one step to avoid the use of solvents or flammable substances. In addition, this method does not require critical temperatures or pressures to reach the reaction conditions. Topology 3 showed to be the most unsafe routes for biodiesel production from microalgae evaluated in this research.

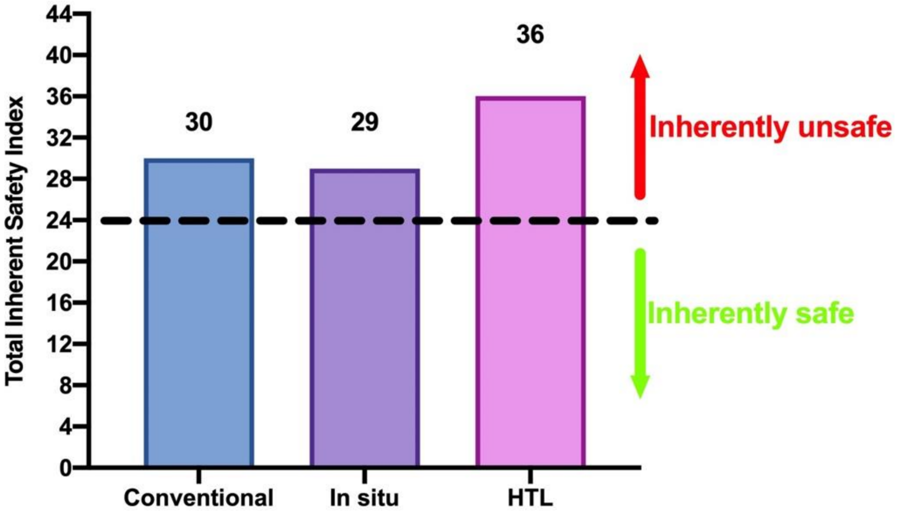

Figure 7. Total inherent safety index for three topologies for biodiesel production from microalgae.

Similar studies related to biodiesel production from residual biomass confirm the low performance of these processes from a safety perspective. The inherent safety assessment of biodiesel production from waste oil revealed that the process is unsafe, indicating that the amount of chemicals and their flammability characteristics represent the main hazard along the route [59]. The emerging risk analysis for a bio-diesel production process by transesterification of virgin and renewable oils concluded that the topology is highly unsafe and identified that the main risk is associated with methanol fire and explosion [60]. Furthermore, processes for other types of biofuels production showed inherently unsafe performance, such as a biorefinery for ethanol, butanol, succinic acid, among others, from lignocellulosic biomass that exhibited an $I_{TI} = 36$ [61].

The results provide information about the unsafe performance of biodiesel production from biomasses due to the use of highly dangerous substances. To reduce the inherent risks, some intensification options are proposed including the elimination of dangerous substances, such as methanol and sulfuric acid, by the incorporation of supercritical transesterification without using catalysts [62] or with enzymatic catalysts such as Tert Butanol which is equally efficient as acidic and basic catalysts [59]. Furthermore, it is proposed to replace methanol with other alcohols including ethanol, propanol, or n-butanol to reduce the toxicity and flammability hazard [63]. Heterogeneous catalysts are also proposed as an option to overcome the inherent safety issues of biodiesel production from microalgae; these are easily removed from the reaction and increasing the control over the neutralization process [60].

4. Conclusions

In this study, the inherent safety analysis of three emerging topologies for biodiesel production from microalgae was performed. The results revealed that the processes are inherently unsafe achieving total inherent safety index scores of 30, 29, and 36. In particular, it was determined that the main risks for the three processes were associated with the chemical safety index given to the highly exothermic reactions carried out in the transesterification, neutralization (topology 1 and 2), hydrothermal liquefaction, and hydrotreating (topology 3) stages and to the presence of dangerous substances. The inventory represented no risk for the three topologies, while the operating conditions showed no risk for topologies 1 and 2. However, the operating conditions (pressure and temperature) of the hydrothermal liquefaction and hydrotreating stages in route 3 were found to be highly risky variables affecting the process safety. In general, these results were favorable since it was possible to determine that biodiesel production via in situ transesterification showed the best performance from the safety viewpoint, while topology 3 showed the worst performance.

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