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Incorporating Exergy Analysis and Inherent Safety Analysis for Sustainability Assessment of Biofuels

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ABSTRACT: In the design of chemical/energy production systems, a major challenge is how to quantify the sustainability of the systems. Concerns on economic return and environmental impacts have been well received by researchers and practitioners. However, the irreversibility of the process has not been taken into consideration yet. Based on the first and second laws of thermodynamics, exergy analysis allows accounting for irreversibility in the process and provides a detailed mechanism for tracking the transformation of energy and chemicals. Sustainability assessment in the societal dimension is mostly a "soft" activity, as the aspects to be considered and the method of evaluation are frequently subjective. How to assess the societal impact of a process in the early design stage remains as a challenging issue. This paper will present a sustainability assessment method incorporating economic, environmental, efficiency, and societal concerns. The efficiency assessment is conducted through exergy analysis, while the societal concerns are measured by an enhanced inherent safety index method. In conjunction with a multicriteria decision-analysis method, this methodology will provide critical guidance to the designers. The efficacy of this methodology will be demonstrated through a case study on biodiesel production processes. The results show that the new heterogeneous catalyst process performs better than the traditional homogeneous process in every dimension.

■ INTRODUCTION

Sustainability is a global issue for the long-term development of human society and ecosystem. The most widely known definition is given by United Nation in 1987: "Sustainable development is development which meets the needs of the present without compromising the ability of future generations to meet their own needs."[1] This combination of sustainability and development tries to reconcile economic growth with a new concern for environmental protection and societal issues.

In chemical engineering, process systems engineering is always positioned to address the challenges of sustainability, especially in the early design stage. The consistent strictness of environmental regulations and continuing need to reduce costs have been challenging the designers. In sustainable development, measuring the environmental and social impacts of an economic activity using specific and defined indicators is very important. The key question is how to assess sustainability and which indicators should be used. Current research on sustainability assessment are heading toward combining economic, ecological, and social indicators of sustainability. Different indices were proposed.[2−4] Many methodologies for process design assessment and selection have been guided generally by criteria integration, as reported by many researchers (Shah et al., 2003; Azapagic et al., 2006; Narayanan et al., 2007; Carvalho et al., 2008; Halim and Srinivasan, 2008; Sugiyama et al., 2008; Seay and Eden, 2009a,b; Othman et al., 2010).[5−13] In these works, the aspects of sustainability become an integral part of process design. The methodologies they developed have been used in the analysis and selection of design alternatives. These works have paved a way for a systematic assessment methodology. However, there are two issues that remain unsolved: (1) how to address the irreversibility/efficiency of the process and (2) how to address the societal performance of a process. In this work, the authors present a sustainability assessment methodology that addresses these two issues systematically in the early design stage. An overall flowchart is shown in Figure 1a to illustrate the complete assessment process in this work. For practical consideration, this parallel assessment approach can only be used for up to two cases. If there are more than two design cases to be evaluated, the authors would recommend a series flowsheet, as shown in Figure 1b. In this approach, the economic performance will be considered first. The processes with unacceptable economic performance are eliminated from further consideration. The societal impacts are then evaluated followed by the assessment of the environmental dimensions, which include potential environmental impact and the efficiency of the process. This sequence is set because the designer needs to check the inbound safety issues first. If the inbound safety cannot be satisfied, the potential environmental impacts must be undesirable. The efficiency is checked last because there are strict regulations on safety and environmental issues, but no such regulations on efficiency. This series procedure improves the efficiency of screening by eliminating non viable processes at the early design stage. As shown in Figure 1, this research intends to investigate the sustainability of a chemical process from the following aspects: economic, environment, and society. The environmental dimension encompasses two subcategories: potential environmental impact and efficiency. The efficiency assessment is conducted through exergy analysis, while the societal concerns are measured by an enhanced inherent safety index method. In conjunction

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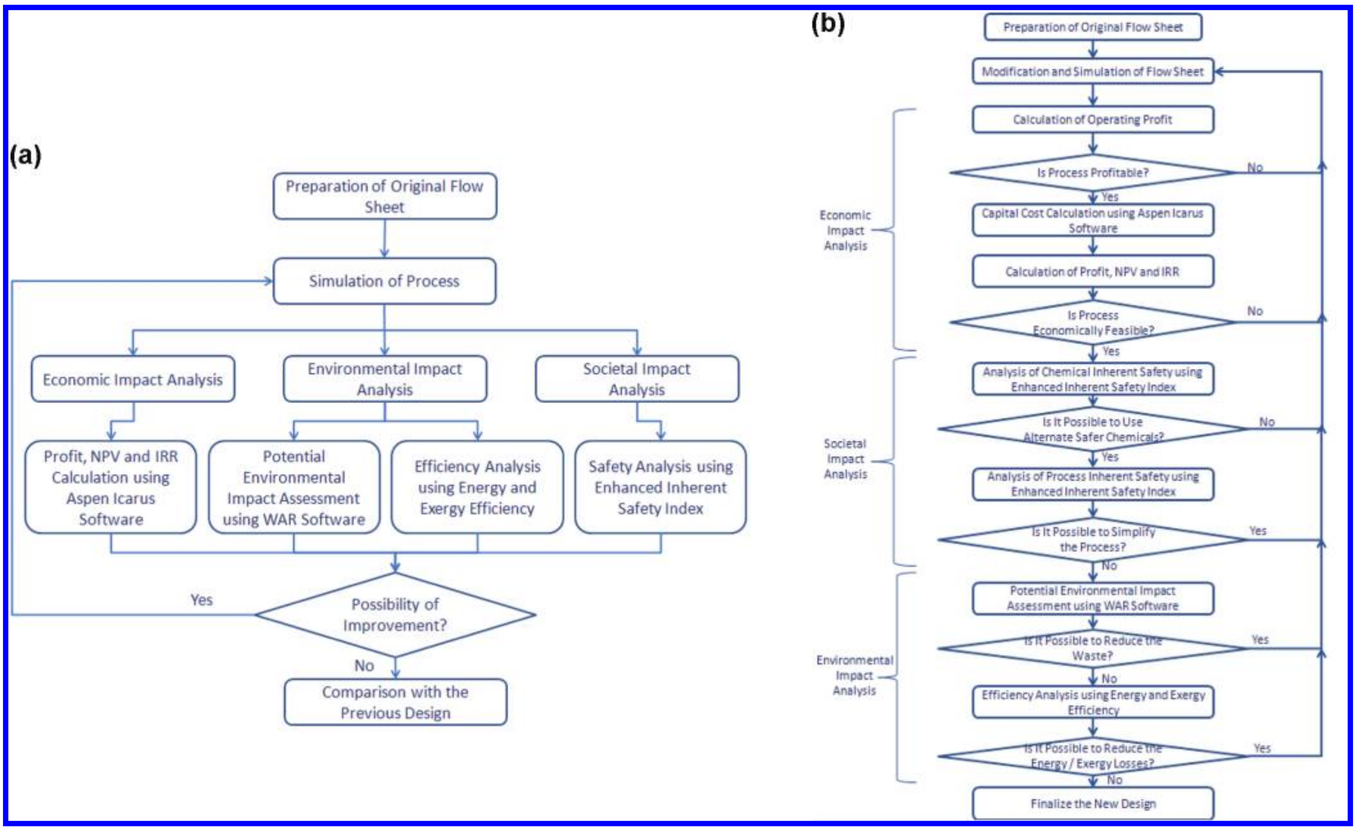

Figure 1. (a) Parallel flowchart for process sustainability assessment. (b) Series flowchart for process sustainability assessment.

with a multicriteria decision-analysis method, this methodology will provide critical guidance to the designers.

SUSTAINABILITY ASSESSMENT

In this section, sustainability indicators regarding economic, environmental, efficiency, and societal concerns will be presented.

Indicators on Economic Performance. Pintarič and Kravanja conducted a survey on the economic objective functions used for the optimization of process flowsheets.[14] Almost half of the papers found were based on simple cost and profit functions, and only 10% used net present value (NPV). Further investigation by Othman et al.[11] on the different indicators to assess economic feasibility reveals that NPV with minimum acceptable discounted cash flow rate of return (DCFRR), also known as internal rate of return (IRR), is probably the most appropriate indicator since it takes into account the overall project's economic life cycle including initial investment, annual profit, annual depreciation, salvage value, and interest on investment. When using NPV for profit calculation, a positive value means that the project is feasible and negative values indicate otherwise. Therefore, when comparing between alternatives, one with the largest positive NPV value will be the best choice. IRR is designed to reflect the highest, after-tax interest or discount rate at which the project can just break even.[15] Apparently, a project that yields IRR with higher value is considered to be profitable. Therefore by combining profit, NPV, and IRR together, a comprehensive economic assessment can be conducted.

Indicators on Environmental Performance. The authors view that environmental performance of a process encompasses two subcategories: potential environmental impact and efficiency. The indicators used in these two subcategories are presented below.

Potential Environmental Impact. Based on the material flow and energy flow information, the life cycle analysis (LCA) method can be utilized to assess the environmental performance of the product, process, or activity from "cradle-to-grave", that is, from raw material acquisition through production, use, and final disposal. Life cycle assessment consists of three complementary components (inventory, impact, and improvement) and an integrative procedure known as "scoping". In 1999, Young and Cabezas (US EPA) introduced a specific and explicit methodology, namely, waste reduction (WAR), algorithm to assess the environmental impact of chemical process.[16] WAR algorithm is designed to evaluate the environmental impact only at the manufacturing stage within the overall life cycle of the chemical production and process. The basic concept of potential environmental impact (PEI) in WAR algorithm is based on the traditional mass and energy balance, which affects the flow of environmental impact across system boundaries. PEI indexes can provide a relative indication of the environmental friendliness or unfriendliness of the chemical process. In WAR algorithm, to evaluate the environmental impact of a chemical process, both the process itself and the energy generation process are considered. To provide an indication of the potential environmental impact of a chemical process, a database of relative environmental impact scores has been created and embedded in the WAR software. As shown in Table 1, the eight different categories are divided into four general environmental impact categories.[16]

Using environmental indicators allows the users to compare different process alternatives with different capacities based on the potential environment impact emitted by the process. In general, processes with lower PEI indexes will be more environmentally friendly. However, the need to design processes with

Table 1. Impact Categories in WAR Algorithm[14]

general impact category	impact category	measure of impact category
human toxicity	ingestion	LD_{50}
	inhalation/dermal	OSHA PEL
ecological toxicity	aquatic toxicity	fathead minnow LC_{50}
	terrestrial toxicity	LD_{50}
global atmospheric impacts	global warming potential	GWP
	ozone depletion potential	ODP
regional atmospheric impacts	acidification potential	AP
	photochemical oxidation potential	PCOP

Table 2. Energy and Exergy Efficiency in Different Natural Gas Fired Combustion Plants[27]

technology	electricity output [%]	heat output [%]	heat output temperature [K]	energetic efficiency η_{fuel}	exergetic efficiency η_{exergy}
heat plant	0	90	343	0.90	0.18
power plant	55	0		0.55	0.55
CHP (heat led)	20	60	473	0.80	0.45
CHP (power led)	50	12	473	0.62	0.55

lower PEI must be constrained by the considerations of engineering economics and the market demand for the products. The environmental impact of the waste streams, the byproduct streams, and the energy consumed by the process should all be minimized.

It must be pointed out that neither the WAR algorithm nor other existing indicator sets include a very important type of efficiency analysis: exergy analysis. The authors argue that exergy analysis is particularly necessary for the assessment of energy/fuel production systems. The authors intend to justify the use of exergy analysis below.

Efficiency. Different kinds of energy display different qualities. For example, high temperature steam can produce more potential work than low temperature steam. These differences are clear in their ability to feed and drive energy processes and to be converted into other kinds of energy. As we all know, the first law of thermodynamics states that energy can be neither created nor destroyed; it just changes forms. The law does not provide enough information about the potential work producible by a form of energy or that lost during energy transformation processes. Exergy is defined as the maximum amount of work that can be extracted from a stream as it flows toward equilibrium.[17] This follows the second law of thermodynamics, which states that not all heat energy can be converted to useful work. In a process, the portion of energy that can be converted to useful work is referred to as exergy, while the remainder is called nonexergy input. Exergy analysis will allow accounting for irreversibility in a process and provide a more detailed tracking mechanism for energy and chemical generation and consumption. Defined as the maximum amount of work available from a stream, exergy analysis differentiates the qualities of energies and chemicals. Engineering applications of exergy methods to the analysis of energy-conversion and chemical process are abundant in the literature. To name a few, Hellstrom presented an interesting study of reciprocating steam engine.[18] Luminosu and Fara presented an exergy analysis of renewable energy cycles.[19] Fuel cells are a system often subject to an exergy analysis.[20,21] Exergy analysis is well suited to perform a systematic study of heat exchange processes.[22,23] In the most recent years, the research work is being shifted toward an exergetic or thermal-economic analysis of specific chemical process applications, for example, ammonia synthesis, ethanol production, methane conversion, CO_2 removal, corn-to-ethanol distillation process.[24−28]

In the application of exergy analysis to different processes and cycles, a key issue is to calculate the exergy value of process streams. The exergy value of a material system depends on the reference state that one takes for its components. The selection of the reference state is important, as different reference states will give different results in exergy analysis. In the seminal work by Szargut et al., the reference state is chosen at T_0 = 298.15 K and P_0 = 1 atm.[17] The mean composition of the earth's atmosphere, the mean composition of seawater, and the mean composition of the earth's crust are set as the reference state for chemical equilibrium. Exergy analysis can unify the efficiency concerns in energy and chemical conversion. Efficiency can be defined as the ratio of output to input for any given system. From the concept of the exergy, the consideration of energy quality leads to the concept of exergy. Energy efficiency does not include the usability of the converted energy, and exergy efficiency includes the quality level of the converted energy. Both of them are important for the sustainability assessment. As shown in Table 2, in different natural gas fired combustion plants, the values of energy and exergy efficiency can be very different.[29]

In a chemical process, there are three types of streams: the material streams, the power streams, and the heat streams. The exergy of a material stream should be a sum of chemical exergy, physical exergy, and the mixing exergy (Figure 2). The exergy of a power stream (electricity) is simple to calculate, as 1 kW of electricity represents 1 kW of exergy. The exergy of a heat stream with a constant temperature at the reference pressure can be obtained based on the concept of Carnot efficiency. All the equations on how to calculate exergy are clearly documented in the Szargut's book and ExerCom manual.[15,30]

According to this efficiency analysis, those process steps with a relatively large exergy loss can be pinpointed, and system improvement opportunities can be readily identified. In this

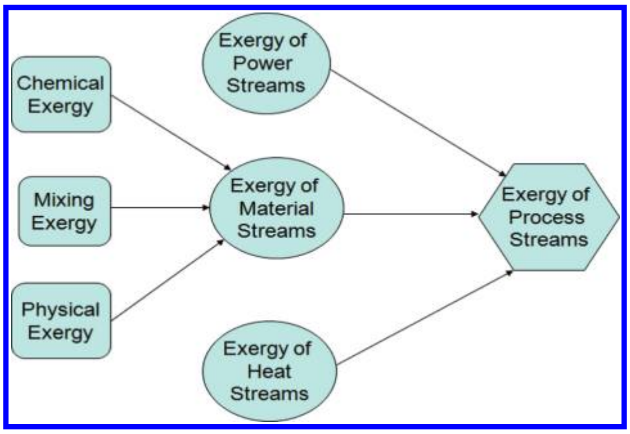

Figure 2. Exergy of Process Streams.

project, exergy efficiency, in conjunction with energy efficiency, will be used as an integral part of the overall environmental sustainability assessment.

Indicators on Societal Performance. Social indicators involve many soft criteria, which are based on human intuition, and it is normally influenced by the decision maker's knowledge and experience. It is difficult to quantify these criteria in numerical equations, but it can be scaled based on specific and distinctive measurement. Herder and Weijnen performed a study to explicitly define soft quality criteria in process design decision making.[31] Since some criteria, such as acceptable for environment, efficient use of raw material, and total life cycle aspects, have been already included in the environmental impact assessment and efficiency analysis, the authors view social assessment consideration is mainly about safety analysis in the chemical process. For chemical industries, social sustainability encompasses many aspects, including chemical safety, process equipment safety, possibility of working accidents, occupational disease, toxicity potential of the process, and so forth. Efforts have been made to estimate the probability of accidents and risk analysis of occupational accidents.[32] However, the assessment of all these factors will be difficult during the early design stage of a chemical process, when only limited information is available. Moreover, the possibility of working accidents, occupational disease, toxicity potential of the process are all rooted from the inherent safety aspects of the chemical and the process equipment. In this work, we used a simpler method which focuses on the inherent chemical and process equipment safety to quantify the social dimension of a process.

Safety is the second nature of the chemical industry. To prevent casualty and injury is of paramount importance. In addition, there are always legal issues and concerns on companies' images for which safety should be considered at the design stage. To evaluate safety at the design stage will help minimize potential undesirable consequences. Safety analysis is a systematic examination of the structure and functions of a process system, aiming at identifying potential accident conditions, evaluating the risk, and identifying measures to mitigate or eliminate risk. Figure 3 illustrates the steps of a classic safety and risk analysis.[33]

There are many safety analysis methods available. Dow Fire and Explosion Hazard Index and Mond Index are two of the widely used methods in process industries.[34,35] These indices are mainly related to fire and explosion rating of a plant and are best suited at later design stage when equipment, chemical, and process conditions are known. Another accurate method for safety

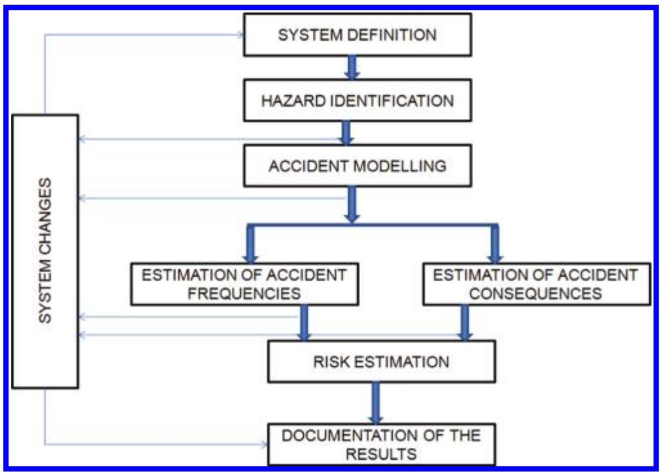

Figure 3. Steps in a safety and risk analysis.

Table 3. Structure of Inherent Safety Index

	symbol	score
chemical inherent safety index, I_{CI}		
heat of main reaction	I_{RM}	0−4
heat of side reaction, max	I_{RS}	0−4
chemical interaction	I_{INT}	0−4
flammability	I_{FL}	0−4
explosiveness	I_{EX}	0−4
toxic exposure	I_{TOX}	0−4
corrosiveness	I_{COR}	0−2
process inherent safety index, IPI		
inventory	I_I	0−5
process temperature	I_T	0−4
process pressure	I_P	0−4
equipment safety	I_{EQ}	
Isbl		0−4
Osbl		0−3
safe process structure	I_{ST}	0−5

analysis is HAZOP (Hazard and Operability Analysis). Normally HAZOP studies are conducted using P&ID (Piping and Instrumentation Diagrams) to find out possible process disturbances and their consequences. Since a very minute detail about plant operating conditions and control is required for HAZOP study, it is not suitable to be used in the early design stage. Prototype Index of Inherent Safety (PIIS) developed by Edwards and Lawrence is also a good safety analysis method.[36] PIIS is mainly used to analyze raw materials used and sequence of the reaction steps. This method focuses on reaction, and it is not suitable for safety analysis of the whole process plant. Details of process plant operations and control are normally not fully available at the early design stage. Nevertheless, safety of all the chemicals and equipment should be considered. In choosing any safety analysis method, requirement of minimum data and coverage of all the aspects of safety should be the main criteria. Heikkilä proposed a very good safety analysis method named inherent safety index, which requires less information compared to other methods while it covers many aspects of safety.[37] As suggested in the report by Heikkilä, this method is suitable for comparison between various alternative designs of a process. In inherent safe design, the main

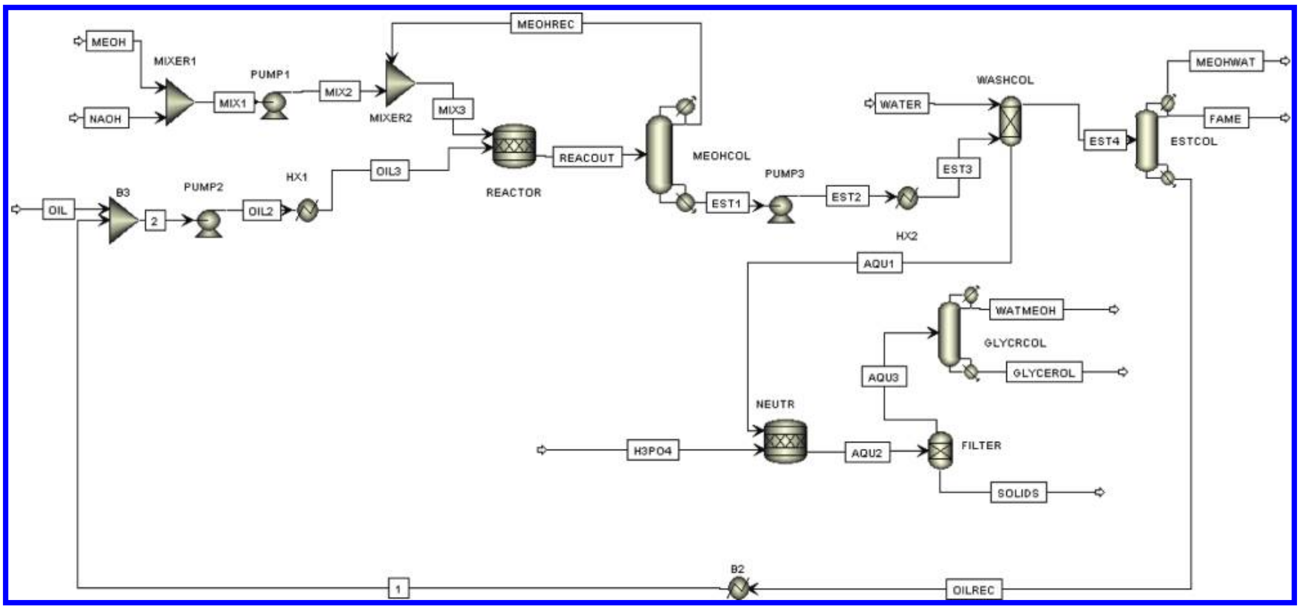

Figure 4. Conventional biodiesel production process.

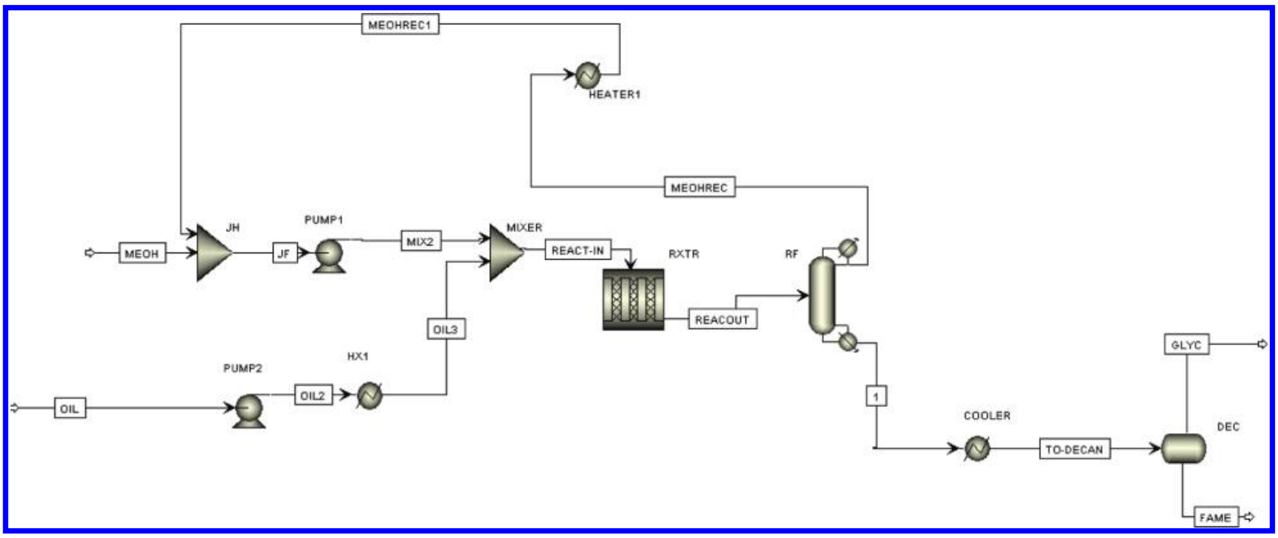

Figure 5. Heterogeneous catalyst biodiesel production process.

principles are to avoid the use of hazardous materials and aim for a simpler process. The possibility of affecting the inherent safety of a process decreases as the design proceeds and more and more engineering and financial decisions have been made. Implementing the principles of inherent safety during the conceptual design phase will help the designers root out inferior designs at the earliest stage.

As shown in Table 3, calculation of inherent safety index is divided into two subindices: chemical inherent safety index and process inherent safety index. These subindices are further divided into other subindices. Chemical inherent safety index covers parameters related to hazards presented by the chemicals in the plant, and process inherent safety index deals with the hazards due to equipment and inventory in the plant. Scores are given for subindices based on the parameters of the individual components. Calculated by adding all the subindices together, the resulting total inherent safety index can be used to compare the safety of different designs. A lower score indicates safer design. Nevertheless, the original inherent safety index method has its own limitations as will be illustrated in the case study. An enhanced inherent safety index method was proposed by the research team to enhance its functionality.

Normalization of the Indexes. Normalization is the process of organizing data in a database. It is a systematic way of ensuring that a database structure is suitable for general-purpose querying and free of certain undesirable characteristics. Many researchers defined the normal form and conducted the data normalization.[38,39]

As different indicators have different values, which may spread over several orders of magnitude, it is necessary to normalize the values to a unified scale to compare them easily. Most often, weights to each criterion are chosen subjectively for each indicator. A normalized vector value indicates the percentage importance of a criterion in the overall decision of its parent level. A typical way of normalization is using the following formula

$$\bar{\mathbf{F}}(\mathbf{x}) = \frac{F(x) - F_{\min}}{F_{\max} - F_{\min}} \quad (1)$$

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Table 4. Feed Specifications and Reaction Conditions

	traditional process	new process
	feed cond.	
oil (triolein)	1050 kg/h	1050 kg/h
methanol	121 kg/h	114 kg/h
NaOH	44.5 kg/h	
H_3PO_4	34.2 kg/h	
water	50 kg/h	
	reaction cond.	
T, °C	60	48
P, bar	4	4

Table 5. Cost Information of the Raw Materials and Utilities

cost of raw materials	vegetable oil	0.830 ($/kg)
	methanol	0.347 ($/kg)
	sodium hydroxide	0.174 ($/kg)
	biodiesel	1.3114 ($/kg)
	glycerol	0.190 ($/kg)
cost of utilities	water	0.1 ($/GJ)
	gas	0.5 ($/kg)

Table 6. Economic Comparison between Two Processes

parameters	conventional process	new process
total capital investment ($)	8 247 978	3 901 402
total feedstock cost($)	7 968 949	7 975 347
total utilities cost ($)	230 387	166 780
total waste management cost ($)	61 763	779
total labor cost ($)	1 510 080	755 040
total maintenance cost ($)	663 962	314 063
total operating overheads ($)	170 625	84 387
property taxes and insurance cost ($)	164 960	78 028
depreciation ($)	412 398	195 070
general expenses ($)	362 604	362 742
total production cost ($)	11 545 728	9 932 235
total sales ($)	12 086 807	12 091 390
total profit ($)	541 079	2 159 155
net present value ($)	(1 834 893)	9 340 064
discounted cash flow rate of return (%)	7	40

where $F(x)$ is the original value and F_{min} and F_{max} are the user specified lower and upper bounds of the range, respectively. $\overline{\mathbf{F}}(\mathbf{x})$ is a normalized value between the range of [0,1]. For economic evaluation, a normalized indicator with a higher value suggests higher economic viability. On the contrary, for environment and safety evaluation, a lower normalized score suggests a more environmentally friendly and safer process. The normalized value of each subindicator will be aggregated to generate the overall score of each dimension. This is conducted by assigning each subindicator a weighting factor based on its perceived importance or relevance. Different methods of assigning the weighting factors have been reported.[11] In this work, the authors assume all the subindicators in each category are equally important.

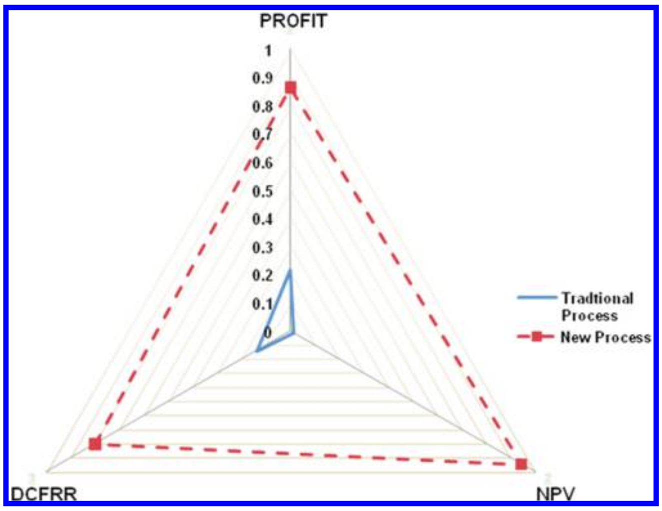
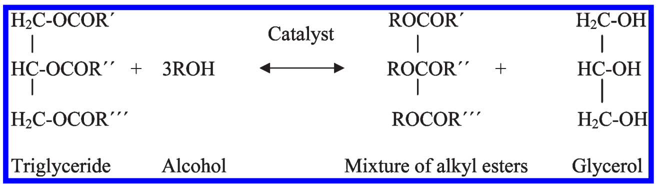


Figure 6. Normalized score for economic evaluation comparison between two processes.

■ ILLUSTRATIVE CASE STUDY: BIODIESEL PROCESSES

Biofuels are valuable sources of renewable energy. Interest in renewable energy has risen tremendously due to the perspective of a dramatic shortage of oil reserves, in conjunction with an accelerated worldwide demand on fuels, especially in emerging economies. One of the promising alternative biofuels is biodiesel. Biodiesel is a renewable fuel suitable for both centralized and distributed production at a wide range of scales. Currently, the most common method to produce biodiesel is by transesterification reaction of vegetable oils (e.g., canola, palm, jatropha, palm kernel, sunflower, and waste vegetable oils), the main component of which is triacylglycerol (TAG). When TAG reacts with alcohol, fatty acid methyl esters (FAME, or biodiesel) and glycerol will be generated. The catalyst can be either enzymes, acids, or bases.[40] The transesterification reaction is illustrated as follows:[41]



In order to test the functionality of the assessment approach, two cases of biodiesel process alternatives were selected. The first case is the conventional homogeneous process, which produces biodiesel using alkali based catalyst. Alkali-catalyzed transesterification (also known as alcoholysis) uses an alkali such as NaOH or KOH as catalyst to convert TAG into biodiesel.[42] The preferred methanol to oil molar ratio is 6:1. At 65 °C, a 93−98% conversion of TAG is achieved within 1 h. In comparison to both the enzyme- and acid-catalyzed transesterification reactions, the high yield in a relatively short reaction time and the relative low cost makes the alkali-catalyzed method the dominating production method in current industrial practice. The transesterification reaction requires a low water (<0.06 wt %) and free fatty acid (FFA) content (<0.5 wt %) in the feedstock. Thus, pretreatment of the feedstock is usually needed. Finally, due to the presence of excess methanol and glycerol byproduct, post-treatment of the biodiesel mixture is required. The main limitations of this homogeneous process include the following aspects. First, the FFA

Table 7. Environmental Assessment Results Comparison between Two Processes

	PEI output rate (PEI/h)	PEI generation rate (PEI/h)	PEI output/mass of product (PEI/kg)	PEI generation/mass of product (PEI/kg)
conventional process	146.7	82.25	0.1392	0.07800
new process	137.7	75.74	0.1305	0.07179

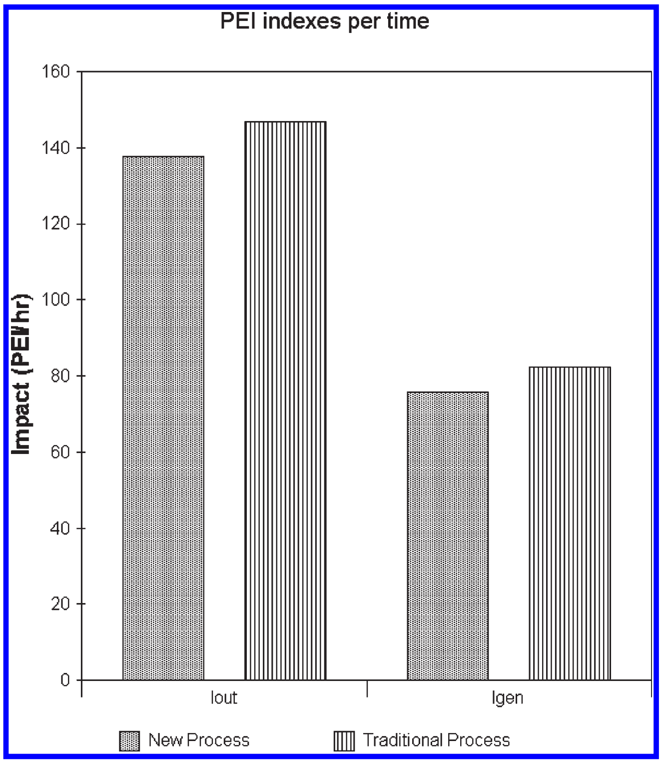


Figure 7. PEI indexes per time of the two processes.

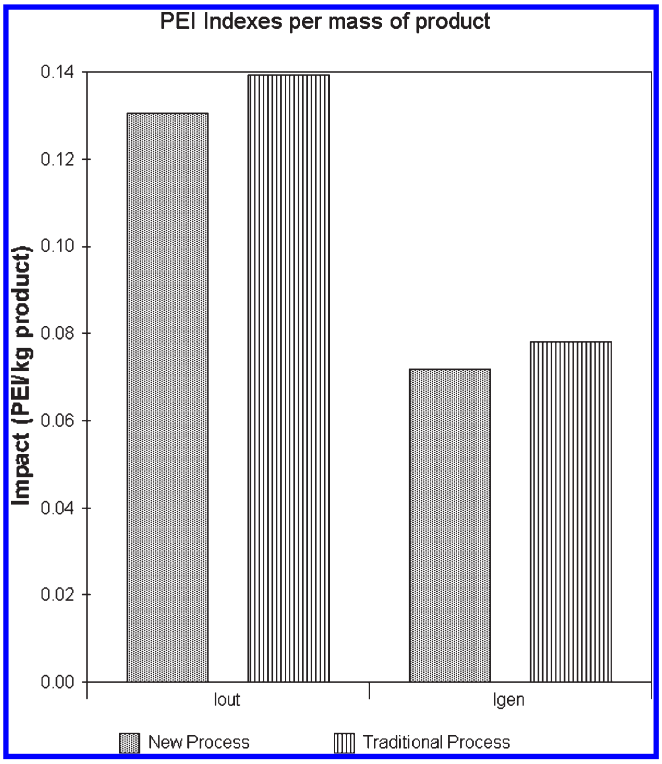


Figure 8. PEI indexes per mass of product of the two processes.

content of the triglyceride stock should be below 0.5 wt % for the alkali transesterification process to be efficient, since the presence of FFA competes with the transesterification reaction by consuming alkali to produce soaps and water, which subsequently causes emulsion formation. NaOH and glycerol together will form emulsion which creates problems in the downstream separation and purification of biodiesel. Second, the conventional transesterification reaction tends to be slow and phase separation of glycerin is time-consuming. Developing a continuous process leads to the use of additional equipment, which ultimately contributes to the capital cost. Third, the catalyst dissolves fully in the glycerin layer and partially in the FAME layer. As a result, raw biodiesel is usually cleaned through a slow, tedious, and environmentally unfriendly water washing process. Certainly purified glycerin can be converted to other value-added products; however, catalyst contaminated glycerin has little value in today's market and is increasingly becoming a disposal issue. Another negative aspect of the homogeneously catalyzed process is that the catalysts are not reusable.

The second case is a heterogeneous catalyst process. Unlike homogeneous catalysts, heterogeneous catalysts (i.e., Na_2O, MgO) can be operated in continuous processes and they can be reused and regenerated. Metal hydroxides, metal complexes, metal oxides such as calcium oxide, magnesium oxide, and zirconium oxide, and supported catalysts have been investigated. The continuous transesterification of triglycerides and simultaneous esterification of free fatty acids with very low residence times was reported.[43] A variety of less expensive feedstocks that often contain high levels of free fatty acids, such as tall oil and algae oil, can be used. Based on the kinetics data reported by Singh, Na_2O was chosen as the catalyst and a process flow sheet was designed using Aspen Plus software.[41]

In this case study, a comprehensive sustainability assessment was conducted on the economic, efficiency, environmental, and social dimensions of two biodiesel processes, that is, the homogeneous catalyst process and the heterogeneous catalyst process.

Process Simulation. In this case study, the process simulator Aspen Plus is used to model and simulate these two chemical processes. Using process simulators saves time as they are equipped with an advanced and user-friendly graphical user interface (GUI), advanced computation techniques, comprehensive thermodynamic packages, and large component libraries that could provide reliable information for process design and operations. The outputs of process simulators provide the inventory data needed to perform process assessment and selection. The Aspen flowsheets of these two biodiesel production processes are provided as Figures 4 and 5.[44] Table 4 shows the design parameters, feed conditions, and reaction conditions of these two processes. One thing to be noted is that the feasibility of biodiesel industries is much influenced by vegetable oil price and price of biodiesel. The capital cost of the two processes was estimated using Aspen Icarus Process Evaluator 2006. In this work, the costs of the raw materials and utilities based on information in 2008 are provided in Table 5.

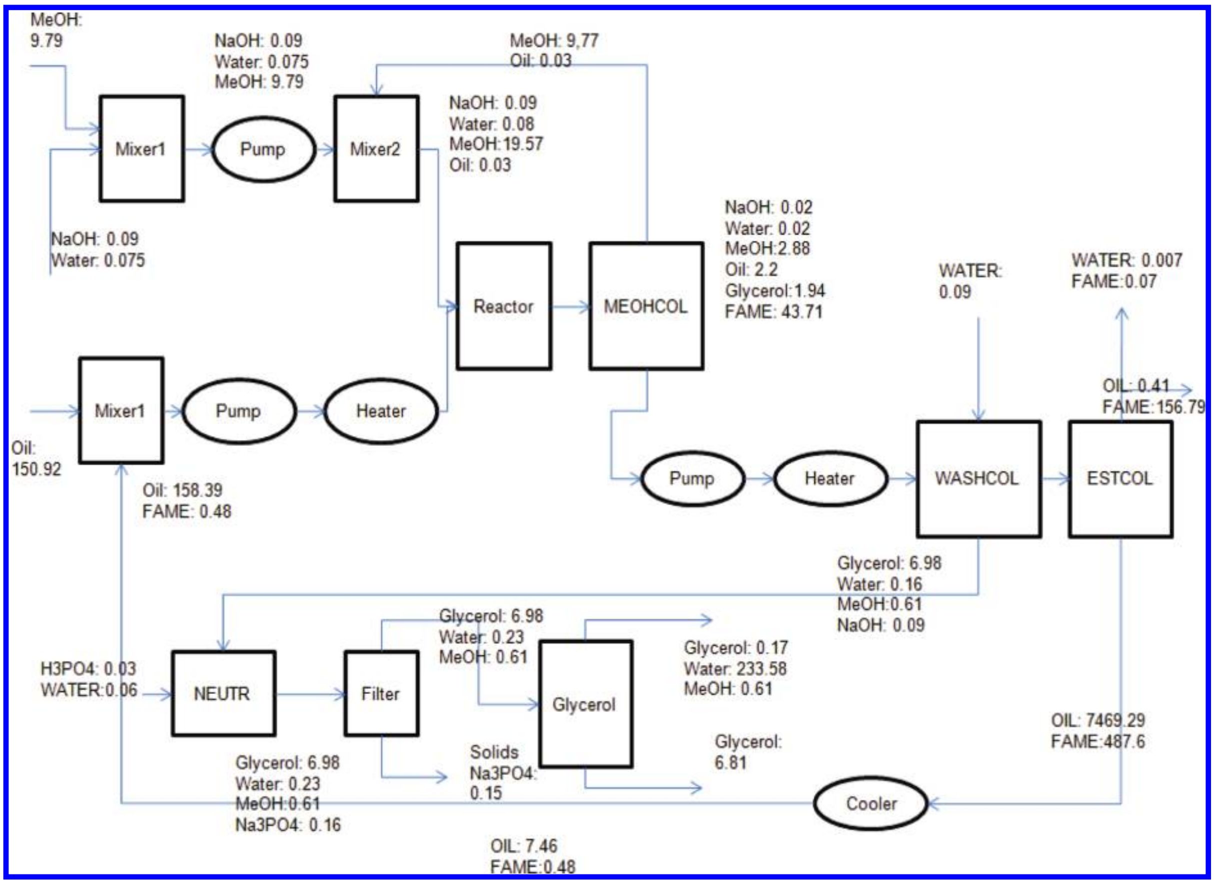


Figure 9. Exergy flow diagram for the conventional biodiesel process.

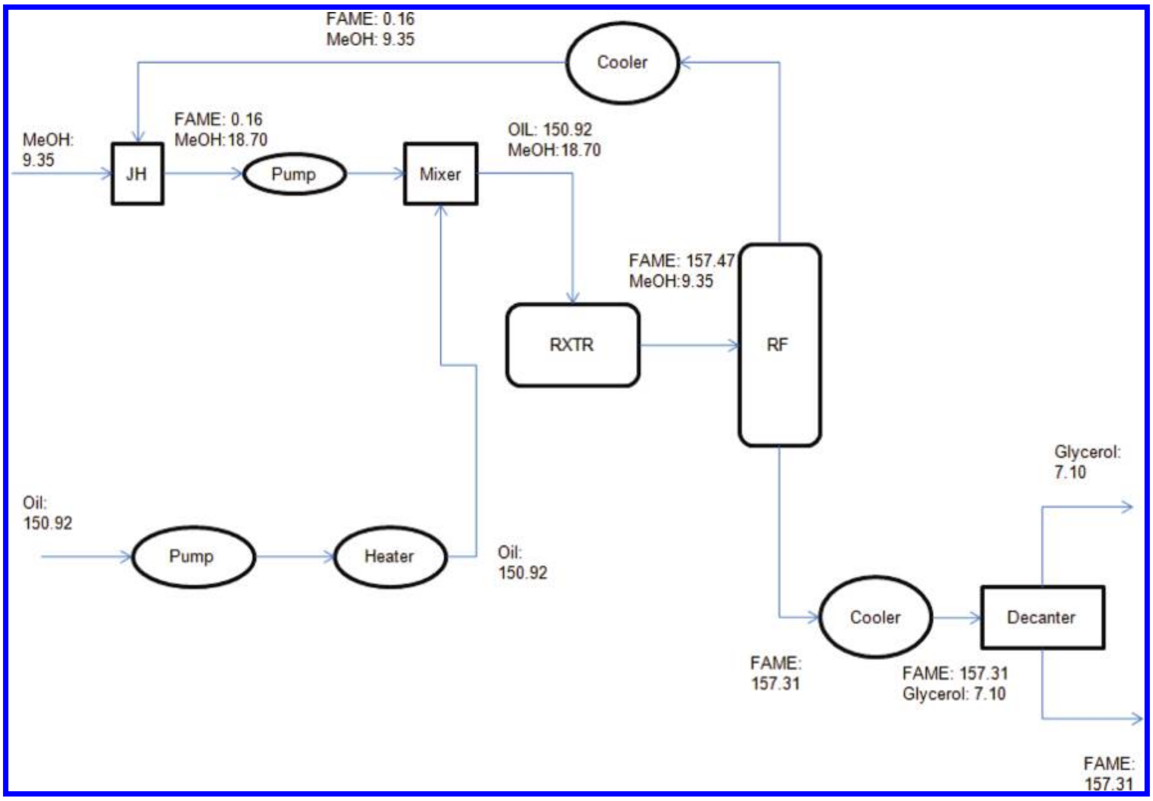


Figure 10. Exergy flow diagram for the heterogeneous catalyst process.

Table 8. Exergy Efficiency of Both Processes

		exergy in (MW)	exergy out (MW)	exergy efficiency (%)
traditional process	including chemical exergy	161.57	157.16	97.27
	excluding chemical exergy	0.43	0.16	37.21
new process	including chemical exergy	160.77	157.18	97.77
	excluding chemical exergy	0.42	0.18	42.86

Table 9. Comparison of Two Processes Using the Original Inherent Safety Index Method

inherent safety subindices	symbol	score range	conventional process	heterogeneous catalyst process	remarks
chemical inherent safety index, I_{CI}					
heat of main reaction	I_{RM}	0−4	–	–	
heat of side reaction	I_{RS}	0−4	–	–	
chemical interaction	I_{INT}	0−4	–	–	
flammability	I_{FL}	0−4	3	3	methanol
explosiveness	I_{EX}	0−4	2	2	methanol
toxic exposure	I_{TOX}	0−6	2	2	methanol
corrosiveness	I_{COR}	0−2	1	0	NAOH, H_3PO_4, methanol
Total chemical inherent safety index, I_{CI}			8	7	
process inherent safety index, I_{PI}					
inventory	I_I	0−5	2	2	inventory 5.9 t
process temperature	I_T	0−4	3	3	distillation column bottoms temp, 375.9 and 351 °C
process pressure	I_P	0−4	0	0	pressure 4 bar
equipment safety	I_{EQ}				
ISBL		0−4	2	2	reactor
OSBL		0−3			
safe process structure	I_{ST}	0−5	2	2	no safety data available
total process inherent safety index, I_{PI}			9	9	
total inherent safety index, I_{TI}			17	16	

Assessment Results. In economic analysis, following the principles and estimation methods illustrated in the seminar book "Product and Process Design",[45] the following factors were considered: sales revenue, cost of feed stocks, utilities, waste treatment, labor-related operations, maintenance cost, property taxes and insurance, and depreciation.

The total sales revenue comes from the sales of biodiesel as the main product and glycerol as the byproduct. The major feed stocks are vegetable oil, methanol, and sodium hydroxide in the conventional process and the heterogeneous catalyst in the new process. The costs of the feed stocks and utilities are reported in Table 5.

The cost of wastewater treatment and solid waste treatment is estimated at \$0.037/kg[11] and \$0.15/kg[11], respectively. The costs of labor-related operations include direct wages and benefits calculated from the hourly wages of the operators. It is estimated that the conventional process requires four operators while the new process requires only two operators. Maintenance cost is estimated from the total capital cost investment.[45] The annual property taxes and insurance were estimated as 2% of the total capital cost. The straight line depreciation method was calculated for a period of 20 years. The annual pretax earning is the difference between annual sales revenue and the annual production cost. A combination of federal and state sales tax of 37% was considered.[45] An interest rate of 10% is used in the calculation of NPV.

Table 6 compares the economic performance of both cases. All the indicators, that is, profit, IRR, and NPV, show that the heterogeneous catalyst process is a promising alternative from the economic point of view. As shown in Table 6, the profit, NPV, and IRR values are not at the same level, so these values are normalized to the range of [0,1]. The normalization procedure is presented below: (1) The total profit is \$541 079 for the conventional process and \$2 159 155 for the new process. The upper and lower bound of total profit is specified as 0 and 2 500 000, respectively. By applying eq 1, the two profit values of the processes are normalized to 0.2164 and 0.8637, respectively. The NPV value for the conventional process is −1 834 893, which means this process is not economically viable. The NPV value for the new process is \$9 340 064. The upper and lower bounds of NPV value are set at −2 000 000 and 1 000 000 each. Thus, the two NPV values are normalized to 0.01376 and 0.9450, respectively; the IRR values are 7% for the conventional process and 40% for the new process. The upper and lower bounds of IRR value are set at 0 and 50% each. Then IRR values of the two processes are normalized to 0.14 and 0.80, respectively. The normalized score for economic evaluation comparison between these two processes is shown in Figure 6. If we choose the weighting factors for the profit, NPV, and IRR at one-third each, then the normalized value of the economic indicator is

Table 10. Modified Inherent Safety Index of the Conventional Homogeneous Catalyst Process

chemical	chemical inherent index, I_{CI} index: flammability, I_{FL}	explosiveness, I_{EX}	toxic limit, I_{TOX}	corrosiveness, I_{COR}	chemical inherent index, I_{CI}
methanol	0.35	0.23	0.23	0	0.81
oil, triolein	1.05	0.00	5.25	0	6.30
FAME, methyl oleate	1.05	0	5.26	0	6.31
glycerol	0.11	0	0.42	0	0.53
NaOH	0.00	0	0.2	0.05	0.25
water	0.00	0	0	0	0.00
H_3PO_4	0.00	0	0.25	0.05	0.30
Na_3PO_4	0.00	0	0.07	0	0.07
total chemical inherent safety index, I_{CI}	2.56	0.23	11.68	0.10	14.6

equipment	process inherent index, I_{PI} index: inventor, I_I	process temperature, I_T	process pressure, I_P	equipment safety, I_{EQ}	process inherent index, I_{PI}
pump	2	0	0	3	5
heat exchanger	2	0	0	3	5
reactor	1	0	0	4	5
distillation column	2	5	0	3	10
separator/extractor	1	0	0	1	2
total process inherent safety index, I_{PI}	8	5	0	14	27
total inherent safety index, I_{TI}					41.6

$[(0.2164 \times 0.3333) + (0.01376 \times 0.3333) + (0.14 \times 0.3333)] = 0.1234$ for the traditional process and $[(0.8637 \times 0.3333) + (0.9450 \times 0.3333) + (0.80 \times 0.3333)] = 0.8696$ for the new process.

In the environmental dimension, potential environmental impacts of both cases are shown in Table 7. Using the WAR algorithm, the following indices were calculated: the total output rate of PEI, PEI output/mass of product, the generation rate of PEI, and PEI generation/mass of product. It was shown that the indices of new process are always lower than the traditional process, which indicates that the heterogeneous catalyst process is more environmental friendly than the conventional biodiesel production process. Figure 7 compares the PEI indexes per time, and Figure 8 compares the PEI indexes per mass of product. The lower and upper bounds of PEI values are set at 0 and 150, respectively. In this research, we set the weighting factors for the total output rate of PEI, PEI output/mass of product, the generation rate of PEI, and PEI generation/mass of product at 0.25 each. Then normalization was conducted using the same procedure illustrated in the economic part. The normalized value of the potential environmental impact is 0.7436 for the traditional process and 0.6929 for the new process.

Another subcategory of environmental performance is efficiency. In this work, the software ExerCom was used to calculate the exergy of the process streams except the chemical exergy.[30] The standard chemical exergy values of biodiesel, methanol, and oil feed stock were collected and calculated from the literature,[17] and their values are listed below: methanol, 718 kJ/mol; oil, 35 354.62 kJ/mol; FAME, 12 282.91 kJ/mol; glycerol, 1640.63 kJ/mol; NaOH, 74.9 kJ/mol; water, 9.5 kJ/mol; H_3PO_4, 104 kJ/mol, Na_3PO_4, 518.14 kJ/mol. Then the exergy flow diagrams of the two processes are shown in Figures 9 and 10. Table 8 shows the exergy efficiency of both cases. As chemical exergy takes a large part of the exergy value of the input and output streams (more than 90% as shown in the table), we use two types of exergy efficiency indicators to illustrate the difference. The first indicator includes chemical exergy, and the second indicator excludes chemical exergy. In both situations, heterogeneous process has a larger exergy efficiency value when compared to the homogeneous process. On the other hand, the energy efficiency of the heterogeneous process was 91.43%, while that for the homogeneous process was 87.92%.

It is demonstrated that the heterogeneous process is better than the conventional process from either exergy efficiency or energy efficiency point of view. This indicates that the new process is more efficient. In this case study, the weighting factors for both exergy efficiency and energy efficiency are set as 0.5. So the normalized value of the efficiency indicator is $[(0.9727 \times 0.5) + (0.8792 \times 0.5)] = 0.9259$ for the traditional process and $[(0.9777 \times 0.5) + (0.9143 \times 0.5)] = 0.946$ for the new process.

For analysis of the processes using the inherent safety index method, the heat of main and side reaction and chemical interaction are ignored because those values are same for both of the processes and will not affect safety analysis while comparing both processes. Safety indices of both cases are shown in Table 9, which shows that the scores of both processes are almost the same. This is because the original inherent safety index only considers the worst case, that is, maximum scores for chemicals. Since methanol is the chemical leading to safety concerns and it presents in both process, the score is almost the same for both processes. The scores of

Table 11. Modified Inherent Safety Index of the Heterogeneous Catalyst Process

chemical	chemical inherent index, I_{CI} index				
	flammability, I_{FL}	explosiveness, I_{EX}	toxic limit, I_{TOX}	corrosiveness, I_{COR}	chemical inherent index, I_{CI}
methanol	0.36	0.24	0.24	0	0.85
oil, triolein	1.05	0.00	5.25	0	6.30
FAME, methyl oleate	1.05	0	5.27	0	6.33
glycerol	0.11	0	0.44	0	0.55
NaOH	0.00	0	0	0	0.00
water	0.00	0	0	0	0.00
H_3PO_4	0.00	0	0	0	0.00
Na_3PO_4	0.00	0	0.00	0	0.00
total chemical inherent safety index, I_{CI}	2.58	0.24	11.20	0.00	14.0
equipment	**process inherent index, I_{PI} index**				
	inventory, I_I	process temperature, I_T	process pressure, I_P	equipment safety, I_{EQ}	process inherent index, I_{PI}
pump	1	0	0	2	3
heat exchanger	2	0	0	3	5
reactor	1	0	0	2	3
distillation column	1	3	0	1	5
separator/extractor	1	0	0	1	2
total process inherent safety index, I_{PI}	6	3	0	9	18
total inherent safety index, I_{TI}					32.0

process inherent safety index were expected to be different, and that of the heterogeneous catalyst process should be lower because of less complexity of the process and less amount of equipment. However, using the original inherent safety index, the process safety index is the same for both processes because this method only deals with the worst case scenario. This experience discloses that the original inherent safety index method has some limitations. The original chemical inherent safety index method does not consider the quantity of the materials or chemicals used, and it just considers the maximum value of the parameters, including flammability, explosiveness, and toxicity. Similarly, the process inherent safety index in the original inherent safety index does not consider the amount of equipment in the plant and the complexity of the process. As illustrated in the flow sheet, two reactors and three distillation columns are present in the conventional biodiesel process and only one reactor and one distillation column is present in the heterogeneous catalyst process. However, using the original process inherent safety index, the scores of both processes are the same. This is because the most hazardous equipment in both processes is the same, that is, reactor and distillation column, while this method ignores the hazard presented by additional equipment in the plant.

Based on the analysis, an enhanced inherent safety index (EISI) was proposed to overcome these limitations, and it is used for the comparison of the safety aspects of conventional and heterogeneous catalyst biodiesel processes. In the EISI method, again two subindices, that is, the chemical inherent safety index and the process inherent safety index, are given similar to ones in the inherent safety index. In chemical inherent safety index, the scores are calculated by multiplying the severity (i.e., flammability) of the chemicals with the flow rates of the chemicals instead of considering only maximum value. All the scores for individual chemicals are added together to obtain the total chemical inherent safety index. In the process inherent safety index, scores are given for individual equipment and multiplied by the number of equipment. The scores of all equipment are added together to get the total process safety index. In this case study, heat of the main and side reaction, chemical interaction, and process structure are ignored because they are the same for the conventional and heterogeneous catalyst process. Results of the analysis are shown and compared in Tables 10−12.

As shown in Table 12, using the modified inherent safety index, the score of the heterogeneous catalyst process is higher. It is also shown that score of the total chemical inherent safety index for both processes is almost the same. This is due to the fact that chemicals used in large quantity (methanol) are the same in the two processes. The total process inherent safety index for the conventional process is much higher because the conventional process uses more reactors and distillation columns than the heterogeneous catalyst process. The lower and upper bounds of the total inherent safety index are set at 0 and 50 respectively. After the normalization, the overall value of the safety indicator is 0.832 for the traditional process and 0.64 for the new process. From the results, it can be concluded that heterogeneous catalyst process is inherently safer than the conventional process.

Figure 11 shows the normalized score for each indicator and the final result comparison between the two processes. As shown in the figure, the new process is more sustainable than the traditional process, especially in the society and economic aspects.

Table 12. Comparison of Two Processes Using the Modified Inherent Safety Index Method

inherent safety subindices	symbol	conventional process	heterogeneous catalyst process
		chemical inherent safety index, I_{CI}	
heat of main reaction	I_{RM}	–	–
heat of side reaction	I_{RS}	–	–
chemical interaction	I_{INT}	–	–
flammability	I_{FL}	2.6	2.6
explosiveness	I_{EX}	0.2	0.2
toxic exposure	I_{TOX}	11.7	11.2
corrosiveness	I_{COR}	0.1	0.0
total chemical inherent safety index, I_{CI}		14.6	14.0
		Process inherent safety index, I_{PI}	
inventory	I_I	8	6
process temperature	I_T	5	3
process pressure	I_P	0	0
equipment safety	I_{EQ}		
ISBL		14	9
OSBL		–	
safe process structure	I_{ST}	–	–
total process inherent safety index, I_{PI}		27	18
total inherent safety index, I_{TI}		41.6	32.0

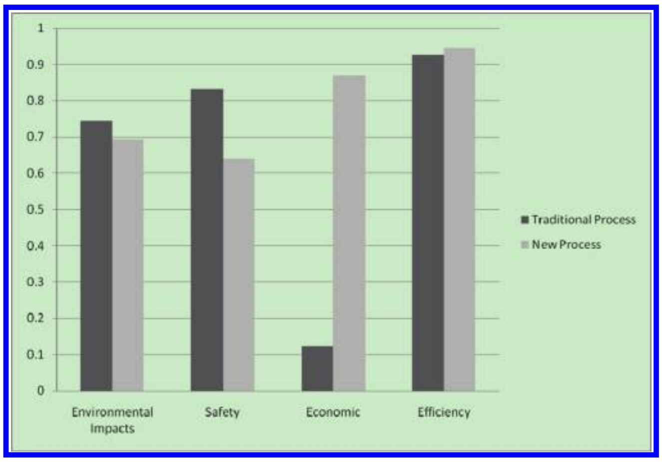


Figure 11. Overall comparison of the two processes.

CONCLUSION

A systematic approach for sustainability assessment of chemical and energy production process has been presented. This methodology incorporates exergy analysis to quantify the efficiency of a process and an enhanced inherent safety index to quantify the societal impacts of a process. Adopting this sustainability assessment method will make a positive impact on the sustainable development of chemical and energy industries.

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