Sustainability assessment and decision making in chemical process design

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Abstract

Sustainability in industries offers a big challenge to engineers and managers. Particularly in process system engineering (PSE), it is important to address the challenges of design for sustainability especially in the early stages of process development. Considering sustainability in process design is about finding the best solution that not only considers its techno-economic performance but also the environmental and social impacts. In the light of this, we proposed a concept called sustainability assessment and selection (SAS) which perform sustainability assessment to several design alternatives and adopting analytic hierarchy process (AHP); a multi criteria decision making (MCDM) methodology, to systematically select a sustainable design. In doing so, we first proposed a set of indicators; hard (quantitative) and soft (qualitative), which suitable for early process design assessment. Having the indicators and AHP as the basis of our research we further expand it by developing a systematic and modular sustainability assessment and decision making tool utilizing state of the art process simulators and spreadsheets. The tool was successfully tested in assessing and selecting sustainable option of two biodiesel process designs; alkali-based system and supercritical methanol. Apart from that, our research also touches several aspects on decision making. One of them is to found out the effect of different decision model topology to solution preferability. We compared two methods; ours and IChemE sustainability metrics (2002), assessing the same biodiesel case study and our observation shows that the problem model does affect the design preferability. It suggested, for a more meaningful result to clearly define the indicators and the assessment boundaries. Other than that, we also proposed a score-based scoring methodology to overcome negative preferences in AHP evaluation step. Using a rule-based approach, the scores which may span over positive and negative values are treated to elicit the final selection and ranking solution. Its functionality were successfully implemented for selection and ranking of several biodiesel process designs in presence of various positive and negative scenarios. We also proposed a new set of decision model that include interdependency indicators which are determinant to engineers and managers. Using analytic network process (ANP), it able to capture those complexities and interacting environment for ranking and selecting sustainable biodiesel process design. Apart from that, we also introduce the concept into chemical engineering education. In a computer aided process design (CAPD) course at TU Berlin, we conduct a 1-day course to process engineering students to find out their response to the idea. From the evaluation form we found that the course was able to attract the interest of these students. We believed this approach is potentially useful and would add an extra edge to the students for their future career.

Zusammenfassung

Die Nachhaltigkeit stellt eine grosse Herausforderung für Ingenieure und Manager in der Industrie dar. Gerade auf dem Gebiet der Prozessentwicklung oder dem Prozess-System Engineering (PSE), ist die Nachhaltigkeit des Prozessdesigns vor allem in den frühen Phasen der Prozessentwicklung von enormer Bedeutung. Bei der Nachhaltigkeit im Prozess-Design geht es um das Finden der besten Lösung, die neben der techno-ökonomischen Leistungsfähigkeit, gerade die ökologischen und sozialen Auswirkungen betrachtet und bewertet. Hierfür wird ein Konzept bestehend aus: Nachhaltigkeit, Bewertung und Auswahl (SAS) vorgeschlagen, in dem die Bewertung der Nachhaltigkeit mehrerer Design-Alternativen mittels eines methodischen Ansatzes, des Analytic Hierarchy Process (AHP) durchgeführt wird. Eine Multi Criteria Decision Making (MCDM) Methodik führt hierbei zur systematischen Auswahl eines nachhaltigen Designs. Dabei werden zunächst eine Reihe von Indikatoren vorgeschlagen, sogenannten harte (quantitative) und weiche (qualitative) Indikatoren, die sich für das frühe Prozess-Design Assessment eignen. Die Indikatoren und der AHP bilden die Grundlage der Forschungsarbeit, und werden zu einem Arbeitswerkzeug durch eine systematische und modulare Nachhaltigkeitsbewertung unter zu Hilfenahme von Entscheidungshilfen, wie moderner Simulationsverfahren und Tabellenkalkulationen weiterentwickelt. Das Programm wurde erfolgreich in der Beurteilung und Auswahl einer nachhaltigen Option zweier Biodiesel Prozess-Alternativen getestet, ein Alkali-basiertes System und einem überkritischem Methanol. Daneben beschäftigt sich diese Arbeit auch mit Aspekten der Entscheidungsfindung. So wurde die Wirkung der verschiedenen Entscheidungsprozesse auf die gefundene Lösung untersucht. In der Arbeit wird die entwickelte Methode mit der IChemE Nachhaltigkeit Metriken (2002) für die Beurteilung der gleichen Biodiesel Fallstudie miteinander verglichen. Es zeigt sich, dass das Problem-Modell die Gestaltung nachhaltig beeinflusst. Es wird vorgeschlagen, die Indikatoren klar zu definieren, ebenso wie die Beurteilungsgrenzen vorzugeben. Daneben wird eine Score-Scoring-Methode vorgeschlagen, um negative Entscheidungen in dem AHP Auswertungsschritt zu verhindern. Mit Hilfe eines regelbasierten Ansatzes werden die Lösungen gewichtet, wobei sowohl positive und negative Werte auftreten, um die endgültige Auswahl und die Ranking-Lösung zu erhalten. Die Funktionalität wurden erfolgreich für die Auswahl und Platzierung von mehreren Biodiesel Prozess-Alternativen in Gegenwart von verschiedenen Szenarien getestet. Daneben wurde eine neue Reihe von Entscheidungsmodellen vorgeschlagen, in der die Abhängigkeit der Indikatoren im Bestimmungsprozess für Ingenieure und Manager enthalten sind. Mit dem Analytic Network Process (ANP), können komplexe Strukturen und Verknüpfungen erfasst werden, für die Bewertung und die Auswahl eines nachhaltigen

Biodiesel Prozess-Design. Das Konzept wurde in die chemische Ingenieurausbildung eingebunden und getestet. In einem computergestützten Prozess-Design (CAPD) an der TU Berlin, wurde ein 1-Tages-Kurs integriert, um die Bewertung der Studenten auf die neue Idee zu erhalten. Es konnte festgestellt werden, dass im Rahmen des Kurses das Interesse der Studenten für Nachhaltige Entwicklung in der Prozessindustrie gewonnen werden konnte. Der entwickelte Ansatz besitzt grosses Potenzial ist und eröffnet Studenten die Möglichkeit schnell Lösungen zu erarbeiten. Damit besitzen die Studierenden erste praktische Erfahrungen auf dem Gebiet der Nachhaltigkeitsanalyse.

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Contents

List of Tables

List of Figures

Nomenclature

Acronyms

AHP	analytic hierarchy process
ANP	analytic network process
CEI	chemical exposure index
CEO	chief executive officer
DfS	design for sustainability
ESH	environment, health and safety
HAZOP	hazard and operability study
LCA	life cycle analysis
PDM	process decision making
PSE	process system engineering
SAS	sustainability assessment and selection

Abbreviations

ABET	Accreditation Board for Engineering and Technology
ACGIH	American Conference of Industrial Hygienists
ACS	American Chemistry Society
AP	acidification potential
APP	applicability to other product and processes
ASW	Aspen simulation workbook
ATP	aquatic toxicity potential
BAHP	bipolar analytic hierarchy process
BOCR	benefit-opportunity-cost-risk
BOD	biological oxygen demand
DALY	disability adjusted life years
DCFRR	discounted cash flow rate of return
DMLSD	design meet location specific demands
DS module	decision support module
EIA module	equipment and inventory analysis module
FAME	fatty acid methyl ester
FFA	free fatty acid
FFP	fit for puspose
GWP	global warming potential
HCFC	hydrochloroflorocarbon
HTPE	human toxicity potential by inhalation/dermal exposure
HTPI	human toxicity potential by ingestion

HVHD	higher-value-higher-desirability
IEAust	Institute of Engineers Australia
IEEA	inverse exergoeconomical and environmental analysis
IF	impact factor
L/D	length/diameter
LVHD	lower-value-higher-desirability
Maint	maintenance
MCDM	multi criteria decision making
MSDS	material safety data sheet
m-SAS	modular - sustainability assessment and selection
NIOSH	National Institute for Occupational Safety and Health
NPV	net present value
ODP	ozone depletion potential
OLE	object linking and embedding
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbons
PC	project champion
PCOP	photochemical oxidation (or smog formation) potential
PS module	process simulator module
SCENE	simultaneous comparison of environmental and non-environmental process criteria
PEI	potential environment impact
PO	plant operability
RA	resource availability
RC	required competence
SO	safety during operation
SPM	suspended particulate matter
SSS	safe startup and shutdown
TG	triglyceride
TGP	total generated/product
TLV	threshold limit value
TM	time to market
TOP	total output/product
TRG	total rate of PEI generated
TRO	total rate of PEI output
TS	technical success
TTP	terrestrial toxicity potential
TWA	time-weighted averages
VOC	volatile organic compound
WAR algorithm	waste reduction algorithm

List of symbols

Symbols in sustainability assessment

α	ratio of electrical energy to steam energy
β	impact category weights
$\hat{I}$	rates of PEI per unit mass of product [PEI/kg]

$[Score]$	average value of chemical impact
ψ^s	specific PEI of chemical component
C	cost [$]
C_A	total annual income cash flow [$]
E	energy requirement [kW]
EC	energy consumption [kW]
EF	emission factor
I	rates of PEI [PEI/hr]
IS	input stream
M	mass flowrate [kg/hr]
m	year
n	project life time
NPS	non-product stream
OS	output stream
PS	product stream
r	interest rate [%]
$Score$	value of chemical impact
x	mass fraction

Symbols in chemical reaction

AL	alcohol
E	activation energy [J/kmol]
ES	ester
DG	diglyceride
GL	glycerol
k_n	specific reaction rate [s^{-1}]
MG	monoglyceride
N_{Re}	Reynolds number
T	temperature [K]
R	gas constant [J kmol^{-1}K^{-1}]
TG	triglyceride

Symbols in AHP/ANP

λ	largest eigenvalue
a	alternative
i	criteria
I	score index
j	indicator
k	number of alternatives
n	priority value of subordinates
p	priority value of the parent's level
PV	priority value
V	assessment score
v	assessment value
V_N	normalized assessment score
w	eigenvector

$\mathbf{A}$	matrix of pairwise comparison
$\mathbf{W}$	supermatrix
T_a	highest assessment value margin
T_b	lowest assessment value margin
V_a	highest score margin
V_b	lowest score margin
V_{neg}	negative assessment score
V_{pos}	positive assessment score

List of Sub/Superscripts and Operations

a	alternative
c	chemical component
cp	chemical mass process
ep	energy generate process
FCC	fixed capital cost
g	gas pollutants
gen	energy generation process
h	stream
i	impact category
in	input
l	lower value
m	direct energy streams
n	indirect energy streams
out	output
p	product
ROR	rate of return
t	total
TCI	total capital investment
TPC	total production cost
u	upper value
WCC	working capital cost
we	waste energy lost

Chapter 1

Introduction

1.1 Motivation

Decades of unhealthy mismanagement of human economic activities has lead to serious environmental problems. Depletion of non-renewable resources, global warming, forest depletion, water contamination and air pollution are some of the most serious problems faced today. Aware of this fact, the global community has now realized that sustainable development has become of utmost importance globally. In 1987, The Brundtland Commission define sustainable development must *'meet the needs of the present without compromising the ability of future generations to meet their own needs'*. The central concept of sustainability, or sustainable development, is the so called "triple bottom line" balance, which is to achieve simultaneously: economic prosperity, environment friendliness, and social responsibility. Inherently, leaders in the global business community have begun to realize the effect of sustainability to their business survival and growth. Many CEOs have asserted a belief that sustainable business practices will improve both enterprise resource productivity and stakeholder confidence [9].

Design for Sustainability (DfS) is a concept and also a design philosophy. By this, a variety of design methodologies have been developed for improving process design, product design, material design, etc., at different scales of time and length. In chemical engineering, process system engineering (PSE) is perhaps best positioned to address the challenges of DfS, especially at its early stage of development. Such efforts can help ensure that a selected design is sustainable for deployment. In such endeavors, it is of great importance to identify necessary indicators in assessing sustainable design. Conventionally, evaluation of process design is performed using techno-economic criteria [10, 11]. It becomes more and more obvious that the resulting design may not be sustainable; other aspects of sustainability should also become an integral part in process design selection [12, 13, 14, 15, 16, 17, 18, 19].

There are many methodologies that exist today to assess sustainable performance of an industrial system. Net present value (NPV), production cost and manufacturing cost are some common methods to assess economic feasibility. For environmental assessment, methods such as life cycle analysis (LCA) or Eco99 were also adopted. On the other hand, assessing social criteria is rather complex since the definition of social is already broad. One can define social criteria as responsibilities, and others, for example chemical engineers, can also include safety or operability as part of social indicator. Nevertheless, within each definition there should exist an assessment method. For example, safety could be assessed using a hazard operability (HAZOP) study or fault tree analysis (FTA). It is important to note however, defining suitable indicators is non-specific. It depends very much on the stage of the project development. At an early design stage for example, indicators with less extensive data search should be used. As the project development progresses and more information are available, a more in depth indicator can be introduced.

Needless to say, research and development has become an integral part of process development. Through research, science and technology evolve. New and innovative alternatives were invented. Assessing sustainability of those alternatives can be done using various tools or methodologies. However, selecting one that is most sustainable is not easy and straightforward. Attaining sustainability often creates conflicting objectives which poses a multicriteria problem in decision making. Generally, there are two known ways to derive an answer [20]. One is by using deductive logic with assumptions and carefully deducing an outcome from them. The second is by laying out all possible factors in a hierarchy or in a network system and deriving answers from all possible relative influences. The former is commonly used and adopted but it has its drawbacks whereby the lack of information on how to bring the different conclusions into an integrated outcome can elucidate inaccurate and under justified conclusions. Therefore, it is very important to have a convincing method for decision making since what we decide today shapes the future world.

In 1980, Thomas L. Saaty [21] introduced a decision making methodology called analytic hierarchy process (AHP), based on the second approach. AHP and its successor analytic network process (ANP) is a multicriteria decision making (MCDM) methodology that performs decision trade-off between multiple objectives in a hierarchically/network structure. It accepts any particular constitutive criterion for inclusion and allows individual decisions to be aggregated into overall criteria, which allows other members to review and participate in that aspect of the decision-making process at an appropriate level of detail. Its hierarchical and systematic method makes it a popular technique to solve MCDM problems and have been successfully implemented in various fields from education, business, sports and even military purposes.

With the global movement towards sustainability driven by various levels of society from politicians to scientists, the awareness is ever increasing. Along the journey, decision makers may confront multiple option alternatives in which they have to decide only on a single option. The question is how to systematically decide the one that best fits the purpose of sustainability. Doing so is not straightforward since many factors influence a decision. With its systematic approach, AHP/ANP is a promising MCDM methodology to be used in conjunction with sustainability. In relation to PSE, our work is basically aiming at performing sustainability assessments for process designs, and introducing the concept of decision making focusing on the selection of sustainable process design. We named this approach process decision making (PDM). In doing so, we try to touch various aspects in the domain of PSE which include computer aided process engineering and chemical engineering education to test the effectiveness of PDM as an alternative tool in designing for sustainability.

1.2 Research objectives and scopes

Aiming at performing sustainability assessment and introducing the concept of decision making in selection of sustainable process design, our work will cover the following scopes:

1. Development of a computer aided sustainability assessment and selection tool to support sustainability assessment and decision making.
2. Study the effect of adopting different sustainability assessment methodology towards design preferability and also handling of negative values in AHP.
3. Solving dependencies among the elements within the decision framework using ANP.
4. Introduction of process decision making into chemical engineering education.

The first scope of our work involves the development of a modular sustainability assessment and selection (m-SAS) tool. In recent years, process design sustainability analysis using state-of-the-art process simulators have emerged [16, 22, 23]. However, the known methodologies are yet to be more systematic. While most of process simulators focus on design assessment, few efforts exist that combine both process assessment and decision making. Hence, by incorporating sustainability assessment and decision making into a process simulator, it will help process engineers or managers in making a holistic decision for fulfilling the concept of DfS. At present, specifically in the PSE, few tools are available that incorporate both sustainability assessment and decision making under one environment. Development of such a tool could greatly support engineers or managers in assessing and selecting sustainable design options. Creating such tool from programming language i.e. C, C++, visual basic is tedious. However, it can be simplified by utilizing spreadsheet and process simulation software. Doing so will effectively integrate model development, data acquisition and analysis, team contribution assessment and decision support. The efficacy of the proposed approach tool will be demonstrated by the assessment and selection of biodiesel process alternatives.

Our second scope covers two issues that we found related to design preferability. First, we touch on the effect of using different sustainability assessment methodologies towards selection preferability. Generally in decision making, indicators are used to represent the decision hierarchy in the problem decomposition. Different assessment methodologies create different decomposition structures and possibly elucidate different results. In such, we perform a comparison between two different sustainability assessment methodologies. The aim is to observe the effect of different assessment methodologies in relation to the overall decision making result. For the second issue, we will highlight a novel method in handling of negative values in AHP. Although AHP is known for its systematic and hierarchical structure for handling multicriteria decision making (MCDM), it is limited to handle only positive preferences. Inclusion of negative values could possibly create spurious and inconsistent results. One way of handling negative preferences is by using the BOCR (benefit-opportunity-cost-risk) method. In this work, we proposed a different approach by using a rule-based scoring methodology.

In the third scope, we propose a new decision model that includes the sustainability indicators and also elements that are important to engineers and managers as well. In addition, we also include interdependencies relationships that exist among and between levels of attributes. However, such inclusion makes the decision making more complex. Since AHP only considers a uni-hierarchical relation, we solve this problem using ANP which is a more accurate approach for modeling complex decisions especially when interactions exist in the problem environment. To test its functionality, we demonstrate its capability in selecting four biodiesel process design options obtained from literature.

In relation to the fourth scope, we observe that engineers, researchers or even managers constantly encounter situations in choosing the best options. This may imply selection of process plant design, suppliers, supply chain, etc. Although decisions can be achieved through discussions or meetings, the decision methodology is still unclear and subject to a lot of subjective preference. Even though such an approach is normally practiced, it will be much better when the decision is made in systematic way. We believe by introducing AHP into the engineering curriculum, it would add an extra advantage to engineering students especially in systematically solving multi-optional problems they may encounter during their career. In conjunction to that, we introduce sustainability assessment and decision making concepts to chemical engineering students at Berlin Institute of Technology. The aim is to observe their response to this novel approach whether or not it actually brings an extra benefit to their career or life in the future.

1.3 Overview of major contributions

The major contributions of this thesis are summarized as below:

- Proposal of a set of indicators combining hard (quantitative) and soft (qualitative) based evaluations to assess the sustainable performance of a process design.
- Extension of the waste reduction (WAR) algorithm by considering both the electrical and steam consumption of a process.
- Systematic approach in selecting sustainable design option that consider the trade-offs between the decision elements.
- Development of a systematic and modular tool that utilize process simulators and spreadsheets to assist decision makers in assessing and selecting sustainable design options.
- Study the effect of different sustainability assessment methodologies towards design selection preferability.

- Introduction of a score based approach to accommodate the presence of positive-negative value in AHP evaluation step.
- Proposal of a new set of decision models, from engineers and managers perspectives that contain interdependencies and solve it using ANP.
- Introduction of the sustainability assessment and selection (SAS) methodology into chemical engineering education.

1.4 Thesis overview

Overall this thesis contain ten chapters including an introduction in the first chapter and summary in the last chapter. The second chapter discusses the indicators to evaluate the sustainability performance of process design. Although there exist varieties of indicators that explicitly represent each of the sustainability criteria, we purposely chose indicators which are substantial at early design stage. The chosen indicators are simple in methodology and require less extensive data but still maintain their relevancy. The indicators including an explanation and equations will be detailed in this chapter. On the other hand, chapter three focus on the AHP methodology. An introduction to AHP is given at the beginning followed a step by step guideline on how to perform the analysis. A short example is also given.

In the fourth chapter, the development of a m-SAS (modular-Sustainability Assessment and Selection) tool will be discussed. By combining the sustainability assessment and decision making methodology discussed earlier, a tool is developed that fully utilizes spreadsheets and process simulation techniques. The tool's framework and algorithm will be presented in detail in this chapter.

In chapter five, we will demonstrate the use of m-SAS for the assessment and selection of two biodiesel process designs. This chapter will cover the fundamental aspects of biodiesel production from chemical reactions, process design and production. In addition, details on process simulation of the two processes will also be presented. Step by step guidelines of using m-SAS for assessing and selecting a sustainable option will also be described in this chapter.

The sixth and seventh chapters discuss the two issues in the second scope of this thesis. Chapter six primarily discusses the effect of using different assessment methodology towards decision preferability. Two sustainability assessment methodologies are chosen and will be compared using the two biodiesel cases presented in chapter five. Some interesting results were found and will be presented in further details in this chapter. Chapter seven on the other hand, primarily discusses on the handling of negative values in AHP using a score-based methodology. An overview of the methodology will be given followed by an example. The example which is based in literature contains some negative-positive values which is then used to test the functionality of the proposed method.

Chapter eight presents the use of analytic network process (ANP) to decision making. As a successor to AHP, an introduction to ANP will be given including a step by step guideline to perform the analysis. Again, a biodiesel process will be used to demonstrate the functionality of the approach and the results will be presented. Chapter nine focuses on the introduction of sustainability assessment and decision making process into chemical engineering education. A lecture is given to process engineering students at Berlin Institute of Technology. Their responses will be analyzed and presented in further detail in this chapter. Finally, chapter ten summarizes all the findings in this work, and I will conclude with some remarks for further research in this area.

Chapter 2

Sustainability Assessment

2.1 Introduction

Galileo Galilei once stated, *'Measure what is measurable, and make measurable what is not'* [24]. In sustainability assessment, measuring environmental and social impacts of an economic activity is of great importance. In such an endeavour, selection of necessary indicators is critical. Arguably, sustainability indicators can be divided into two groups: hard and soft. Hard indicators give a quantitative evaluation of a process using numerical information and formulas, such as net present value (NPV) and rate of return (ROR) used for economic performance assessment, life cycle assessment (LCA) and waste reduction (WAR) algorithm for environmental performance assessment, and fault tree assessment (FTA) and chemical exposure index (CEI) for safety related social responsibility assessment. More recent efforts of using hard indicators in biodiesel systems assessment can be found in some recent publications [25, 26, 27].

Soft indicators on the other hand give qualitative evaluation which depends heavily on designers' knowledge and experience (mostly heuristic). The indicators are frequently very subjective because of different interpretations, but eventually they play an important role in obtaining an agreeable solution. Although difficult to be transferred into formulas or equations, this type of soft indicator may be also numerically scaled using appropriate scaling techniques.

In sustainability assessment methodology development, several papers [13, 14, 15, 17, 19] applied both types of indicators. It is important to note that, defining suitable indicators to assess sustainability is non-specific. The selection of indicators very much depends on the level of assessment. At early design stages a less extensive data search should be used as the indicators. As the project development progresses and more information becomes available, more in depth indicators can be introduced. In this work, we proposed specific indicators which are suitable to assess the sustainability performance of process plant design at the early stages of development.

2.2 Economic indicator

In product development, economic performance is the most assessed and important attribute when evaluating a process design. Although with the emergence of the concept design for sustainability, economic feasibility is still one of the most influential factors that determine the continuation of a product development.

The methodology to measure economic performance has come a long way. There are many established and good methodologies proposed by various authors in various fields. One may use capital costs or manufacturing costs, but others may adopt a more comprehensive method such as NPV. Normally, at early design stages the economic feasibility is estimated. It is based on the development of a process flow and rough sizing of major process equipment without inclusion of plant details such as plant layout, process instrumentation diagram or piping and instrumentation information. Such estimation has an accuracy range from +30% to 20%. Thus, results from such preliminary evaluation may not accurately reflect the final profitability of a chemical plant but can be used as a tool for comparison of several process alternatives [28].

According to Pintarić and Kravanja [29], in process flowsheet optimisation frequently uses simple capital and operating costs and profit functions. However, further investigation indicates that NPV and discounted cash flow rate of return (DCFRR) are more favorable as they take into account the overall projects economic life cycle. This includes initial investment, annual profit, annual depreciation, salvage value and interest on investment. Furthermore, they are among those favored by entrepreneurs as they can provide more appropriate profitability measurement in design alternative evaluation [10, 11]. Both indicators should be used together and thus provide a comprehensive profitability measurement, and can also be used to compare alternatives. For the reasons above, these two indicators will be used to describe the economic performance of a process design. Details on both indicators will be given next.

2.2.1 Net present value

NPV can be calculated by summation of the present values of all incomes subtracted by the summation of the present values of all expenditures as shown below.

$$NPV = \sum_{m=1}^{n} \frac{C_{A,m}}{(1+r)^m} - C_{TCI} \tag{2.1}$$

where C_A is the total annual income cash flow after the base year for year m; r is the interest rate (%); n is the project life time after the base year. C_{TCI} is the total capital investment cost before the base year and is the summation of the total fixed capital cost, C_{FCC}, and the working capital cost, C_{WCC}.

Fixed capital cost represents the cost of constructing a new plant. According to Ulrich [11] and Turton et al. [28] fixed capital cost consists of three parts: total bare module capital cost, contingencies and fees, and costs associated with auxiliary facilities. Total bare module capital cost is the sum of the cost of each piece of equipment in the process. Contingencies and fees are defined as a fraction of the total bare module capital cost to cover unforeseen circumstances and contractor fees. Expenses of auxiliary facilities include items such as the purchase of land, installation of electrical and water systems and construction of all internal roads. They are usually represented by 30% of the total basic module cost (i.e., the sum of total bare module capital cost and contingency and fees).

Working capital cost or also known as total production investment (TPI), refers to the cost of the day-to-day operation of a chemical plant and is usually divided into three categories: direct manufacturing costs, indirect manufacturing costs (or fixed manufacturing cost) and general expenses [11, 28]. Direct manufacturing costs consist of raw material costs, catalyst and solvent costs, operating labor fees, supervisory and clerical labor fees, utilities (including waste disposal), maintenance and repairs, operating supplies, laboratory charges, and expenses for patents and royalties. In brief, all charges related to materials and labors belong to this category. Indirect manufacturing costs include overhead, packaging, storage, local taxes, insurance and depreciation. All of the items in this category are independent of the production rate in a plant. The last category, general expenses, includes administrative costs, distribution and selling costs, and research and development charges. Similarly, items pertaining to indirect manufacturing costs and general expenses were also computed and multiplied by various constant factors, which are commonly applied to economic assessments [11, 28].

2.2.2 Discounted cash flow rate of return

While NPV describes the profitability of a plant, DCFRR on the other hand, is designed to reflect the highest after-tax interest or discount rate at which the project can just break even [28]. It is defined as the discount rate at which the NPV of a project equals to zero as shown in equation 2.2. At that point, the values of interest, r or interest rate of return (ROR), r_{ROR}, can be readily determined. This so called internal rate interest is usually determined by corporate management and represents the minimum acceptable rate of return that the company will accept for any new investment. The acceptance of this discount rate depends on many factors, such as economic situation, environmental regulation, and social needs. Obviously, a project that yields DCFRR greater than the internal interest rate is considered to be profitable. Clearly, a combined used of both NPV and DCFRR can reflect a comprehensive economic assessment that includes the rate of return and its investment scale.

$$0 = \sum_{m=1}^{n} \frac{C_{A,m}}{(1 + r_{ROR})^m} - C_{TCI} \tag{2.2}$$

2.3 Environmental indicator

For the last two hundred years, industrial systems have achieved massive growth in prosperity and manufactured capital, but at the severe cost of the rapid declining of natural capital [30]. Realizing this, the movement towards an environmentally conscious society is ever increasing and the driving forces are coming from all segments of society. Consumers, stakeholders, competitiveness, legislation, energy and material price are some of the driving forces that push companies or even countries to adopt various environmental initiatives. In chemical industries such factors have urged decision makers to implement various cost or environment reduction strategies from operation or design while maintaining product quality. While implementing such strategies, there is a need of specific assessment methodology to assess the extent of their initiatives. Such assessment is important to gauge the environmental performance of a system to any design or operation modifications. Moreover, it enables one to compare the environmental impacts of different initiatives and finally choose the one that fits the criteria of design for sustainability.

As a part of sustainability, there are some well-known and widely used methodologies to assess environmental performance. LCA for example, is a holistic approach for environmental assessment that offers systematic guidelines for analysts to investigate and evaluate the impacts of product, process or service to the environment. A complete life cycle assessment, also known as cradle-to-grave assessment, considers a larger scope of chemical production starting from extraction of raw materials phase until disposal phase (see Figure 2.1a). It begins with the gathering of raw materials from the earth to create the product and ends at the point when all materials are returned to earth.

Performing LCA assessment involves four phases and starts with goal definition and scoping, inventory analysis, impact assessment and interpretation (see Figure 2.2). Specifically by performing LCA, it enables to, among other things, assist in identifying significant shifts in environmental impacts between life cycle stages and environmental media, and compare the health and ecological impacts between two or more rival products/processes, or to identify the impacts of a specific product or process. Although LCA is a good tool for environmental assessment, and has been implemented widely, it has several critics. Besides being time consuming and costly, the most critical and controversial step in life cycle impact assessment (LCIA) is the weighting step [6]. In this step, how the impact categories are to be weighted is much less clear. Thus, it frequently leads to unambiguous interpretation of the LCA results. To overcome these limitations the Eco-indicator 99 or Eco-indicator 95, its predecessor, is introduced.

Eco-indicators are actually an LCA weighing method with a top-down approach. The top-down approach starts by defining the required result of the inventory phase assessment and the rest is set up to accommodate the best weighting procedure. Figure 2.3 shows the different procedure and (intermediates) results of the methodology. According to Goedkoop and Spriensma [6] there are two ways the Eco-indicator methodology solves the problems in LCA. The first is by transforming the inventory table into damage scores, namely damages to human health expressed as DALY (disability adjusted life years), damages to ecosystem quality and resources extraction which can be aggregated, depending on the needs and choice of the user, to damage scores per each three comprehensive damage categories, or even to one single score. Secondly, is by calculating standard indicator values for a large number of frequently used materials and processes. By doing this, the number of environmental problems that are to be weighted is limited to just three. Furthermore, the environmental

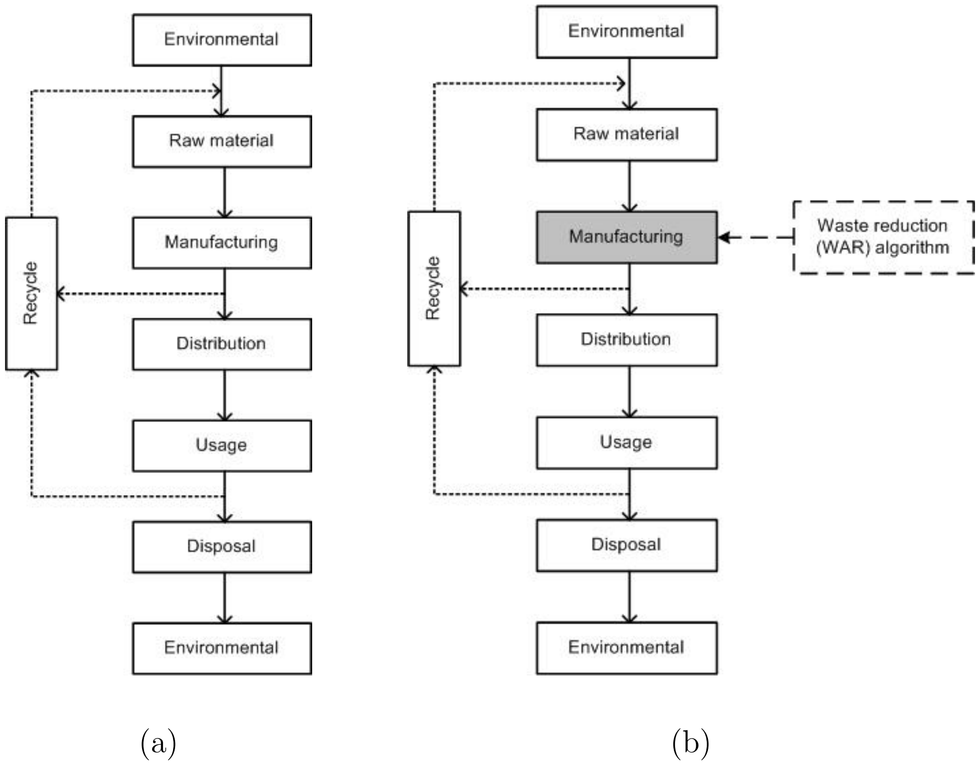


Figure 2.1: System boundaries for environmental impact assessment (a) LCA (b) WAR algorithm.

problems are defined at their endpoint level, in terms of damages to human health, ecosystem quality and resources. Definitions at this level are much easier to comprehend that the rather abstract definitions of greenhouse effect and acidification used in LCA.

In 1999 Young and Cabezas [31] introduced a so-called waste reduction (WAR) algorithm for assessing environmental impact of a chemical process design. The concept of potential environment impact (PEI) in the WAR algorithm is based on the conventional mass and energy balance conducted at the manufacturing level (see Figure 2.1b). PEI is a relative measure of the potential for a chemical to have an adverse effect on human health and environment. The result of the PEI balance is an impact index that provides quantitative measure of the impact of the waste generated in the process. Unlike the Eco-indicator, it does not describe the extent of damages to the surroundings, but it is useful to measure the effectiveness of process design to design modifications etc., to be more environmentally friendly. It is important to note that in this method the product life cycle is partial, as it covers the stages only from manufacturing to the factory gate (before transported to consumers) as can be seen in Figure 2.1b. This algorithm adopts simple to use algorithms and easy to find parameters. Furthermore, it is inherently flexible, which allows the user to emphasize or de-emphasize the individual impact categories in the calculation of the pollution indices to address their specific needs. Because of its suitability in assessing environmental performance at the design stage, the WAR algorithm has been integrated into several process simulators such as ChemCAD, Integrated Computer Aided System (ICAS) and AspenTech (under negotiation). A

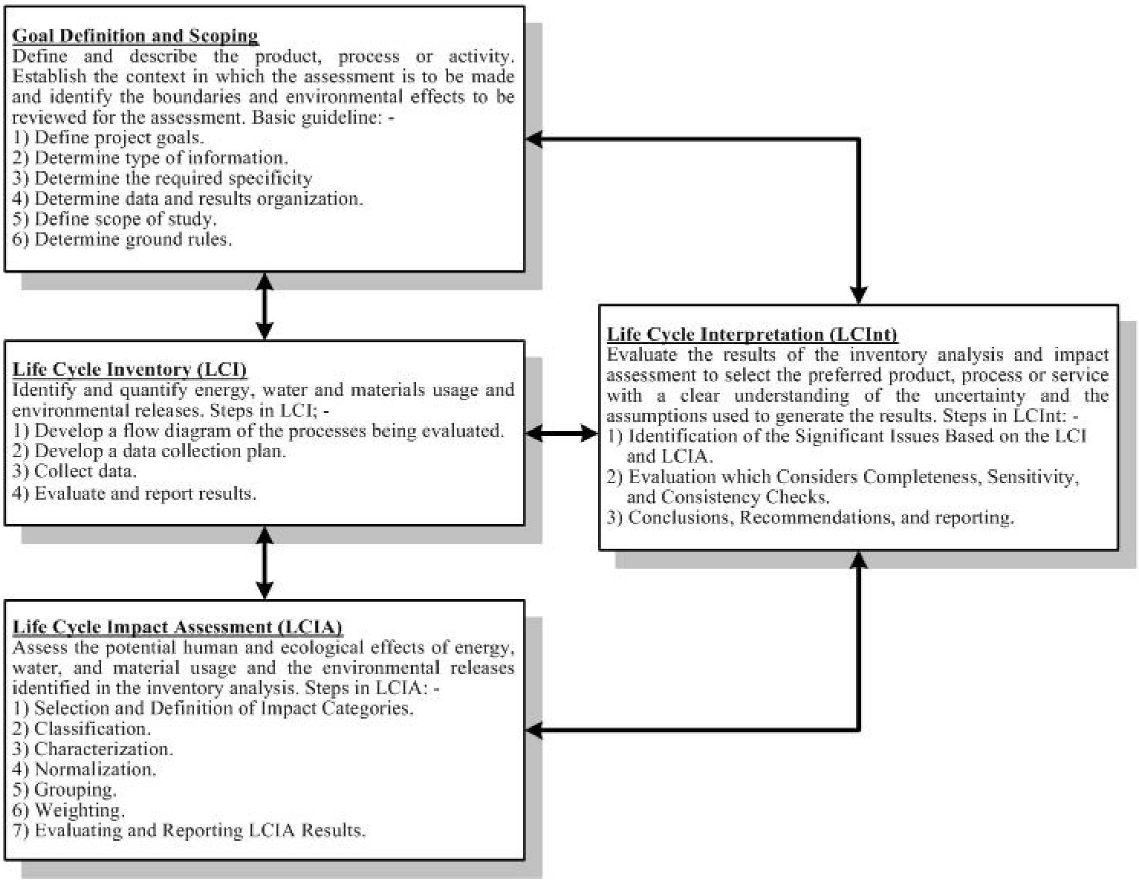


Figure 2.2: Phases and guidelines of LCA.

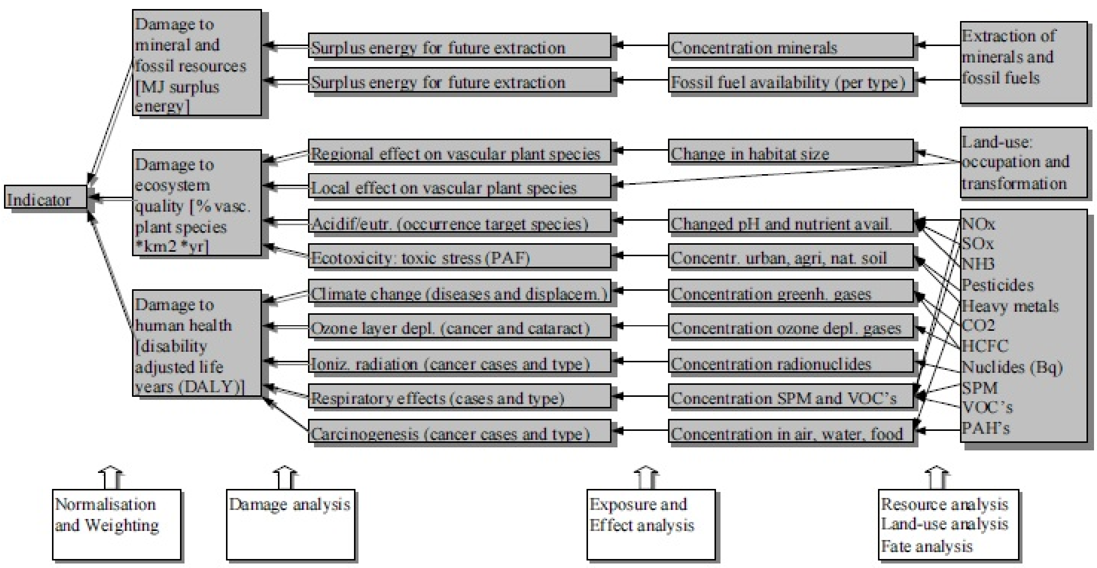


Figure 2.3: General representation of the Eco-indicator 99 methodology. The white boxes refer to procedure; the other boxes refer to intermediate results [6].

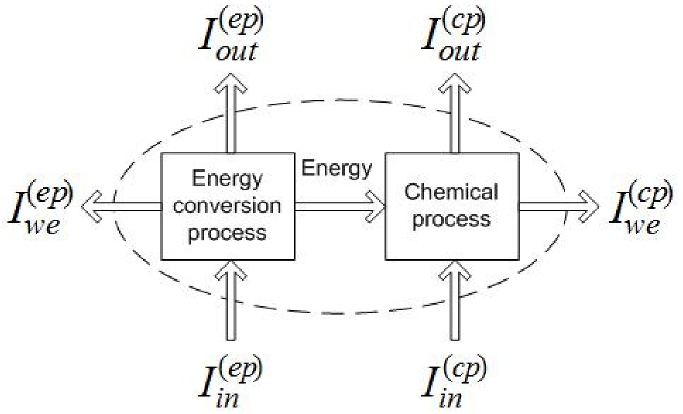


Figure 2.4: Mass and energy balance for the calculation of the PEI at the manufacturing level.

download version of WAR software can be found at the US EPA website [32].

The methods mentioned above offer very specific and detailed environmental assessments. However, they are strongly affected by weights or preference. There are other efforts to describe environmental performance using singular indicators. One of them is exergy. Although has long been introduced, exergy analysis still has an important role in understanding and increasing utilization of green energy and technologies for sustainable development. As energy analysis alone cannot provide information on the location, magnitude and source of thermodynamic inefficiencies, exergy play its role by improving the overall efficiency and cost effectiveness of a system, or for comparing the performance of various systems [33]. This is particularly important at early design stages before it is used as the primary design option. An exergy analysis obviously cannot indicate how much the process can improved, however it can indicate where the process can be improved and what areas should receive technical attention [34]. Meyer et al. [35] have extended the exergy to exergoenvironmental analysis that combine exergy analysis with Eco-indicator 99. In a latest development, Schöneberger et al. [36] introduced a novel approach called IEEA (Inverse Exergoeconomical and Environmental Analysis) by combining ecological indicators and an inverse economic analysis with exergetic analysis. By using these as key indicators, improvement strategies can implement to further improve the process.

Another singular index to measure the environmental performance of an industrial system is emergy. Emergy analysis originated from the study on agricultural and natural ecological systems. It is based on the evaluation of the energy used for making products or services. In other words, emergy is the available energy of one kind previously required, directly and indirectly, to make the products or services. The unit of emergy is emjoule. Calculation of unit emergy values can be categorized into several types, including transformity (seJ/J), specific emergy (seJ/g), emergy per unit money (seJ/\$) and energy per labor (seJ/yr or seJ/\$). For example, if 10.000 solar emjoules are required to generate a joule of wood, then the solar transformity of that wood is 10.000 solar emjoules. Based on this concept, Lou et al. [37] introduce new indexes to improve the applicability and the effectiveness to industrial systems. Their observation shows that emergy analysis could provide a common platform to quantitatively express the economic values as well as the environmental factors. However, emergy is not free from criticisms. Some researchers are reluctant to accept quality corrections of other forms of energy besides oil, i.e., using calories of sunlight. Others questioned the possibility to quantify the amount of sunlight that is required to produce a quantity of oil. This creates concern about the uncertainty involved in such quantification.

Unlike economic measurement, establishment of standardized and commonly accepted environmental methodology has a long way to go. There are still efforts to identify or improve ways to measure environmental performance of a system. None of the fore mentioned methodologies have become a standard or approved method to assess environmental effects of a process design. Different organizations or individuals may use different methods based on their preferences. The adoption of a particular indicator is significantly important, especially in the initial stages of process design, so that the indicator presents a direct correlation among flows and impacts and reduces the requirement of complex models [38]. In this work, the WAR algorithm is adopted to assess the environmental performance of a process design. The reason is because of its ability to describe the environmental impact of the input-output material and energy stream in a simple approach, thus making it suitable especially at early design evaluation. Moreover, it uses less extensive data which can be found in open literature and could greatly facilitate design comparison to modified or new processes. More on the WAR algorithm is described next.

2.3.1 Waste reduction algorithm

The concept of potential environment impact (PEI) in the WAR algorithm is based on the conventional mass and energy balance (see Figure 2.4). The key formulations of the algorithm are briefly reviewed below.

At the steady state, the algorithm can be expressed as:

$$I_{in}^{cp} + I_{in}^{ep} - I_{out}^{cp} - I_{out}^{ep} - I_{we}^{cp} - I_{we}^{ep} + I_{gen}^{t} = 0 \tag{2.3}$$

where I_{in}^{cp} and I_{out}^{cp} are, respectively, the mass input and output rates of PEI of a chemical process; I_{in}^{ep} and I_{out}^{ep} are, respectively, the energy input and output rates of PEI of the energy conversion process; I_{we}^{cp} and I_{we}^{ep} are, respectively, the outputs of PEI associated with waste energy lost from the chemical process and the energy conversion process; I_{gen}^{t} is the total rate of energy of PEI inside the system, representing the creation and consumption of PEI by chemical reactions. According to Young and Cabezas [31], I_{we}^{cp} and I_{we}^{ep} can be neglected since chemical plants usually do not emit large amounts of waste energy and the potential environment impact of mass is much greater than the emission of energy. Thus, the above equation can be simplified as,

$$I_{gen}^{t} = I_{out}^{cp} - I_{in}^{cp} + I_{out}^{ep} - I_{in}^{ep} \tag{2.4}$$

For the mass expressions,

$$I_{in}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,in} \sum_{c}^{Comp} \left(x_{c,h}\psi_{c,i}^{s}\right) \tag{2.5}$$

$$I_{out}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,out} \sum_{c}^{Comp} \left(x_{c,h}\psi_{c,i}^{s}\right) \tag{2.6}$$

where M_h is the mass flow rate of the stream h, either input or output stream; $x_{c,h}$ is the mass fraction of component c in stream h; $\psi_{c,i}^{s}$ is the specific PEI of chemical c for impact category i. Details on calculation of the specific PEI of chemical components is further described in section specific PEI of chemical component. Note that equations 2.5 and 2.6 only involve PEI associated with pure components and additional expression is needed if involve mixtures of components.

PEI of energy consumption

Potential environmental impact for energy is calculated by summing up all the energy requirements of the system, such as the energy used by compressors, reboilers, heat exchangers, cooling and reboiler pumps, refrigeration units, turbines, etc. Typically, energy sources for these can be classified as direct energy (e.g., electricity) and indirect energy (e.g., steam at different pressures and natural gas). In Young and Cabezas [31], only electrical energy is considered. As an extension, this work includes both electrical energy and steam. For sources of energy conversion in a coal-fired power plant, the amount of emission must be considered, which contains SO_2, NO_x, CO_2, CH_4 and Hg [1]. Some modifications are made to the original equations, whereby the input and output energy PEI are expressed by:

$$I_{in}^{ep} = \sum_{h}^{ep} I_{h}^{in} = \sum_{h}^{ep} M_{h,in} \sum_{c} \left(x_{c,h}\psi_{c,i}^{s}\right) \tag{2.7}$$

$$I_{out}^{ep} = \sum_{h}^{ep} I_{h}^{out} = \sum_{h}^{ep-g} I_{h}^{out} + \sum_{h}^{ep-s} I_{h}^{out} \tag{2.8}$$

where I_{in}^{ep} is the potential environmental impact of the combustion source (the energy conversion process); I_{out}^{ep} is the potential environment impact of energy output that is used by the process plant. From equation 2.8 we can see that the energy PEI output, I_{out}^{ep} is calculated by summation of all gaseous output streams, $ep-g$ and all solid output streams, $ep-s$ from the power plant. Calculation of each stream is given by:

$$\sum_{h}^{ep-g} I_{h}^{out} = \sum_{h}^{Streams} \zeta_{gas} \sum_{c}^{Comp} \left(EF_{c,h}\psi_{i}^{s}\right) \tag{2.9}$$

$$\sum_{h}^{ep-s} I_{h}^{out} = \sum_{h}^{Streams} \zeta_{solid} \sum_{c}^{Comp} \left(x_{c,h}\psi_{i}^{s}\right) \tag{2.10}$$

Gas pollutants	emission factor (EF), kg/h.kW
SO_x	0,00272
NO_x (NO_2 and NO)	0,00181
CO_2	0,3719
HCl	9,0 x 10-5
Methane	0,4763
Mercury (Hg)	4,944 x 10-9

Table 2.1: Emission factor for the coal-fired power plant [1].

where

$$\zeta_{gas} = \left[\sum_{h}^{ep-g} E_{h,in}^{Direct} + \sum_{h}^{ep-g} \alpha E_{h,in}^{Indirect} \right] \tag{2.11}$$

$$\zeta_{solid} = \left[\sum_{h}^{ep-s} E_{h,in}^{Direct} + \sum_{h}^{ep-s} \alpha E_{h,in}^{Indirect} \right] \tag{2.12}$$

E is the energy requirement of h direct energy streams and indirect energy streams consumed by the unit operations or facilities; EF is an emission factor for gas pollutants g (in kg/h.kW for coal-fired power plants, see Table 2.1); α is the ratio of electrical energy to steam energy for plant utilities produced through burning the same amount of coal (this coefficient is used to consider the energy lost from steam that is used for generating electrical energy before being used for heating purposes in the plant).

The energy conversion process which is assumed to be coal-fired uses mainly coal, air and water as raw materials. Since water and air have no chemical PEI, the only one that has significant chemical PEI is the coal feed stream. According to Young and Cabezas [31], coal ought to have a significant chemical PEI because of the presence of hazardous materials i.e., metals, sulfur, and organic compounds. Fortunately, all of these components are locked in a solid form which makes them unavailable to cause environmental impacts in the way that liquids and gases would. Therefore, it is assumed that solid compounds are intermediate pollutants as the hazardous components are locked in a solid mixture, having no or negligible negative environment impact. Such an assumption makes I_{in}^{ep} and the second term on the right hand side of equation (2.8) approximately zero. This simplifies the calculation of PEI energy of a process design to only take into account the potential environmental impact of energy output, I_{out}^{ep} in equation 2.13 below:

$$I_{out}^{ep} = \sum_{h}^{ep} I_{h}^{out} = \sum_{h}^{ep-g} I_{h}^{out} \tag{2.13}$$

Specific PEI of chemical components

To implement WAR algorithm, the specific PEI of each chemical over certain impact category, $\psi_{c,i}^{s}$ needs to be determined. The impact categories to measure the affect to environment are based on a study by Heijungs et al. [39] which is generally categorized into two categories: global atmospheric and local toxilogical. The global atmospheric category involves indicators, namely global warming potential (GWP), ozone depletion potential (ODP), acidification potential (AP) and photochemical oxidation (or smog formation) potential (PCOP). In the local toxilogical level, the indicators include human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation/dermal exposure (HTPE), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP).

The calculation of ψ^s is based on scores using the following normalization scheme:

$$\beta_i \psi^s_{c,i} = \frac{Score_{c,i}}{[Score_c]_i} \tag{2.14}$$

where β_i represents the relative weighting factor of impact category i that should be use to emphasize or de-emphasize specific impact categories. $Score_{c,i}$ represents the value of chemical c on some arbitrary scale for impact category i and $[Score_c]_i$ represents the average value of all chemicals in category i. This normalized value will ensure that values of different categories contain the same units and a proper normalization will also ensure that values from different categories will have the same value on average equivalent scores. Without the second condition, implicit weighting factors could be present in the chemical database causing unintentional bias in the calculation of the PEI indexes.

The mechanism for finding the scores can be found in different sources. The impact factor (IF) data for the four global atmospheric impact categories; GWP, ODP, AP and PCOP, can be found in Heijungs et al. [39] whereas the other can be found in MSDS datasheet. To further understand the mechanism a brief summary of their methodology for determining these parameters is presented next.

Definition of impact categories

The GWP is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent that CO_2 absorbs infrared radiation over its respective lifetimes. The half-lives of each of these chemicals was factored into the calculation for determining the GWP. Since, chemicals have different atmospheric half-lives the length of time over i.e., 100 years, which comparison is made will change the GWP of a chemical.

The ODP is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. For a chemical to have ODP it must exist in the atmosphere long enough to reach the stratosphere. It also must contain a chlorine or bromine atom. The PCOP or smog formation potential is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical (OH·) to the rate at which a unit mass of ethylene reacts with OH·. The AP or acid rain potential is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2.

Two categories were used to estimate the potential for human toxicity: ingestion and inhalation: dermal exposure. These two categories were used to estimate toxicity potential because they considered all of the primary routes of exposure of a chemical. As a general rule, HTPI were calculated for a chemical if it existed as a liquid or solid at a temperature of 0°C and atmospheric pressure, and an exposure potential, HTPE, was determined for that chemical if it existed as a gas at those conditions. Some chemicals, however, were assigned values for both categories if it was warranted.

For the toxilogical level the lethal dose, LD50 was used as an estimate for the HTPI and TTP whereas lethal concentration, LC50 was used for ATP category impact. By inspection of this scale, it is quite apparent that a chemical with a higher value represents a chemical with lower toxicity. This scale is inverted from the manner in which the WAR algorithm is presented where a higher score represents a greater potential environmental impact. Thus, the score for chemical c for HTPI and TTP can be calculated by:

$$Score_{c,HTPI,TTP} = (LD50)_c^{-1} \tag{2.15}$$

whereas for ATP:

$$Score_{c,ATP} = (LC50)_c^{-1} \tag{2.16}$$

This inversion assigns scores to chemicals in the database so that the more toxic chemicals have higher scores, which follows with the concepts of the WAR algorithm. This inversion also maintains a proportional relationship between chemicals. To estimate the HTPE, time-weighted averages (TWA) of the threshold limit values (TLV) were used. These values were obtained from OSHA, ACGIH, NIOSH and represent occupational safety exposure limits. This was considered to be an adequate measuring stick for comparison of chemicals that would pose a threat to human health through inhalation and dermal exposure routes. Recall, only a relative comparison within categories is needed for this methodology. These estimations of human toxicity potential should be considered to be a first-order approximation only.

Environmental indicators definition

From previous equations we can conclude that the total rate of PEI generated, I^t_{gen} and total PEI output, I^t_{out} can be expressed as:

$$I^t_{gen} = I^{cp}_{out} - I^{cp}_{in} + I^{ep}_{out} \tag{2.17}$$

$$I^t_{out} = I^{cp}_{out} + I^{ep}_{out} \tag{2.18}$$

The indices presented to this end are in terms of rate PEI/h. To evaluate on a product basis (PEI/kg), a simple transformation can be made to the index by,

$$\hat{I}^t_{gen} = \frac{I^{cp}_{out} - I^{cp}_{in} + I^{ep}_{out}}{\sum M_p} \tag{2.19}$$

$$\hat{I}^t_{out} = \frac{I^{cp}_{out} + I^{cp}_{out}}{\sum M_p} \tag{2.20}$$

where M_p is the mass flowrate of product p. Using equations (2.17) - (2.20) allows us to measure the environmental impact of a chemical process. The value of total rate of PEI output, I^t_{out}, enables us to identify an appropriate site for a plant (a plant with low I^t_{out} should be located in an ecologically sensitive area).

On the other hand, $\hat{I}^t_{out}$ measures the efficiency of material utilization by a specific process per unit mass of products; it decreases when the mass rate of PEI, I^t_{out}, is reduced or the production rate is increased. This means that improving material utilization efficiency through process modification/innovation tends to lower the PEI output per unit mass of products. This suggests that engineers design process systems through a careful selection of process operating conditions, which directly affects the magnitude of I^t_{gen} (an indicator useful in comparing processes based on how fast they generate impact). On the other hand, $\hat{I}^t_{gen}$ is used for comparing processes and products based on the amount of new potential environmental impact generated in product manufacturing. Obviously, the lower the PEI value, the desirable the process.

Note than, the equations considered above count for all products and non-products streams (such as intermediate products, by-products, waste, etc.), because all of them may have potential environment impacts. In some cases, however, when the product of one process is an intermediate of a downstream process, a high demand on the product and when the analysis objective is to reduce waste the product stream should be excluded from the analysis. This is to ensure that a user or producer is not directly penalized for producing chemicals that has a high PEI value [31].

2.3.2 An example

To demonstrate the WAR algorithm methodology, an example of biodiesel purification column will be shown. Figure 2.5 shows the fractionation column and its input and output flow. The feed to the column is the upper product of the decanter after the water washing process. The feed contains triglyceride, fatty acid methyl ester (FAME), natrium hydroxide (NaOH), glycerine or glycerol and water. The feed mass flowrate for each component is shown in Table 2.2. The aim of the column is to produce FAME with purity of more than 99.6%. To achieve this the column uses six theoretical stages with a reflux ratio of 2 and operated under vacuum to maintain product temperature below 250°C. At this stage pumps are not included in the design. The column is model and simulated in Aspen Plus and the results for the waste streams and product stream is shown in Table 2.2.

The PEI value is calculated using equation (2.4). For the mass PEI value for input and output stream is calculated using equation (2.5) and (2.6), respectively. Whereas the PEI for energy is calculated by using equation (2.7) to (2.12). For simplication all solid component is assumed having no or negligible negative environmental impact therefore equation (2.7) and (2.12) is neglected, thus reduced the formulation to only equation (2.13). In equation (2.9), the emission factor (EF) is shown in Table 2.1. The value of α which represents the ratio of electrical energy to steam energy for plant utilities produced through burning the same amount of coal is assumed three. For source of energy the PEI value is shown in Table 2.3. In this example, only steam consumption for the reboiler is considered with heat duty of 1781 MJ/hr. No electric energy was considered in this case. The score of the com-

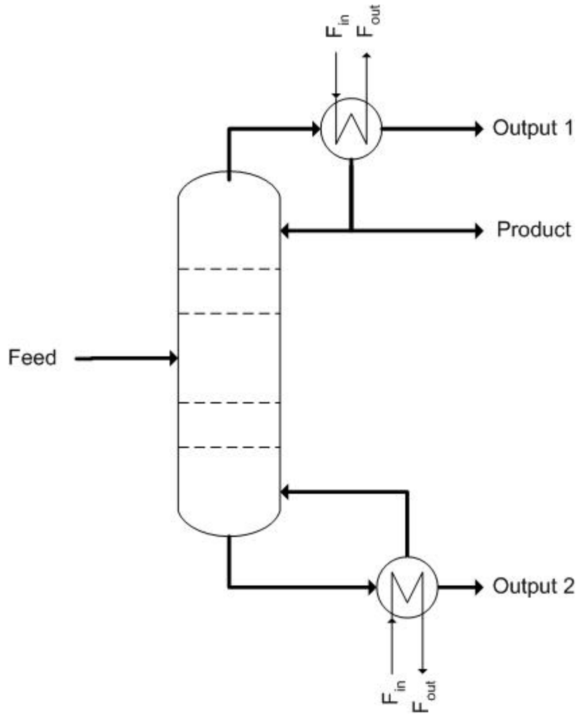


Figure 2.5: Biodiesel fractionation column.

Component	Feed (kg/hr)	Output 1 (kg/hr)	Output 2 (kg/hr)	Prod. (kg/hr)
TG	52,49	0	50,50	1,99
MeOH	0,93	0,66	0	0,27
NaOH	0	0	0	0
Glycerine	1,20	0	0	1,20
FAME	1002,05	0,59	4,57	996,89
Water	0,45	0,21	0	0,23

Table 2.2: Input and output flowrate for the fractionation column

ponent PEI is depicted in Table 2.3 and the calculated specific and normalized PEI of chemical component is shown in Table 2.4. This table also shows the normalized specific PEI of each component calculated using equation 2.14. This normalized value will be used in calculating the PEI value.

Comp.	HTPI[a] (mg/kg)	HTPE[b] (ppm)	ATP[c] (ppm)	TTP[a] (mg/kg)	GWP[d]	PCOP[d]	AP[d]	ODP[d]	EF
TG	-[e]	-	-	-	-	-	-	-	-
MeOH	5628	200	29400	5628	-	0,123	-	-	-
NaOH	-	2	-	-	-	-	-	-	-
Glycerol	12600	10	58,5[f]	12600	-	-	-	-	-
FAME	-	-	-	-	-	0,223	-	-	-
Water	-	-	-	-	-	-	-	-	-
H_3PO_4	1530	1	-	1530	-	-	-	-	-
Na_3PO_4	4150	15	220[g]	4150	-	-	-	-	-
SO_x	1,2	-	-	1,2	-	-	1	-	0,00272
NO_x	0,78	-	-	0,78	-	-	1,77	-	0,001814
CO_2	-	-	-	-	1	-	-	-	0,3719
HCl	-	-	-	-	-	-	0,88	-	0,00009
Methane	-	-	-	-	35	0,007	-	-	0,4763
Mercury	-	0,025	500	-	-	-	-	-	$4{,}90 \times 10^{-9}$

[a]LD50 (Oral-Rat)
[b]TWA-TLV (CGIH)
[c]LC50 (Fathead Minnow)
[d]Classification factors published by Heijungs et al. [39]
[e]Denotes either nonapplicable or nondetermined data
[f]LC50 (Trout)
[g]LC50 (Bluegill Sunfish)

Table 2.3: Score value of the PEI of components.

Comp.	HTPI[a]		HTPE[b]		ATP[c]		TTP[a]		GWP[d]		PCOP[d]		AP[d]		ODP[d]	
	LD50	Norm.	TWA-TLV	Norm.	LC50	Norm.	LD50	Norm.	IF	Norm.	IF	Norm.	IF	Norm.	IF	Norm.
TG	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MeOH	0,00018	0,61717	200	4,38596	0,00003	0,00471	0,00018	0,61717	-	-	0,12300	0,71098	-	-	-	-
NaOH	-	-	2	0,04386	-	-	-	-	-	-	-	-	-	-	-	-
GLY	0,00008	0,27567	10	0,21930	0,01709	2,36612	0,00008	0,27567	-	-	-	-	-	-	-	-
FAME	-	-	-	-	-	-	-	-	-	-	0,22300	1,28902	-	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H_3PO_4	0,00065	2,27020	1	0,02193	-	-	0,00065	2,27020	-	-	-	-	-	-	-	-
Na_3PO_4	0,00024	0,83697	15,00000	0,32895	0,00455	0,62917	0,00024	0,83697	-	-	-	-	-	-	-	-
SO_x	0,83333	0,78788	-	-	-	-	0,83333	0,78788	-	-	-	-	1	0,82192	-	-
NO_x	1,28205	1,21212	-	-	-	-	1,28205	1,21212	-	-	-	-	1,77000	1,45479	-	-
CO_2	-	-	-	-	-	-	-	-	1	0,05556	-	-	-	-	-	-
HCl	-	-	-	-	-	-	-	-	-	-	-	-	0,88000	0,72329	-	-
Methane	-	-	-	-	-	-	-	-	35	1,94444	0,00700	1	-	-	-	-
Mercury	-	-	0,02500	1	0,00200	1	-	-	-	-	-	-	-	-	-	-

[a]LD50 (Oral-Rat)
[b]TWA-TLV (CGIH)
[c]LC50 (Fathead Minnow)
[d]Classification factors published by Heijungs et al. [39]
[e]LC50 (Trout)
[f]LC50 (Bluegill Sunfish)

Table 2.4: Specific and normalized PEI of chemical components.

The overall result is shown in Table 2.5. The parameters that we are interested within this table are the TRO, TOP, TRG and TGP values. The definitions for these parameters are given in Chapter 2.3 and can be used depending on the objective and focus of the assessment. It is important to note that the values do not represent physical or damage as in Eco-indicator. Furthermore, the values do not have any established limits or threshold value. However, it is useful in several ways. First, it can be used as an index to compare several design options and based on that make a decision. The TRO value for example can be used to selects a design that has the least environmental impact to be built in a sensitive area. Secondly, WAR algorithms also allow users to emphasize or deemphasize the impact categories. Depending on the problem and the assessment objective, some impact categories may be highlighted and others may not be significant. For example, in a process that does not involve many toxic materials, the toxilogical categories such as HTPI, HTPE, ATP and TTP can be deemphasized. This will enable the user to focus on reducing the effect of the most influential environmental impact of the design.

Other than that, WAR algorithms are also useful in measuring the extent of any modifications performed to an initial design and as a retrofitting tool by identifying spots where improvement can take place. In doing so, it is important to relate the results with stream mass flow rate or PEI value of chemical component. For example, the TRO value (without product stream) in Table 2.5 shows that the PCOP value dominates the effect to the environment compared to other categories. Further analysis shows that this is due to the presence of FAME in the non-product output stream and also the high value of its specific PEI. By relating such factors, it could assist designers in identifying spots or points in the design for furthering any improvements. In this work, although WAR algorithm can be utilized in many ways as previously mentioned, we focus on utilizing it as comparison tool in selecting environmentally benign design option.

Ind.	IS[a]	OS[b]		EC[c]	With product stream						Without product stream					
		PS[d]	NPS[e]		OS/PS	EC/PS	TRO[f]	TOP[g]	TRG[h]	TGP[i]	NPS/PS	EC/PS	TRO[f]	TOP[g]	TRG[h]	TGP[i]
HTPI	2,03	1,12	0,91	6,45	0,01	0,01	8,47	0,01	12,89	0,01	0,01	0,01	7,36	0,01	5,33	0,01
HTPE	2,80	0,94	1,87	0,00	0,00	0,00	2,80	0,00	0,00	0,00	0,00	0,00	1,87	0,00	-0,94	0,00
ATP	2,41	2,40	0,01	0,00	0,00	0,00	2,41	0,00	0,00	0,00	0,00	0,00	0,01	0,00	-2,40	0,00
TTP	4,06	2,23	1,83	6,45	0,01	0,01	10,50	0,02	12,89	0,01	0,01	0,01	8,27	0,01	4,22	0,00
GWP	0,00	0,00	0,00	1405,52	1,40	1,40	1405,52	2,81	2811,05	2,81	1,40	1,40	1405,52	1,41	1405,52	1,40
PCOP	1292,32	1285,20	7,12	707,07	2,00	0,71	1999,38	2,70	1414,13	1,41	0,71	0,71	714,18	0,72	-578,13	-0,58
AP	0,00	0,00	0,00	7,33	0,01	0,01	7,33	0,01	14,67	0,01	0,01	0,01	7,33	0,01	7,33	0,01
ODP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TOTAL	1303,61	1291,88	11,74	2132,81	3,43	2,13	3436,43	5,57	4265,63	4,26	2,14	2,13	2144,55	2,15	840,94	0,84

[a] Input stream
[b] Output stream
[c] Energy consumption
[d] Product stream
[e] Non-product stream
[f] Total rate PEI output, I^t_{out}
[g] Total PEI output/product, $\hat{I}^t_{out}$
[h] Total rate of PEI generated, I^t_{gen}
[i] Total PEI generated/product, $\hat{I}^t_{gen}$

Table 2.5: Overall PEI result.

2.4 Social indicator

The assessment of sustainability would not be complete without addressing issues concerning social aspects. In general, social criteria reflect other wider aspects of sustainable development responsibilities besides economic and environmental. However, such definitions are still loose and open to a lot of different interpretations. One may include technical issues such as safety and operability, but others may include issues concerning human rights, politics, cultural values and ethics. Considering such dimensions and evaluating social aspects often creates difficulties in measuring its performance. Many of the variables are difficult to quantify and cannot even be defined in physical terms. However, it remains a realistic goal to measure them consistently and in comparable manners, using qualitative indicators [9]. Until now, there are bundles of indicators suggested by researchers to define social performance. Azapagic and Perdan [9] for example suggest several ethical and welfare indicators for an industrial system such as, to name a few, preservation of cultural values, international standards of conduct, work satisfaction and satisfaction of social needs.

IChemE in their sustainability matrix guideline introduced 20 quantitative social indicators for assessing social performance. They reflect the company's attitude to treatment of its own employees, suppliers, contractors and customers and also its impact on society at large [8]. However, some of the indicators are irrelevant at early design stages as they adopted a back-driven approach. This approach requires extensive data search and needs historical operational data. For a new process and design, such data is difficult to find.

When defining the term social, and to explicitly define its relevant indicators, most of the research focuses on safety aspects of chemical plants and their effect on human safety. Particularly in evaluating process design, researchers are more interested in using assessment tools that are already common in PSE domains for example, safety and health assessment. The source of unsafe conditions, known as hazards, usually comes wherever there is latent energy such as kinetic energy, potential energy, work, heat and enthalpy and internal energy. In chemical plants, hazards lay everywhere from piping, storage vessels, furnaces, columns, pumps, heat exchangers, compressors and reactors. It is important to implement inherent safer design concepts to eradicate catastrophic failures that cost human life or money. In some works, for example Tugnoli et al. [38], Sugiyama et al. [19] and Carvalho et al. [16] included quantitative safety indexes in their approach to assess social related aspects at early stages of process design. The parameters involved in the assessment include information on heat of reaction, flammability, corrosivity, temperature and pressure. In 2008, Adu et al. [40] performed a comparison study of different quantitative and qualitative environmental, health and safety (ESH) indicators in early phases of chemical design. Their findings show that the results of the assessments agree well with each other although they have used different approach. Furthermore, they concluded there are no unique merits of one method over another in the EHS assessment.

Other than safety, operability or controllabity also has significant impacts to good process design criteria. In a simple definition, operability is the ease to which a process is operated and controlled. The main aim of operability is to enhance interactions that are beneficial, and eliminate those that are detrimental to the operability of the process [41]. Assessing operability of a process design therefore could help designers in assessing and possibly ranking several design alternatives. Past contributions to operability analysis can generally be classified into linear and non-linear model-based methods. Santoso et al. [42], for example, perform an operability analysis of MTBE reactive distillation column using process simulators. An extensive review of operability methods can be found in Georgakis et al. [41]. However, a widely accepted operability measure which can assist in quantifying the trade-offs between design and control has remained elusive. This is supported by Morari and Perkins [43]: *'More research effort has to be devoted to the development of simple criteria for controllability evaluation and to clearly understand their limitations. Only then it is meaningful to formulate an algorithm synthesis technique to trade off controllability and economics'.* Vinson and Georgakis [44] introduced a simple and yet powerful quantitative approach for operability analysis of nonlinear processes using steady-state models. The advantages of these approaches are that the analysis is performed at early design stages and results in a single numerical value, but this takes a lot of mathematical effort.

In 1998, Herder and Weijnen [45] conducted a study to explicitly define quality indicators for early design decision making. They observed industrial practice case studies and conducted interviews with expert panels and professionals from industry and from academia, and concluded top ten quality indicators. Sorted by ranking, the most important indicator is safety during operation, followed by plant operability, acceptable for environment, safe startup and shut down, fit for purpose, efficient use of raw materials, design should meet location specific demands, control of product quality and quantity, maintenance, and lastly, total life cycle aspects. These qualitative indicators are suitable to assessing a good quality design as they utilize the heuristics knowledge of assessors in process design evaluation. Furthermore, by assessing it in a qualitative manner, it enables a rapid assessment that is hoped to be close to the best possible evaluation without the need for extensive data searches.

In this work, four of the ten quality indicators are adopted and categorized under the socially related criteria namely safety during operation, plant operability, safe startup and shut down, and design meet location specific demands. The acceptable for environment and efficient use of raw materials indicator were excluded to avoid overlapping since both have been considered in the environmental indicator. The maintenance and total life cycle aspects were also excluded since it is considered as a part of NPV calculation. Maintenance is a part of direct manufacturing cost while total life cycle aspects were considered as salvage values. Some of the indicators more or less have the same definition. In such cases, we decide to lump the indicator into a single indicator. Fit for purpose, for example, is lumped together with design should meet location specific demands, while control of product quality and quantity is merged with plant operability.

The indicator for defining social performance of a process design is not rigid. But rather, they can be extended. Additional indicators can be introduced depending on specific problems at hand, or the nature of the process itself. Note that any indicator definition must represent the process accordingly for a meaningful assessment. It is also important to note that these soft-based indicators are difficult to measure

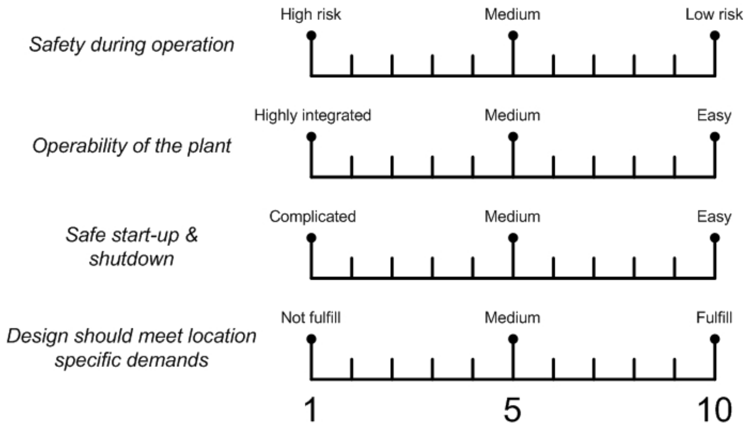


Figure 2.6: Scaling systems for the social indicators.

Indicators	Definition
Safety during operation	The condition or state of being safe; free from danger or hazard; exemption from hurt, injury, or loss. Evaluation of hazards and risks associated, but not limited to chemical compounds, reactions, unit operations and equipment, and operating conditions should include in the assessment.
Operability of the plant	The condition where the plant is able to operate feasibly. Assessment should consider the operation feasibility by workers and also control systems of the plant, especially if tightly integrated, and also in the presence of process variations and uncertainties.
Safe start-up and shutdown	Start-up means the act or process of setting into operation or motion while shut down means cease to operate or cause to cease operating. The degree of difficulties of the procedure depends on the system complexity and workers capability.
Design should meet location specific demands	Local demands may include technology transfer, employment, affect to other related industries, local regulations and policies, legal proceedings, etc.

Table 2.6: General definition of the social indicators.

and formulate, but generally can be converted to numerical numbers using appropriate scaling systems. A scaling system proposed is shown in Figure 2.6. Although not very specific, it acts as a general guideline to assess various types of chemical processes. This type of approach is widely used in process safety engineering. Note also that to conduct an appropriate evaluation of process design, the indicators to be used should be explicitly defined to avoid confusion. As a guideline, each of the indicators is defined in Table 2.6. Although not very rigid, they should be useful to guide decision makers.

2.5 Concluding remarks

Research on sustainability assessment had led to abundant of indicators to evaluate the economic, environmental and social performance of an industrial system. Out of those indicators, we select the most suitable approach to assess sustainability at early stages of chemical process design. The proposed indicators have a simple and easy to use algorithm, and need less excessive data search but still retain their relevance and provide reasonable accuracy. We divided the indicators into two categories, hard and soft indicators. Hard indicators represent indicators which can be represented by mathematical equations. This analytical approach provides a concrete measurement of the system performance. The economy and environmental criteria are assessed in this manner. On the other hand, soft indicators represent assessments that cannot be described by physical approach alone. This qualitative type of assessment is able to capture human heuristic knowledge in assessing a good process design, especially involving the socially related criteria. In conclusion, by combining both analytic and heuristics evaluation, we can provide a more realistic and comprehensive assessment.

It is important to note that, the indicators defined here are non-definitive. It can be extended based on the problem, process and assessment objective. In connection with decision making the selection of indicators define the problem decomposition. Different indicators create different model and may infer different selection results. A working paper has been dedicated to investigate the effect of different assessment methodologies to towards decision preferability, and will be to topic of Chapter 6. The next chapter will discuss further on decision making using the analytic hierarchy process (AHP).

Chapter 3

Decision Making - AHP Methodology

3.1 Introduction

Deciding on an option sometimes is not an easy task particularly when many factors influence the decision. Normally, decision making involves the following elements: the decision makers, criteria or indicators and decision methodology. Like any other members in a society, engineers or managers often face situations in which they have to decide which option best fits their personal or organizational needs. Usually these situations form a complex system with interrelated components, such as resources, desired outcomes or objectives, persons or groups, etc. Presumably, while interacting with such complex scenarios, the better the decision makers understand this complexity, the better the decision will be.

When facing a multi criteria problem, generally, there are two known ways to derive an answer [20]. First is by using deductive logic with assumptions and carefully deducing an outcome from them. Second is by laying out all possible factors in a hierarchy or in a network system and deriving answers from all possible relative influences. The former method is commonly used and adopted, but it has its drawbacks, whereby the lack of information on how to bring the different conclusions into an integrated outcome can elucidate inaccurate and unjustified conclusions. Let us take for example the selection of two biodiesel process design. Case 1 is an alkali-based system while Case 2 using supercritical methanol. Using the sustainability criteria presented in Chapter 2 the assessment result is shown in Table 3.1. Details on these two cases are presented in Chapter 5. Appendix B shows the process flowsheets and also the simulation results. Based on the first methodology we show an example of two typical approaches to decision making. Approach 1 (see Table 3.1) used symbols to designate the preferability between several cases corresponding to an indicator or criteria. Generally, the case with more symbols is preferred. However, choice on the number of symbols is arbitrary. There is no explicit methodology to do so, but generally it is done using deductive logic and carefully inferring the outcome. Using this approach, comparing between the two cases, most of the indicators for Case 1 are given two symbols whereas Case 2 mostly has one symbol. One could give three symbols for some indicators in Case 1, but as explained the definition could be

Indicator	Assm. value		Approach 1		Approach 2	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
NPV, $	3.364 k	4.073 k	$\surd$	$\surd\surd$	0,45	0,55
DCFRR, %	27	18	$\surd\surd$	$\surd$	0,6	0,4
TRO	3023	4125	$\surd\surd$	$\surd$	0,58	0,42
TOP	2,74	3,73	$\surd\surd$	$\surd$	0,58	0,42
TRG	2287	3443	$\surd\surd$	$\surd$	0,6	0,4
TGP	2,07	3,11	$\surd\surd$	$\surd$	0,6	0,4
SO	5	3,5	$\surd\surd$	$\surd$	0,59	0,41
PO	5	6	$\surd$	$\surd\surd$	0,45	0,55
SSS	5	3	$\surd\surd$	$\surd$	0,63	0,38
DMLSD	10	10	$\surd$	$\surd$	0,5	0,5
TOTAL			17 x $\surd$	12 x $\surd$	5,55	4,46

Table 3.1: Assessment result and typical decision making approach.

arbitrary. Overall, summing the number of symbols each case has, Case 1 is chosen as the best sustainable option.

Another typical approach is by using scores (see Approach 2). This is done by normalizing the assessment values of each case corresponding to an indicator. Summation of all normalized scores gives the total score. The one which obtains the highest score is the most preferred. In this case, again Case 1 is selected. Even though both approaches resulted in the same option, the advantage of Approach 2 compared to Approach 1, is the considerations of quantitative difference between the cases. Unlike the first approach which very much influenced by assumptions, the second approach appears to be more quantifiable. While both approaches offer simplicity in deducing answers, the drawbacks lies on its inability to consider the assessor's preferability towards certain criteria or indicators. Often the importance of the elements is neglected. To compliment this drawback, we adopt a decision making methodology called analytic hierarchy process (AHP) in selecting a sustainable design option. Through its hierarchical and systematic approach it provides an excellent option to solve multi criteria problems. Because of this, it has been a popular option for solving multi criteria problems in various fields from sports to engineering problems.

3.2 AHP methodology

When considering sustainable development (SD) in chemical industries, it is important to take into account the triple bottom line of sustainability namely, environmental friendliness and social advantages alongside of economic feasibility. These often conflicting objectives pose a multi criteria problem thus, increasing the complexities in decision making.

Decision selection requires a systematic decision-making methodology. Decision making relies first on effective assessment of design alternatives. Some of the commonly used techniques for MCDM problems are the analytic hierarchy process (AHP), the distance function method and the multi attribute utility theory (MAUT). Among the three techniques, AHP is the most suitable for MCDM problems [17]. AHP was introduced in 1980 by Thomas L. Saaty [21]. As a MCDM

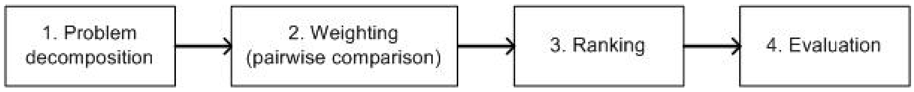


Figure 3.1: Steps for performing AHP.

methodology, AHP performs decision trade-off between multiple objectives in a uni-hierarchical structure. It accepts any particular constitutive criterion for inclusion and allows individual decisions to be aggregated into overall criteria, which allows other members to review and participate in that aspect of the decision making process at an appropriate level of detail. Its hierarchical and systematic method makes it a popular technique for solving MCDM problem. Some of the advantages of AHP are that it:

- Provides a systematic and simple approach.
- Is hierarchy-based
- Offers multiple and specific criteria for decision inclusion.
- Accepts team work participation[46].

The development of AHP for decision making requires four steps, namely, problem decomposition, weighting, ranking and evaluation (see Figure 3.1). Descriptions on each step will be presented next.

3.3 Steps for performing AHP

3.3.1 Problem decomposition

Problem decomposition is very important in decision making. The best and most organized way to decompose a problem is by structuring it into a hierarchical form (see Figure 3.2). It starts at the top or first level with a goal or problem statement and ends with the alternatives to be evaluated. Between these two levels are the top down related elements that describe the system.

A hierarchy is an abstraction of the structure of a system to study the function interactions of its components and their impacts on the entire system [21]. The interaction at the highest level with the elements at the lower level can be in a of a linear hierarchy or non-linear hierarchy. The former is the simplest form, rising from one level of elements to an adjacent level. The latter involves circular arrangements in which an upper level might be dominated by a lower level as well as being in a dominant position. The advantages of hierarchy modeling include [21]:

- Hierarchical representation of a system can be used to describe how changes in priority at an upper level affect the priority of elements in lower levels.
- They give great detail of information on the structure and function of a system in the lower level and provide an overview of the actors and their purposes in the upper level.

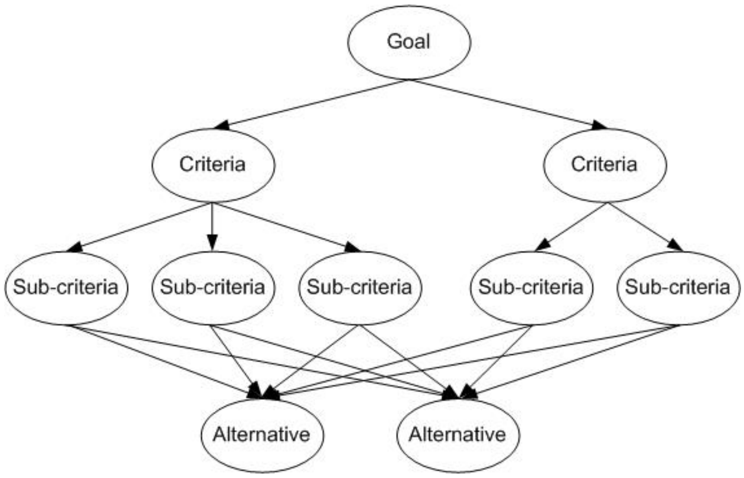


Figure 3.2: Example of hierarchy system.

- Natural systems assembled hierarchically, i.e. through modular construction and final assembly of modules, evolve more efficiently than those assembled as a whole.

- They are stable and flexible; stable in that small changes have small effect and flexible in that addition to a well-structured hierarchy they do not disrupt the performance.

The abstraction of the problem model can range from simple to complex decision tree depending on the problem complexities. However, it must be well defined for a justifiable and accurate outcome. The first level of the decision tree is the problem statement and the last level will be the alternatives or options to be assessed. Between these two levels are the details of the elements describing the decision tree. The problem model used in this work for selection of a sustainable design option is based on the indicators discussed in Chapter 2. Figure 3.3 shows the problem decomposition with five levels in a uni-directional hierarchy structure. It starts with the first level indicating the decision objective, which is to select a sustainable design. The criteria for design selection are then expanded into the second level decision hierarchy, which are economy-, environment-, and social-related. Each of these criteria is then broken into the third level criteria. The fourth level is only defined for the environment criteria that consider the eight environmental impact categories. This is useful, especially when a certain category is of a special focus. The last level is the alternatives to be assessed.

3.3.2 Pairwise comparison

In AHP, an important element within its methodology is the pairwise comparison step. In this step, the assessor is asked to perform pairwise comparisons where two components at a time will be compared with respect to an upper level control criterion. Each criterion is assigned with a weight based on its perceived importance or relevance through a pairwise comparison. Table 3.2 shows a scaling system based on the work by Saaty [21] and also a general guideline to the weights setting. Using

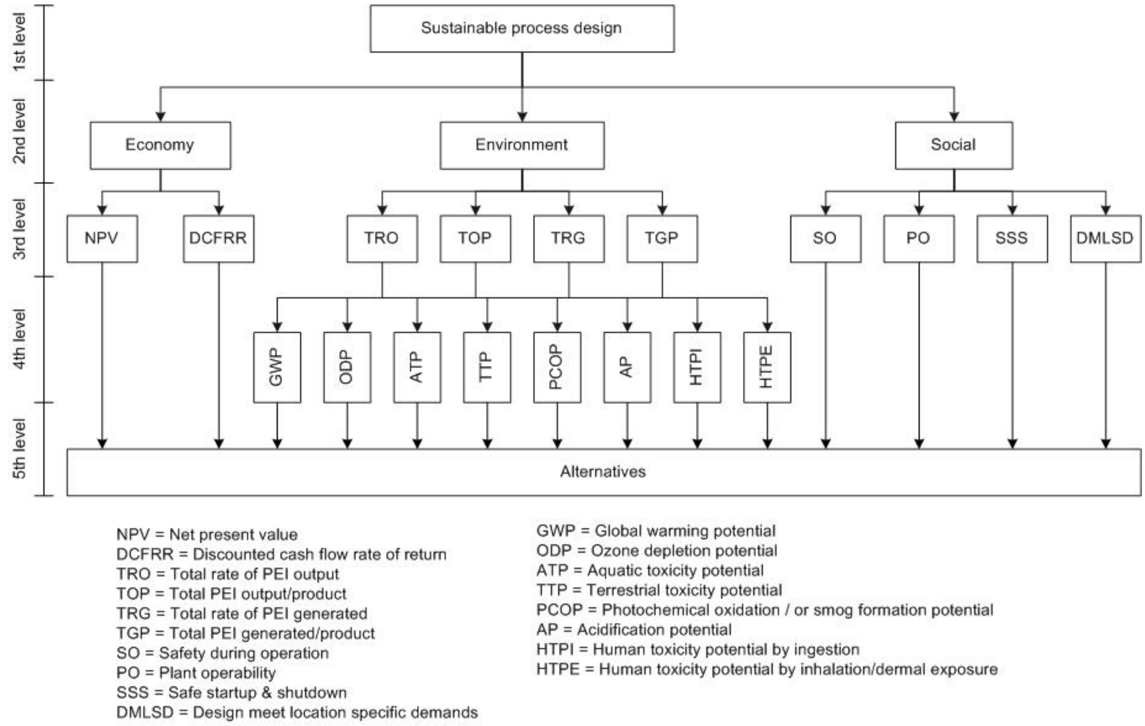


Figure 3.3: AHP sustainability assessment problem decomposition

this scaling system, one needs to identify a value of a_{ij}, which denotes the importance of the i-th element (base criterion), compared to the j-th element (paired criterion) with respect to a control criterion. A value greater than 1 indicates that the base criterion is relatively more important than the paired criteria, whereas a value less than 1 indicates its unimportance compared to the paired case. A reciprocal value is assigned to the inverse comparison, $a_{ji} = 1/a_{ij}$. The pairwise comparison is performed to each decision level. It is important to note that assigning weights to indicators is subjective. Decision makers' knowledge, experience, and judgment ability are critical in weight assignment.

The comparison process can be aided using a series of questions that relates the relationship of the compared elements and the control criterion. For example, in the second level, the question that may be asked is *'How much important is economy compared to environment when selecting a sustainable option?'*. In this question, economy acts as the base criterion while environment is the paired criteria and a sustainable option is the control criterion. Reflecting the posed question, if a value of two is taken (refer Table 3.3), it simply states that, to obtain a sustainable design option, economic feasibility is viewed as slightly more important than the environmental criteria. Whereas when compared to social criteria a value of 1,5 is assigned, which is in the range between equally important and slightly important. However, weights assignment is subjective, nevertheless, to have a meaningful and justifiable comparison, justification and team-work participation among decision makers is very important.

For the process design sustainability problem, an example of the pairwise comparison matrix is shown in Table 3.3. What we are interested in at the end of this

Quantitative scale	Qualitative indicator	Explanation
1	Equal Importance	Two activities contribute equally to the objective
2	Weak or slight	
3	Moderate importance	Experience and judgement slightly favour one activity over another
4	Moderate plus	
5	Strong importance	Experience and judgement strongly favour one activity over another
6	Strong plus	
7	Very strong or demonstrated importance	An activity is favoured very strongly over another; its dominance is demonstrated in practice
8	Very, very strong	
9	Extreme importance	The evidence favouring one activity over another is of the highest possible order of affirmation
2, 4, 6, 8	Intermediate values	
1/3	Weakly less important	May be difficult to assign the best value but when compared with other contrasting activities the size of the small numbers would not be too noticeable, yet they can still indicate the relative importance of the activities
1/5	Moderately less important	
1/7	Strongly less important	
1/9	Absolutely less important	
1/2, 1/4, 1/6, 1/8	Intermediate value etc.	

Table 3.2: Pair-wise comparison and weighting scale

weights assignment step is the priority value, PV, which indicates the importance of each element. From the same table we can see that for the second level decision hierarchy, economy criteria dominates 46% of the decision, while environment and social criteria influence 22% and 32% of the total decision, respectively. Calculation of this PV value will follow next.

3.3.3 Ranking of priorities

Once the weights of each element at each level of the hierarchy have been determined the next step is to calculate the priorities or ranking for each element. The estimation can be done by solving the following equation:

$$\mathbf{A} \cdot w = \lambda \cdot w \tag{3.1}$$

Where $\mathbf{A}$ is the matrix of pairwise comparison, w is the eigenvector and λ is the largest eigenvalue of $\mathbf{A}$. There are several algorithms for approximating w. Chung et al. [47] describe a three step procedure to synthesize priorities. Explanations of the steps are described below taking the value of the second level pairwise matrix in Table 3.3.

2nd level

Goal	Economy	Environment	Social	*PV*
Economy	1	2	1,5	0,46
Environment	0,5	1	0,67	0,22
Social	0,67	1,49	1	0,32

3rd level

Economy	NPV	DCFRR			*PV*
NPV	1	1,5			0,6
DCFRR	0,67	1			0,4
Environmental	TRO	TOP	TRG	TGP	*PV*
TRO	1	2	2	2	0,4
TOP	0,5	1	1	1	0,2
TRG	0,5	1	1	1	0,2
TGP	0,5	1	1	1	0,2
Social	SO	PO	SSS	DMLSD	*PV*
SO	1	2	3	4	0,47
PO	0,5	1	2	3	0,28
SSS	0,33	0,5	1	2	0,16
DMLSD	0,25	0,33	0,5	1	0,09

Table 3.3: Pairwise comparison for the second and third level.

1. Sum of the values in each column of the pairwise comparison matrix.

$$\begin{vmatrix} 1 & 2 & 1,5 \\ 0.5 & 1 & 0,67 \\ 0,67 & 1,49 & 1 \end{vmatrix} \tag{3.2}$$

Column sum =

$$\begin{vmatrix} 2,17 & 4,49 & 3,17 \end{vmatrix} \tag{3.3}$$

2. Divide each element in a column by the sum of its respective column. The resultant matrix is referred to as the normalized pairwise comparison matrix.

$$\begin{vmatrix} 1/2,17 = 0,461 & 2/4,49 = 0,445 & 1,5/3,17 = 0,473 \\ 0,230 & 0,223 & 0,211 \\ 0,309 & 0,332 & 0,315 \end{vmatrix} \tag{3.4}$$

3. Add the elements in each row of the normalized pairwise comparison matrix, and divide the sum by the n elements in the row. These final numbers provide an estimate of the relative priorities for the elements being compared with respect to its upper level criterion.

$$\begin{vmatrix} 0,461 & 0,445 & 0,473 \\ 0,230 & 0,223 & 0,211 \\ 0,309 & 0,332 & 0,315 \end{vmatrix} \tag{3.5}$$

Row sum =

$$\begin{vmatrix} 1,379 \\ 0,664 \\ 0,956 \end{vmatrix} \tag{3.6}$$

Eigenvector =

$$\begin{vmatrix} 1,379/(1,379+0,664+0,956)=0,460 \\ 0,664/(2,999)=0,221 \\ 0,956/(2,999)=0,319 \end{vmatrix} \tag{3.7}$$

Another way of solving w is through multiplication of matrix $\mathbf{A}$ with $\mathbf{A}$ itself as shown below:

$$\begin{vmatrix} 1 & 2 & 1,5 \\ 0,5 & 1 & 0,67 \\ 0,67 & 1,49 & 1 \end{vmatrix} \times \begin{vmatrix} 1 & 2 & 1,5 \\ 0,5 & 1 & 0,67 \\ 0,67 & 1,49 & 1 \end{vmatrix} = \begin{vmatrix} 3 & 6,24 & 4,34 \\ 1,45 & 3 & 2,09 \\ 2,08 & 4,32 & 3 \end{vmatrix} \tag{3.8}$$

The next step is the same as Step 2 and 3 to obtain the relative priorities with the same value as in the previous method. The resulting priority value, PV in this example for the second level, states that the economy and social criteria influence 46% and 31,9% of the total decision, respectively, whilst the environmental influence is 22,1%.

3.3.4 Evaluation

Evaluating alternatives using AHP requires each of the alternatives to be assigned with intensities (e.g., excellent, very good, good, average, poor; or high, medium or low) for each criterion in the decision hierarchy. One can also use quantitative value, if it exists, to replace ratings with intensities. In our work, all the sustainability indicators are measurable or in a quantifiable form, giving a more justifiable decision. The selection of best alternatives depends on the summation of the entire score index, I for an alternative a for each designated indicator, j in the i-th criteria. In general, for a single criteria, i with single subordinate or indicator, j the equation for calculating I is defined by,

$$I_{a,i} = p_i n_{ij} V_{N,ij} \tag{3.9}$$

where p is the priority value of the parents level (criteria), i, n is the priority value of its subordinate (indicator), j and V_N is the normalized assessment score, V of each case.

When performing evaluations, the assessors need to be aware of the contradictory behavior between the value desirability of the indicators. Arguably, this behavior can be categorized as the higher-value-higher-desirability (HVHD) and the lower-value-higher-desirability (LVHD). While the HVHD is obvious, such as profits, the LVHD refers to the inverse behavior which prefers a lower value. This type of behavior is closely related to the environmental indicators, such as CO_2 emission and the PEI. Such proportional and inverse value desirability behavior could create confusion, especially for the selection purpose. Therefore, in order to make the evaluation consistent, a score-based approach is proposed. The approach works by converting the indicator value into a score of 1 to 10. For indicator with the HVHD behavior, a high value is assigned to a high score. Inversely, for a LVHD indicator, a low value is assigned to a high score. The equation involved to convert the assessment value, v to its corresponding score, V is shown below.

For HVHD,

$$V_{HVHD}^{ij} = \frac{v^{ij}}{a_u^{ij}} \left(b_u^{ij}\right) \tag{3.10}$$

and for LVHD,

$$V_{LVHD}^{ij} = \frac{a_u^{ij}}{v^{ij}} \left(b_l^{ij}\right) \tag{3.11}$$

where v^{ij} is the assessment value of j-th indicator of the i-th criteria. a_u^{ij} is the value for the upper value margin of the indicator. b_u^{ij} and b_l^{ij} correspond to the upper and lower score margin for the designated indicators, respectively. Once the assessment score, V for each indicator have been obtained it needs to be normalize against other cases to obtain the normalized score, V_N and then equation 3.9 is adopted to get the score index, I for the corresponding criteria. Summation of I for each criteria gives the overall score for the alternative. The alternative with the highest score is the most preferred. An example of AHP applying all the procedures will follow next.

3.4 An illustrative example

To demonstrate the AHP methodology, two biodiesel process designs; alkali-catalyzed system (Case 1) and supercritical methanol (Case 2), is used as an example. The objective of the assessment is to compare and select one that meets the sustainability criteria. For illustrative purposes, a simplified decision model shown in Figure 3.4 is adopted. It consists of four decision levels. The upper part is the goal followed by the three sustainability criteria. The criteria are further broken down into its corresponding indicators and the last level is the alternatives being evaluated. The resulting assessment value, v is shown in Table 3.5. Note that the details on the process modeling and discussions of the results are not discussed here and will be the subject of Chapter 5. This part primarily focuses on the AHP step and only the results of the AHP analysis will be presented here.

At the initial step of the AHP analysis, pairwise comparison between the elements in the problem decomposition is conducted. The pairwise comparison is performed to each decision levels. Based on the simplified problem model in Figure 3.4, level two has three pairwise comparisons. Level three has a total of 13 pairwise comparisons; one under economic criteria and six for each environmental and social criterion. Table 3.3 shows an example of the pairwise comparison for the second level and third level. Once the pairwise comparisons have been performed, next is to calculate the PV. Using the method presented in Chapter 3.3.3, Table 3.3 shows the priority value, PV for the second and third level decision hierarchy. Before the evaluation step, the assessment value needs to be converted into its corresponding score based on its HVHD and LVHD behavior. Table 3.4 shows the conversion parameters to convert the assessment value to its corresponding score using the proposed score-based approach presented before. Once this is done, the score index, I can be calculated using equation 3.9.

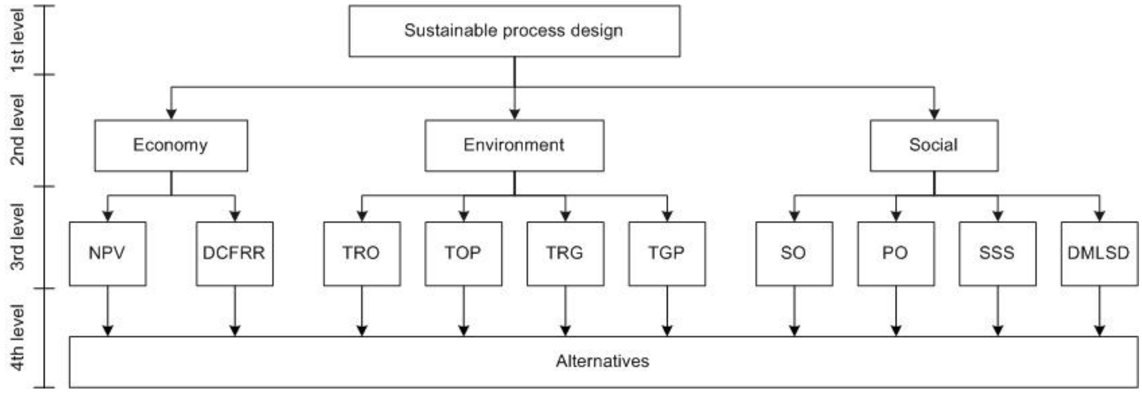


Figure 3.4: Simplified decision model.

Criteria	Indicators	Behavior	Value margin, a		Score margin, b	
			Upper, a_u	Lower, a_u	Upper, a_u	Lower, a_u
Economy	NPV	HVHD	10^6	0	10	1
	DCFRR	HVHD	100	0	10	1
Environment	TRO	LVHD	3000	0	1	10
	TOP	LVHD	3	0	1	10
	TRG	LVHD	3000	0	1	10
	TGP	LVHD	3	0	1	10
Social	SO	HVHD	10	0	10	1
	PO	HVHD	10	0	10	1
	SSS	HVHD	10	0	10	1
	DMLSD	HVHD	10	0	10	1

Table 3.4: Conversion parameters for the proposed score-based approach according to its behavior.

Figure 3.5 shows the individual score index for each criterion and also the overall result. From this figure we can see that for economic criteria Case 2 has a slight advantage over Case 1. However, for the environmental criterion, Case 1 is environmentally friendlier than Case 2. The same preference is also obtained for the social indicators. Overall, by adding the score for each individual criterion Case 1 is chosen as the most sustainable option. Through this approach, AHP were not only able to consider the quantitative differences of the indicators but, with its pairwise comparison and ranking step, it able to capture the importance of each element into the decision making process. Thus, it makes the decision more realistic in which it takes into consideration the uncertainties that influence the decision. This is by far better than the typical decision making methods mentioned early in this chapter.

3.5 Concluding remarks

AHP is mostly related to operations research and management science. However, implementing AHP in PSE is a new idea and can be useful. With sustainability in mind, selection of a process design is not straight forward. There are other factors besides economy that have to be considered and thus make the decision process more complex. With AHP, these complexities can be systematically modeled and

j	p	i	n	v		V_N		I,%	
				Case1	Case2	Case1	Case2	Case1	Case2
Econ.	0,46	NPV,$	0,6	3364	4073	0,336	0,407	12,49	15,12
	0,46	DCFRR,%	0,4	27	18	2,717	1,827	11,00	7,40
Env.	0,21	TRO	0,4	3023	4125	9,93	7,27	5,11	3,75
	0,21	TOP	0,2	2,74	3,73	10,94	8,04	2,55	1,88
	0,21	TRG	0,2	2287	3443	17,96	11,81	2,66	1,77
	0,21	TGP	0,2	2,07	3,11	7,62	11,48	2,66	1,77
Social	0,32	SO	0,47	5	3,5	4,14	6,22	8,77	6,14
	0,32	PO	0,28	5	6	5	6	4,02	4,82
	0,32	SSS	0,16	5	3	5	3	3,17	1,9
	0,32	DMLSD	0,09	10	10	10	10	1,51	1,51

Table 3.5: Assessment and selection results using AHP.

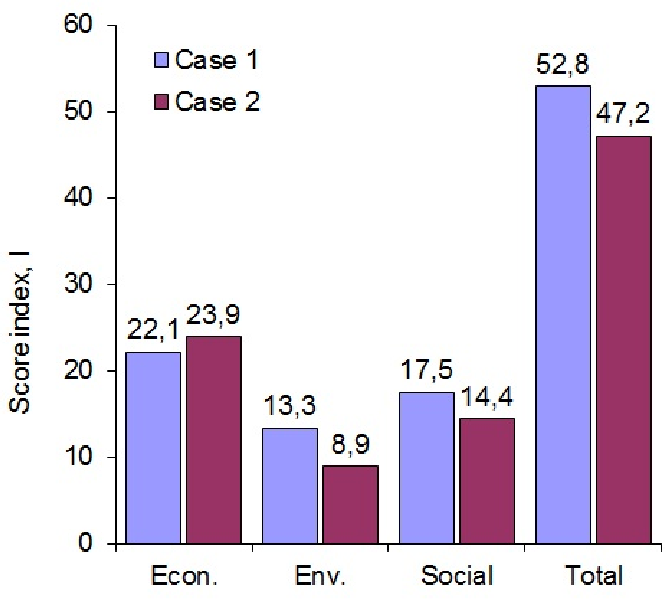


Figure 3.5: Assessment and selection result.

elucidate a meaningful result.

While the general consensus is that it is both technically valid and practically useful, the method does have its critics. One of them involves a phenomenon called rank reversal. In short, rank reversal refers to a condition when an existing ranking of alternatives will not intervene when new alternatives are added to a decision problem. In other words, that 'rank reversal' must not occur. However, this is questionable since there are examples where adding new alternatives changes the rank on the initial ones. There are two schools of thought about rank reversal. One maintains that new alternatives that introduce no additional attributes should not cause rank reversal under any circumstances. The other maintains that there are some situations in which rank reversal can reasonably be expected. Either way is useful according to the problem at hand. Other than that, AHP has the limitation on handling non-positive value which can result in inconsistent answers. Typical ways of handling this are to handle positive and negative values separately and to calculate a benefit to cost ratio. This is also known as the benefit-opportunity-cost-risk (BOCR) method. The second, which is a standard method, is by inverting negative values into positive preferences. We also proposed a new method based on a scoring system and will be explained in detail in Chapter 7.

Chapter 4

m-SAS Framework

The trend towards improving economic, environmental and social aspects of process design has attracted many researchers to develop methods to assess them. Some of the methods involve using heuristic rules [48], others were based on mathematical concepts and optimization methods i.e. mixed integer non-linear programming (MINLP) [49, 50]. Other than that, Lange [51] proposed a method that directly relates the process design alternatives to improvements in sustainability of the processes. Recently, Uerdingen et al. [52, 53] proposed an indicator-based methodology based on mass and energy indicators, which are able to identify and screen processes operating in the continuous mode. To facilitate implementation of these methods, often computational tools or process simulators are used. Such tools can help engineers handle tedious and complex problems more quickly and efficiently. With regards to design analysis, such technology is indeed beneficial. Many assessment methodologies today try to utilize computer technology to aid the assessment process. With emergence of process simulators, spreadsheets and computational software, these were made possible.

In recent years, process design sustainability analysis using state-of-the-art process simulators have emerged. Jensen et al. [22] developed a computer aided system that combined several assessment algorithms, including the Uerdingen et al. [52] method in the same computer environment. The system enables data transfer more efficient and the problem solution is less time consuming. In 2003, Chen et al. [23] developed a software called SCENE (Simultaneous Comparison of Environmental and Non-Environmental Process Criteria) which have been integrated with HYSYS using OLE (Object Linking and Embedding) programming. The tool composed of several modules that perform economic assessment, environmental analysis, process retrofit, process optimization and process decision making in one or several steps in hierarchical manner. The software can perform environmentally-conscious chemical process design and optimization in an efficient and automated fashion. In another work, Carvalho et al. [16] developed an EXCEL-based software called Sustain-Pro that facilitates retrofit generation analysis and evaluation of alternatives for sustainable process design. The methodology behind the software were based on Uerdingen et al. [52, 53] and Jensen et al. [22] with some new improvements. The most significant features are its capability to avoid the typical trade-off between competing design decisions. However, most of the work mentioned here focuses on process retrofit, process synthesis and process optimization. Few tools exist which incorporate sustainability assessment and decision making under one environment. Thus, this work is dedicated to developing a computer aided system that combines sustainability assessment and process decision making using AHP into process design selection. Hopefully, the tool could assist decision makers including engineers and managers to analyze and select sustainable initiatives in a systematic and efficient way.

4.1 m-SAS framework

A modular-Sustainability Assessment and Selection (m-SAS) framework is proposed for systematic assessment and selection of sustainable process design alternatives. Figure 4.1 shows an overview of the framework. It includes four modules which are commonly part of design stages and are systematically integrated to assist case model development, data acquisition and analysis, team contribution assessment and decision support process. It includes Process Simulator (PS) module, Equipment and Inventory Analysis (EIA) module, Sustainability Assessment (SA) module and Decision Support (DS) module. The PS module is basically a process simulator. In this work, we use Aspen Plus process simulator by Aspen Technology. The other remaining modules were developed in EXCEL spreadsheet. The main advantage of the spreadsheet is its capability of integration with other programs, i.e., Visual Basic, SQL, which is suitable for integrated task applications. Specifically for the EIA module, it fully utilizes Aspen Simulation Workbook (ASW), which can be linked directly to Aspen Plus, which made automated data transfer possible.

The EIA and SA module is located in a template file named 'Case' while DS module is developed in a separate template called 'DS Module'. The reason being is that the file 'Case' is a data inventory file developed specifically for a particular case or process design. It collects, stores and calculates all technical data or other information for a particular design. On the other hand, the 'DS Module' acts as a compilation file, where all the results in different 'Case' files will be deposited. In addition, it also includes the decision making procedure which is the pairwise comparison, ranking and evaluation step. The final result overview and its details will also be given in this file. Detailed descriptions of each module are described next.

4.1.1 Process simulator (PS) module

The first module in m-SAS is the Process Simulation (PS) module. The PS module aims to assist process modeling and simulation development by utilizing the capability of the commercial process simulator, Aspen Plus. Aspen Plus is a powerful process simulator tool that provides a flexibility to model, modify or optimize processes but at the same time keeps the data updated, accurate and consistent for further evaluation process. Furthermore, it provides reliable results with computational ease. Using process simulators saves time, especially while performing rigorous modeling as it is equipped with an advanced and easy to use graphical user interface (GUI), advanced computation techniques, comprehensive thermodynamic

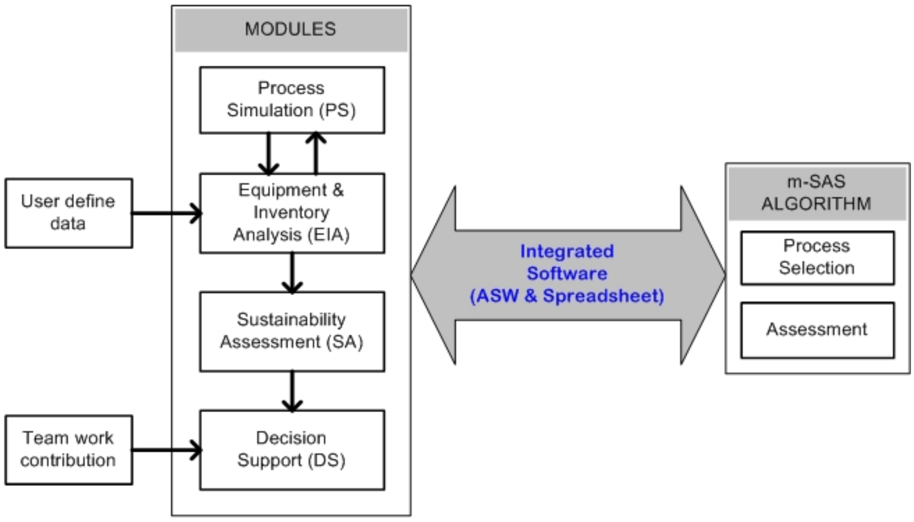


Figure 4.1: m-SAS framework.

packages and large component libraries that could provide reliable information of process design and operations.

Although far from reality, process simulators are used to mimic real processes. Basic steps to process modeling and simulation using process simulators include defining chemical components, selecting thermodynamic models and methods, designing process flowsheet by choosing proper operating units, determining plant capacity and setting up input parameters. All case models for use in this assessment are modeled using Aspen Plus.

4.1.2 Equipment and Inventory Acquisition (EIA) module

The main function of the Equipment and Inventory Acquisition (EIA) module is to acquire and deposit inventory data. It includes data concerning economic and environmental parameters, equipment design specifications, streams and operational information. This module which is developed in EXCEL is divided into two categories, namely EIA module-general and EIA module-equipment design. The former involves general information about the process including economic and environmental parameters while the latter involves detailed information of unit operations involved in the process. This module acts like inventory tables which collect or deposit essential information or parameters for performing design analysis calculations. Generally, the acquired data is obtained in two ways either by user definition or by the process simulator. For user defined data, Figure 4.2 and Figure 4.3, which is both in the EIA module general, shows the input parameter for economic and environmental assessment, respectively. Economic parameters include information about the material price, utilities price and production cost information. For the environmental parameter the user needs to define the $Score_{c,i}$ value of chemical c on some arbitrary scale for impact category i. Definition of this value is given in Chapter 2. Note that, the score for chemical involvement in energy generation is fixed. Figure 4.4 shows an example of EIA module-equipment design module for a distillation column. The parameter that needs to be defined by the user is indicated by gray colored cells with bold frames. For the distillation column example, this includes information on the purchased cost coefficients, material and bare module factors and pressure factor coefficients which can be found in most process design textbooks [11, 12, 28].

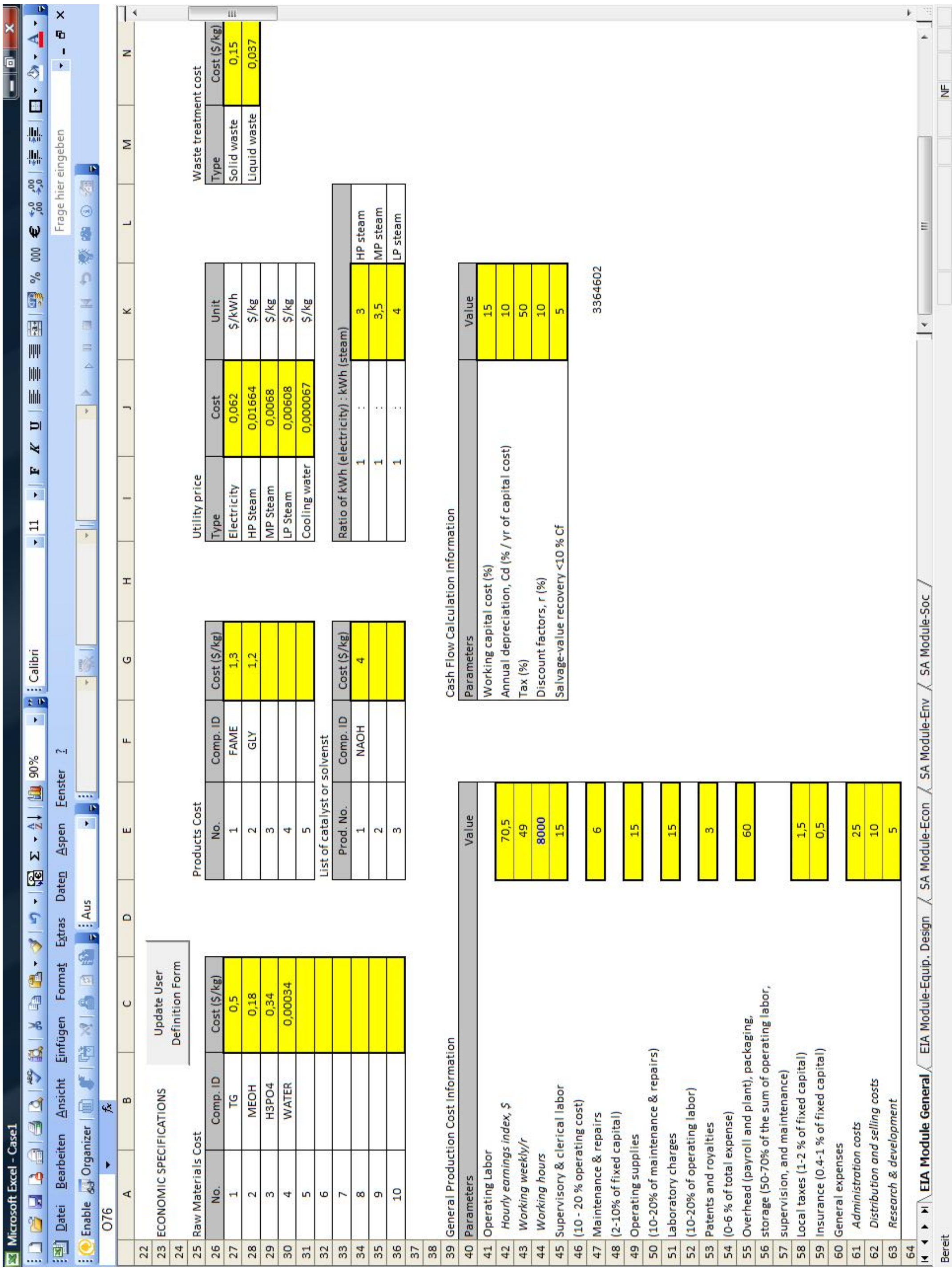
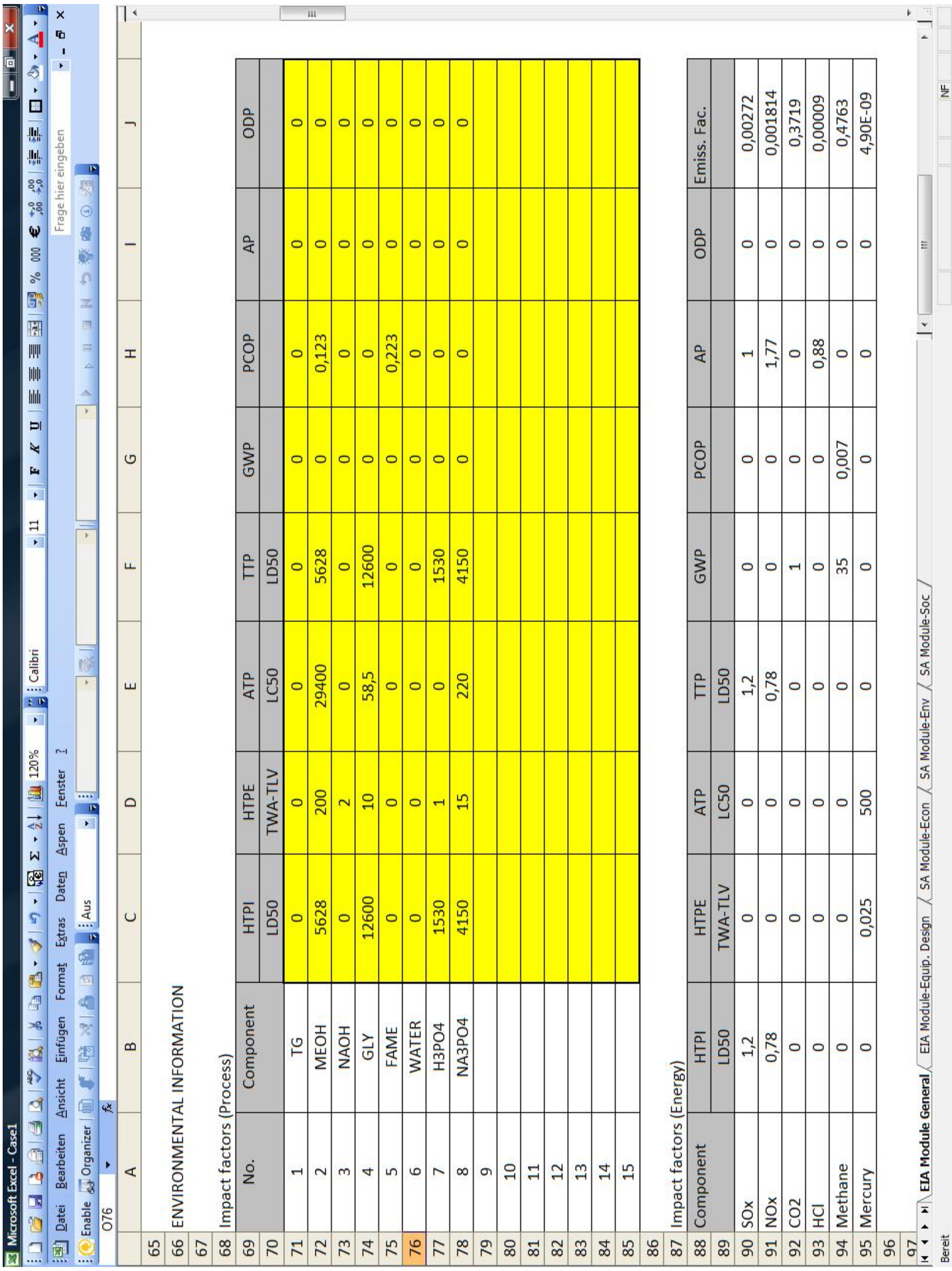


Figure 4.2: m-SAS economic parameters.



ENVIRONMENTAL INFORMATION

Impact factors (Process)

No.	Component	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP
		LD50	TWA-TLV	LC50	LD50				
1	TG	0	0	0	0	0	0	0	0
2	MEOH	5628	200	29400	5628	0	0,123	0	0
3	NAOH	0	2	0	0	0	0	0	0
4	GLY	12600	10	58,5	12600	0	0	0	0
5	FAME	0	0	0	0	0	0,223	0	0
6	WATER	0	0	0	0	0	0	0	0
7	H3PO4	1530	1	0	1530	0	0	0	0
8	NA3PO4	4150	15	220	4150	0	0	0	0
9									
10									
11									
12									
13									
14									
15									

Impact factors (Energy)

Component	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP	Emiss. Fac.
	LD50	TWA-TLV	LC50	LD50					
SOx	1,2	0	0	1,2	0	0	1	0	0,00272
NOx	0,78	0	0	0,78	0	0	1,77	0	0,001814
CO2	0	0	0	0	1	0	0	0	0,3719
HCl	0	0	0	0	0	0	0,88	0	0,00009
Methane	0	0	0	0	35	0,007	0	0	0,4763
Mercury	0	0,025	500	0	0	0	0	0	4,90E-09

Figure 4.3: m-SAS environmental parameters.

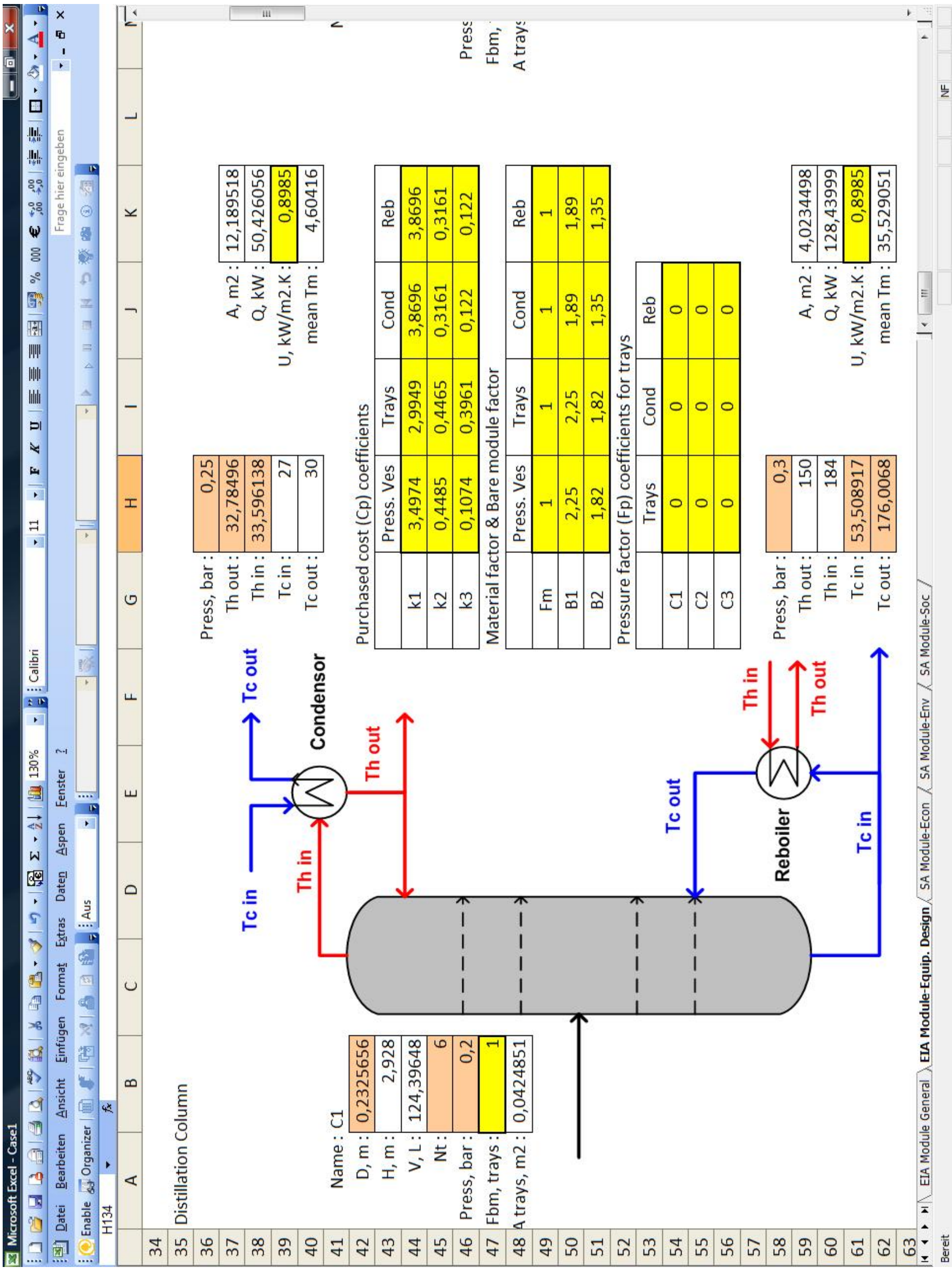


Figure 4.4: m-SAS equipment parameters.

The second way involves automated data acquisition using Aspen Simulation Workbook (ASW). ASW is a computer aided tool that enables the linking between Aspen Plus and EXCEL. Applying ASW offers a huge advantage as the interface in EXCEL allows direct communication with the Aspen Plus simulation engine that is running in the background, thus allowing an automated customized data exchange. Consequently, it enables the development of EXCEL interfaces to process models in Aspen Plus without writing VB programs enabling it to extend its application capabilities. This is a huge advantage as the interface allows direct communication with the Aspen Plus simulation engine that is running in the background, thus allowing automated customized data exchange. Through this program one can perform extra internal programming in EXCEL, such as performing economic analysis which can be combined with the model outputs for various model inputs. Other than that, the program can also be used as a bridge to link models to other tools such as optimization tools, risk analysis modeling, third party simulators and equipment design programs. Non experienced users can also benefit from this as they can use models developed by experts through the EXCEL interface. Detailed descriptions for developing an interface with ASW in EXCEL will not be discussed here. However, interested readers can refer to Aspen Technology documentation for further details. Figure 4.5 shows the general workflow for developing an interface. According to Aspen Technology, ASW adds new functions and macros to EXCEL that enable to:

- Activate models
- Make models visible
- Run models
- Update plant data
- Synchronize models with tags
- Display current simulation status (converged, input changed)

The automation features also allow to further automate, for example to:

- Add buttons to run the model, etc
- Display information about the model in cells
- Write VB programs to automate workflow

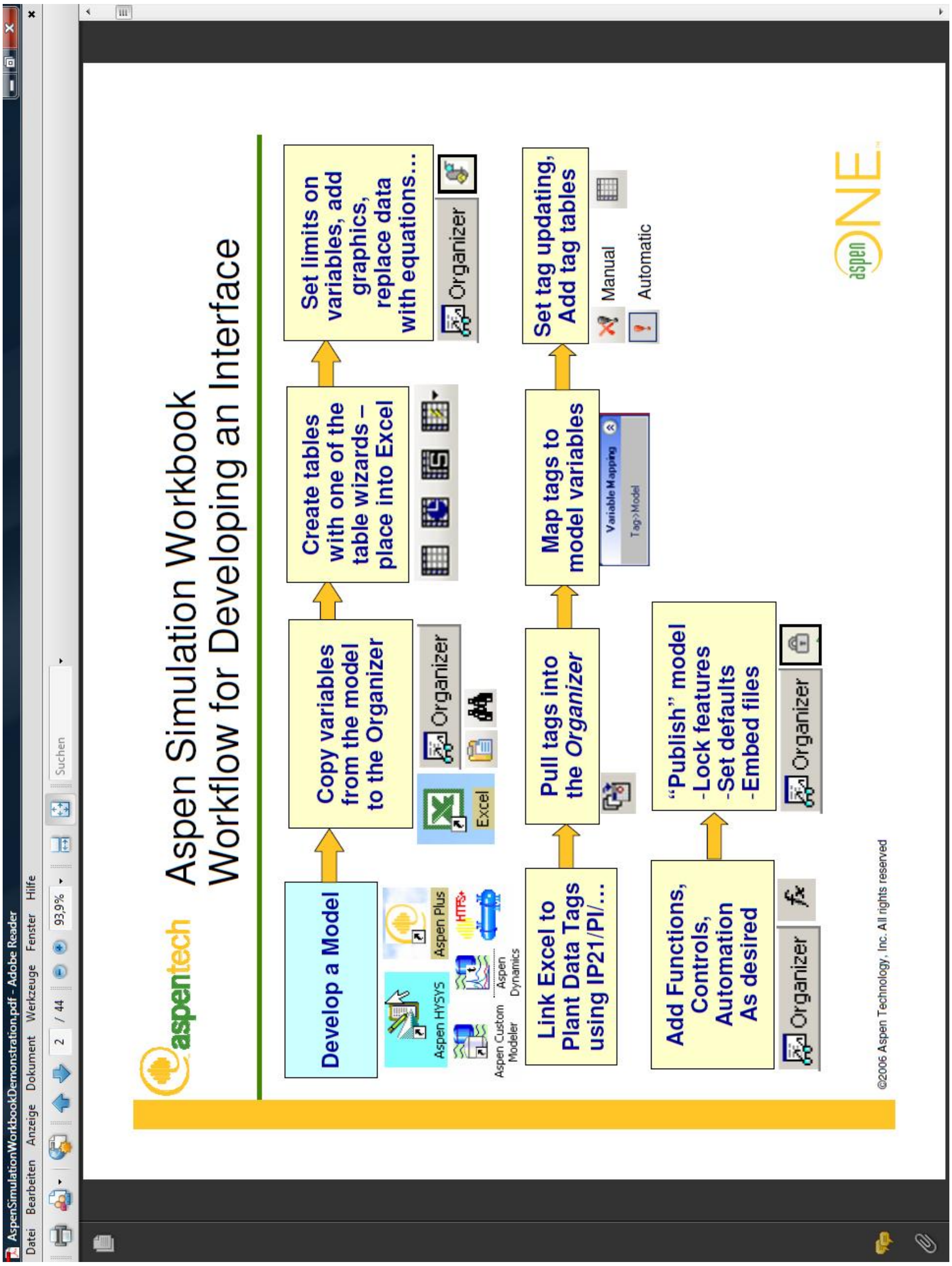
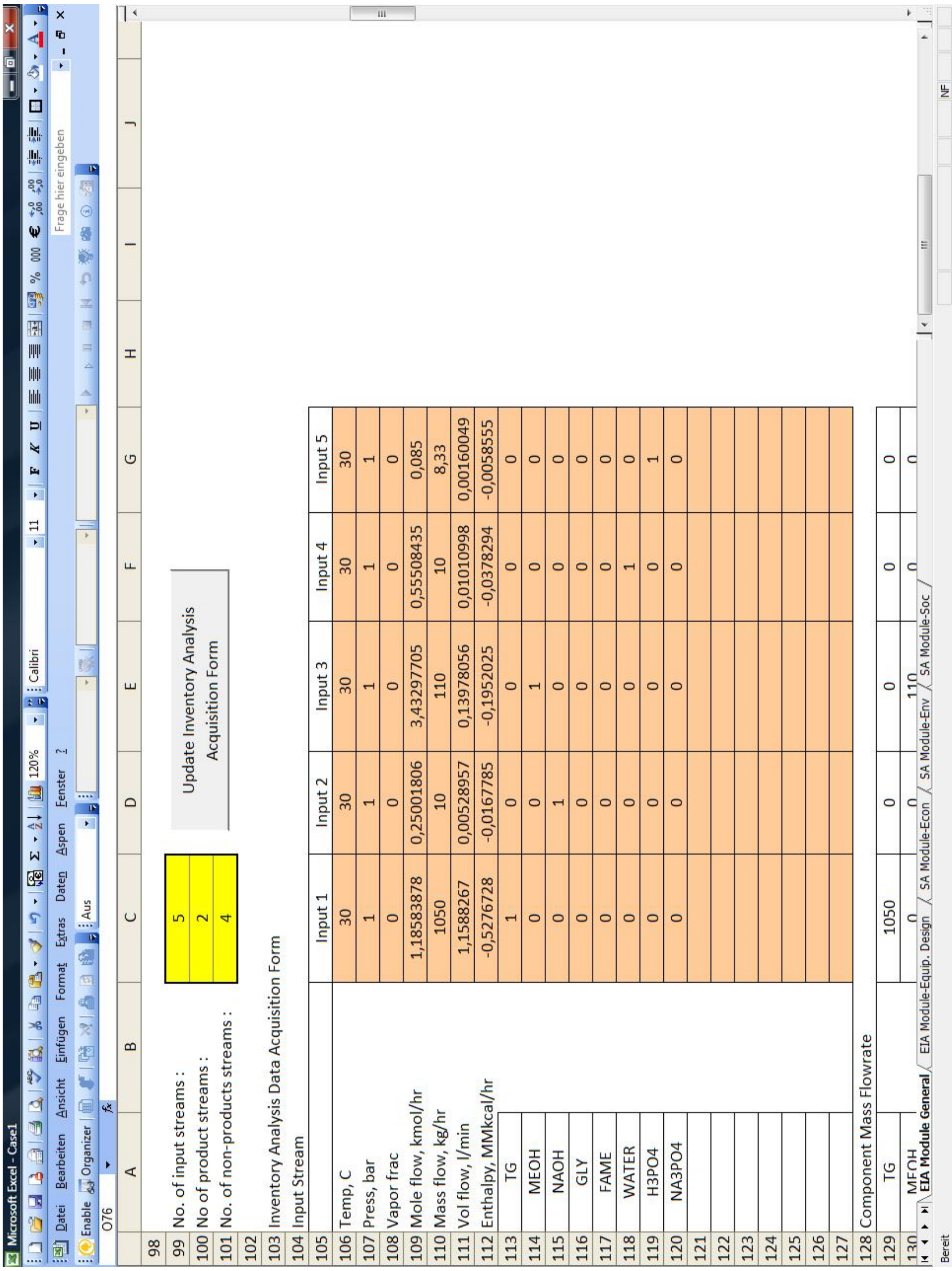


Figure 4.5: ASW workflow overview for developing an interface [7].

These functions are really useful, especially when it involves data exchange, usually for process optimization or process assessment. In the m-SAS system such functions are fully utilized. Specific variables from process models in Aspen Plus are linked with specific inventory cells in EXCEL. Figure 4.6 shows an example of an inventory table for the input stream of a process model. It includes information such as stream temperature and pressure, vapor fraction, mole and mass flow, volume flowrate, enthalpy and mass fraction. Tables for product and non-product (waste) streams are also available in the module. Inventory data for utilities are shown in Figure 4.7. The inventory table is divided into three categories which hold information on utilities needed by column, heat exchangers and pumps such as heat duty, utility type, utility price, etc. Using ASW, any modification altered to the process model automatically updates the value in the corresponding cells. All the inventory information is then summarized as shown in Figure 4.8.



	Input 1	Input 2	Input 3	Input 4	Input 5
Temp, C	30	30	30	30	30
Press, bar	1	1	1	1	1
Vapor frac	0	0	0	0	0
Mole flow, kmol/hr	1,18583878	0,25001806	3,43297705	0,55508435	0,085
Mass flow, kg/hr	1050	10	110	10	8,33
Vol flow, l/min	1,1588267	0,00528957	0,13978056	0,01010998	0,00160049
Enthalpy, MMkcal/hr	-0,5276728	-0,0167785	-0,1952025	-0,0378294	-0,0058555
TG	1	0	0	0	0
MEOH	0	0	1	0	0
NAOH	0	1	0	0	0
GLY	0	0	0	0	0
FAME	0	0	0	0	0
WATER	0	0	0	1	0
H3PO4	0	0	0	0	1
NA3PO4	0	0	0	0	0

Component Mass Flowrate					
TG	1050	0	0	0	0
MEOH	0	0	110	0	0

Figure 4.6: Example of input stream inventory table linked with Aspen Plus model using ASW.

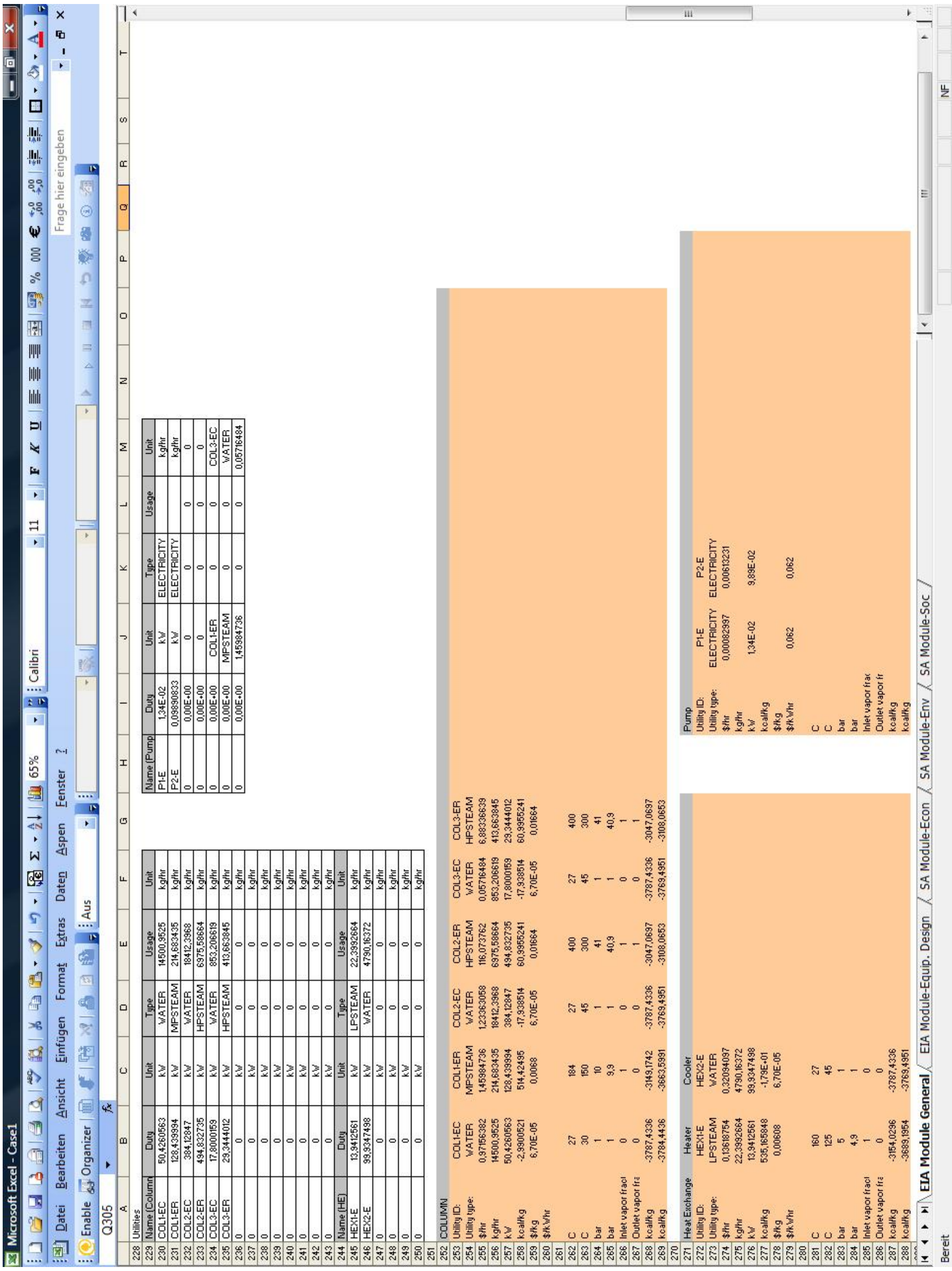
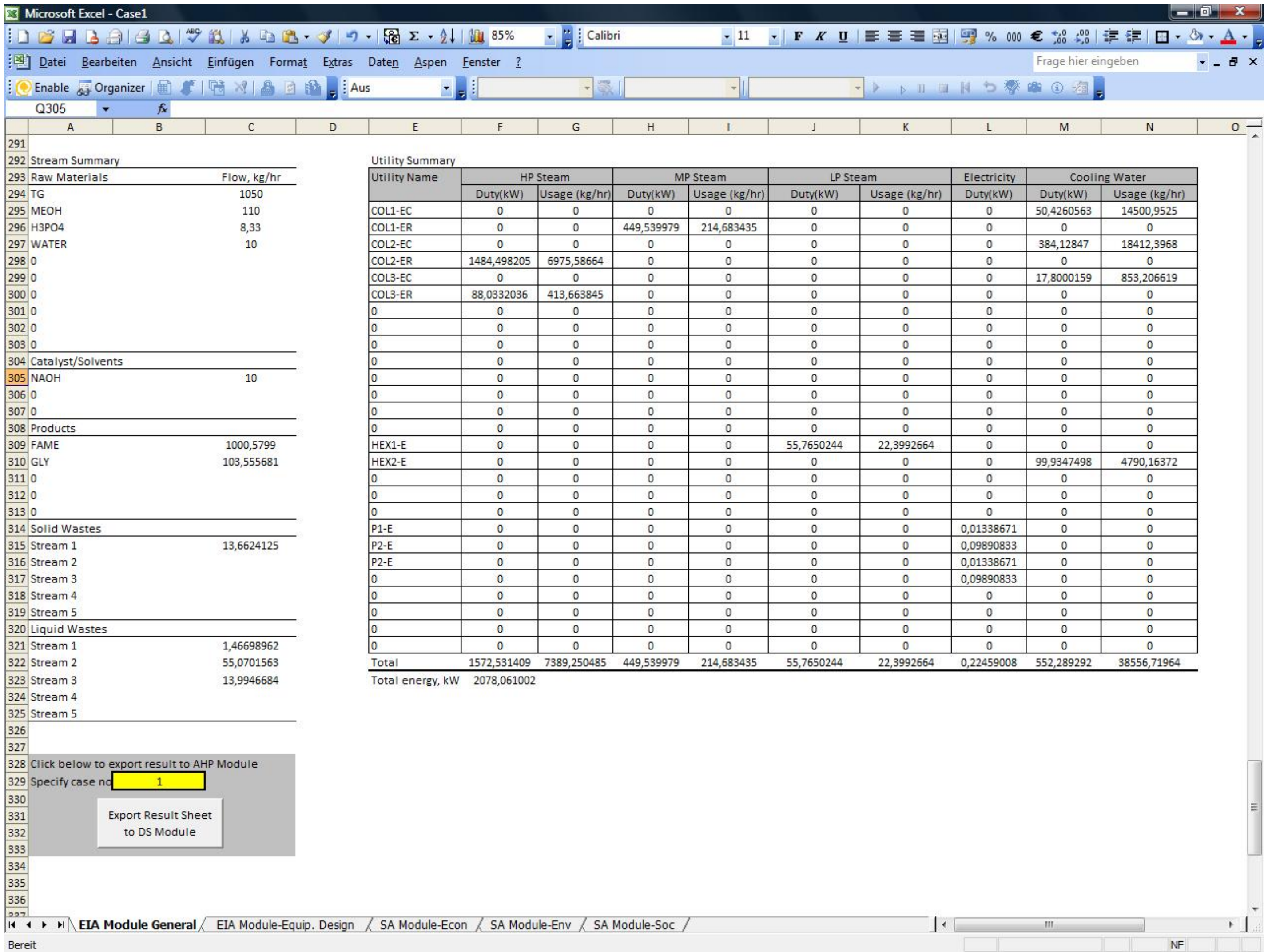


Figure 4.7: Example of utilities inventory table linked with Aspen Plus model using ASW.



Stream Summary	
Raw Materials	Flow, kg/hr
TG	1050
MEOH	110
H3PO4	8,33
WATER	10
0	
0	
0	
0	
0	
0	
Catalyst/Solvents	
NAOH	10
0	
0	
Products	
FAME	1000,5799
GLY	103,555681
0	
0	
0	
Solid Wastes	
Stream 1	13,6624125
Stream 2	
Stream 3	
Stream 4	
Stream 5	
Liquid Wastes	
Stream 1	1,46698962
Stream 2	55,0701563
Stream 3	13,9946684
Stream 4	
Stream 5	

Utility Summary

Utility Name	HP Steam		MP Steam		LP Steam		Electricity	Cooling Water	
	Duty(kW)	Usage (kg/hr)	Duty(kW)	Usage (kg/hr)	Duty(kW)	Usage (kg/hr)	Duty(kW)	Duty(kW)	Usage (kg/hr)
COL1-EC	0	0	0	0	0	0	0	50,4260563	14500,9525
COL1-ER	0	0	449,539979	214,683435	0	0	0	0	0
COL2-EC	0	0	0	0	0	0	0	384,12847	18412,3968
COL2-ER	1484,498205	6975,58664	0	0	0	0	0	0	0
COL3-EC	0	0	0	0	0	0	0	17,8000159	853,206619
COL3-ER	88,0332036	413,663845	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
HEX1-E	0	0	0	0	55,7650244	22,3992664	0	0	0
HEX2-E	0	0	0	0	0	0	0	99,9347498	4790,16372
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
P1-E	0	0	0	0	0	0	0,01338671	0	0
P2-E	0	0	0	0	0	0	0,09890833	0	0
P2-E	0	0	0	0	0	0	0,01338671	0	0
0	0	0	0	0	0	0	0,09890833	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
Total	1572,531409	7389,250485	449,539979	214,683435	55,7650244	22,3992664	0,22459008	552,289292	38556,71964
Total energy, kW	2078,061002								

Figure 4.8: Summary of stream and utilities inventory data.

4.1.3 Sustainability Assessment (SA) module

The Sustainability Assessment (SA) module is designed to calculate the hard indicators using the inventory data deposited in the EIA module specifically in the EIA-general sheet and EIA-equipment design sheet. All the equations involved in calculating the economic and environmental indicators were placed in two separate sheets, namely SA Module-economy and SA module environment. Separating the EIA module and SA module, and developing it as a standalone, allows a rapid calculation despite any data changes in the EIA module, thus aiding users to focus on the real issues in process design development. Clip shots from both modules are shown in Figure 4.9 and 4.10. Other than that, this module also includes the scaled-based social related indicator assessment as shown in Figure 4.11. Since these criteria involves qualitative assessment, the user needs to insert the score based on the given scale to assess the process design. It also includes a column to describe the assessor's justification to the given score.

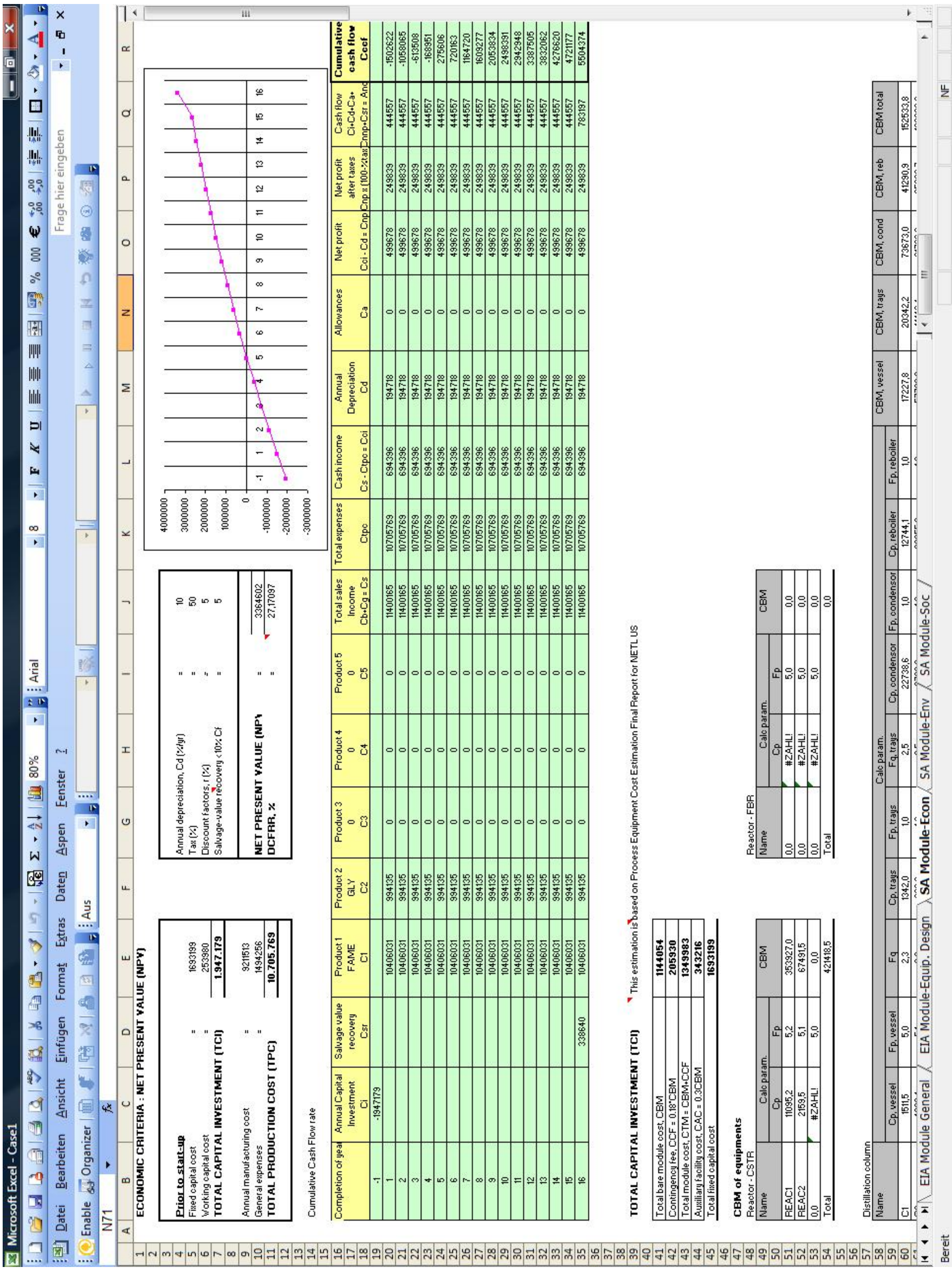


Figure 4.9: SA module for economic assessment.

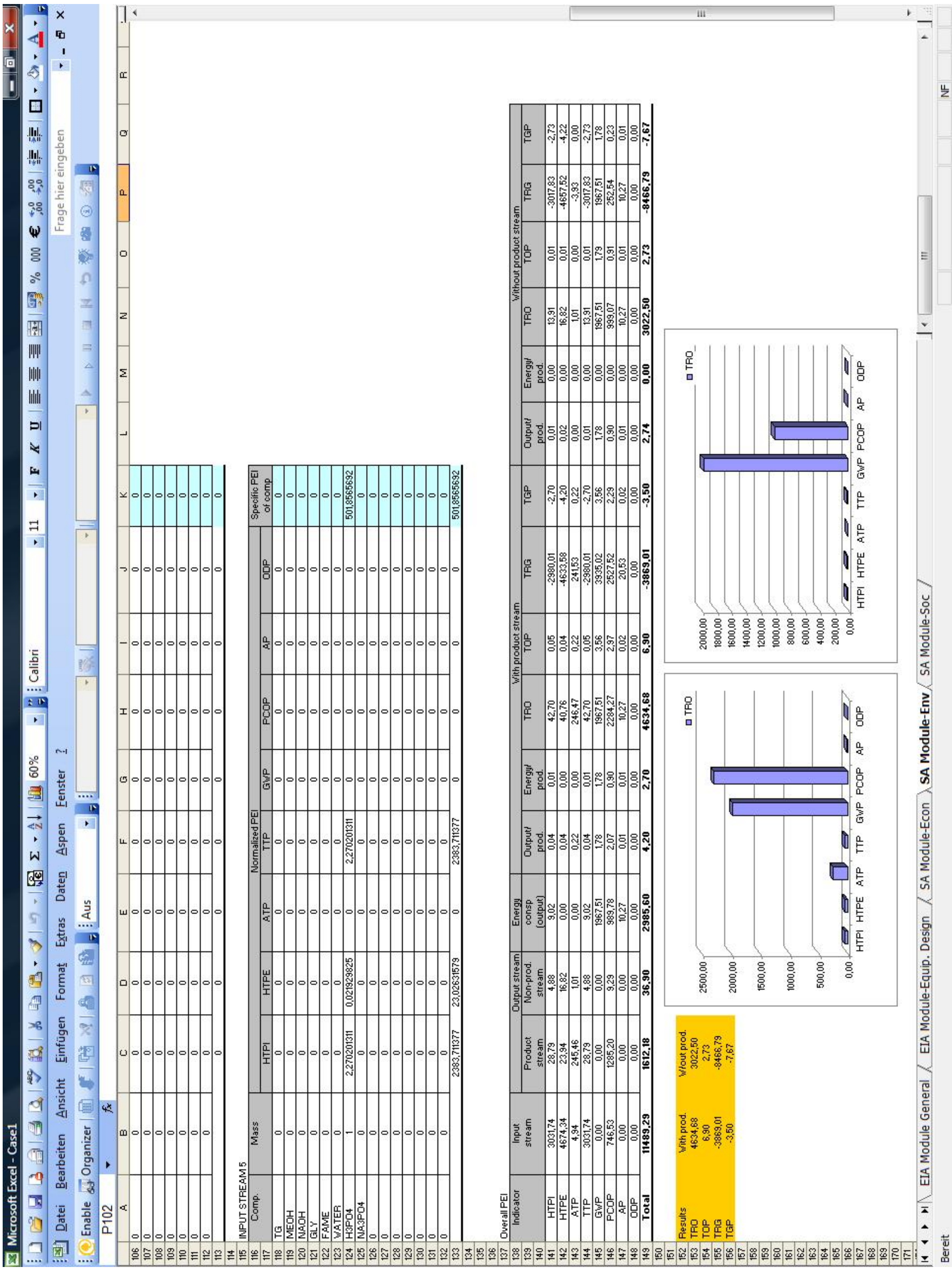


Figure 4.10: SA module for environmental assessment.

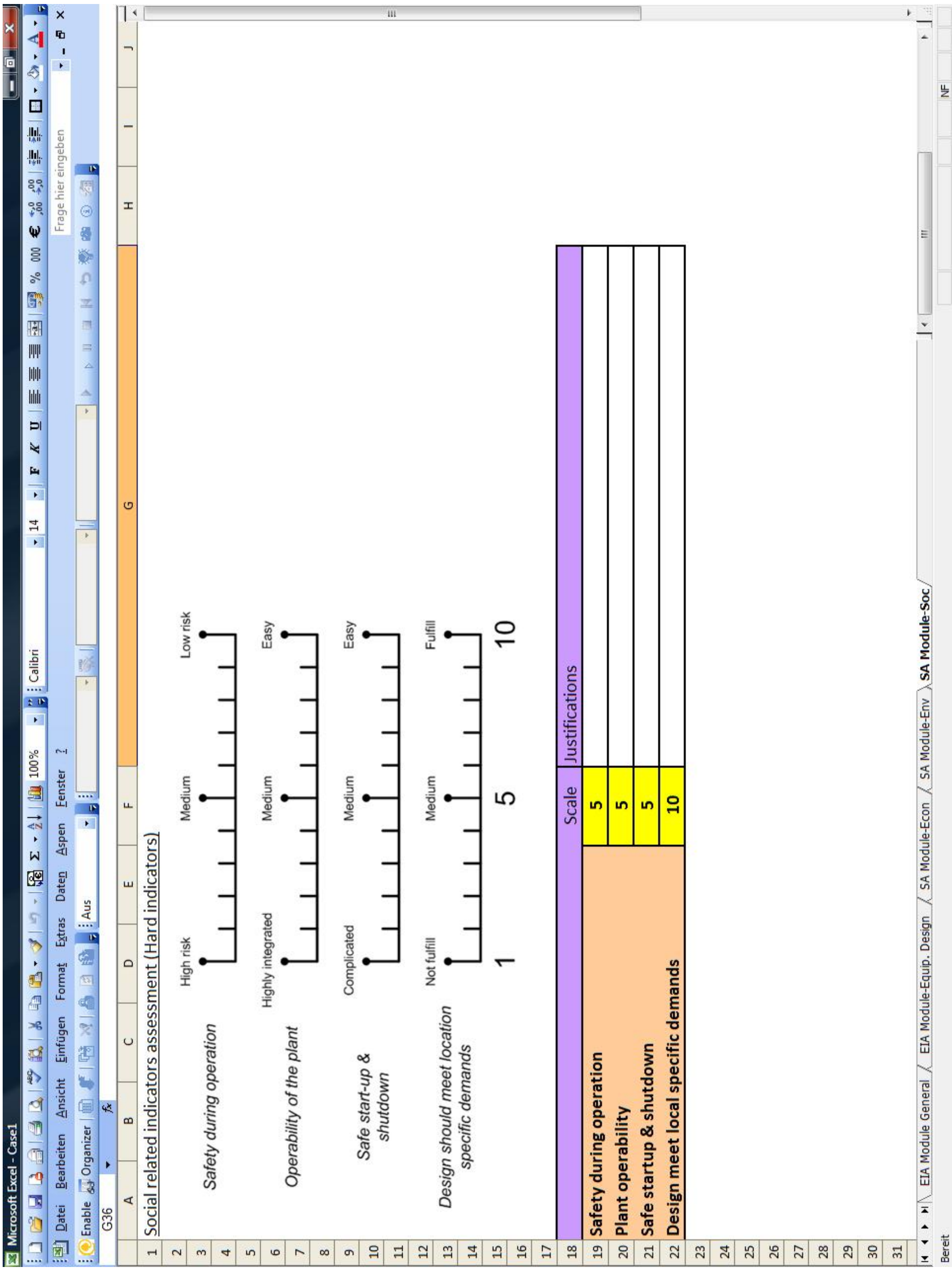


Figure 4.11: SA module - social related indicators assessment.

4.1.4 Decision support (DS) module

The Decision Support (DS) module is developed to support team contributions in decision making. This module serves several functions. The first is to assist decision makers in setting the decision weights. As shown in Figure 4.12, the users need to provide the weights in the corresponding cell for each decision matrix. The eigenvector value or priority value is then calculated automatically. Secondly, the DS module integrates the results from the 'Case' file which consists of the EIA and SA modules. This is done in the 'Case' file by clicking the 'Export Result Sheet to DS Module' button located in the bottom left in Figure 4.8. Clicking this button will transfer all the economy and environmental results to the 'DS Module' in a separate sheet as shown in Figure 4.13. All the relevant results are then linked to a specific cell in the 'DS Module' sheet. Here as shown in Figure 4.14 it calculates the assessment score, V and its normalized score, V^N, provided that the decision makers define the scaling margin of each level. Once the normalized value is obtained, it calculate the final score index, I for each criteria. All the results are shown in a separate spreadsheet table called 'Result Summary'. For example, Figure 4.15 shows the overall and economic performance of each case in a bar diagram. Such illustration could facilitate decision makers in visualizing the performance of each case.

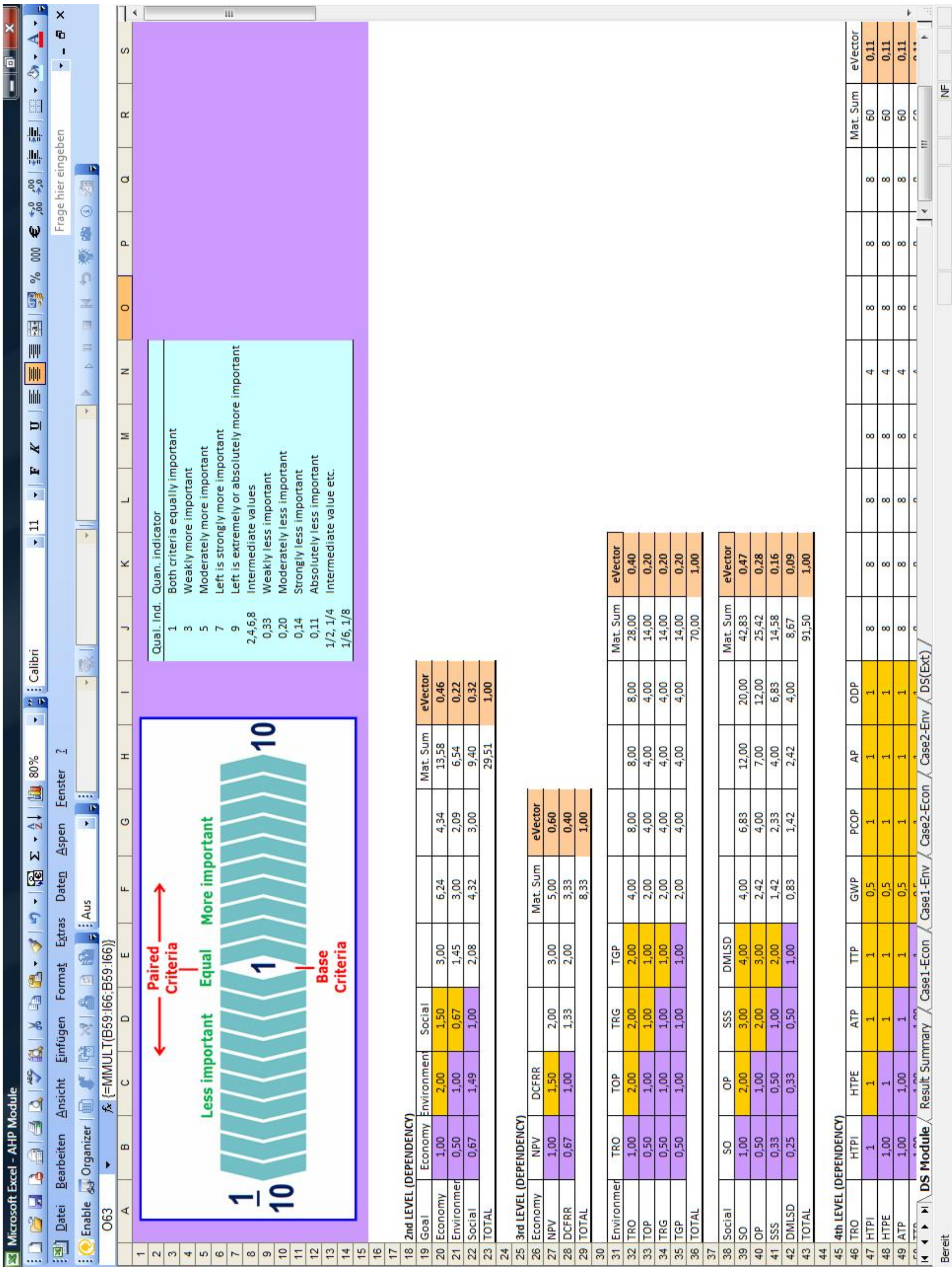
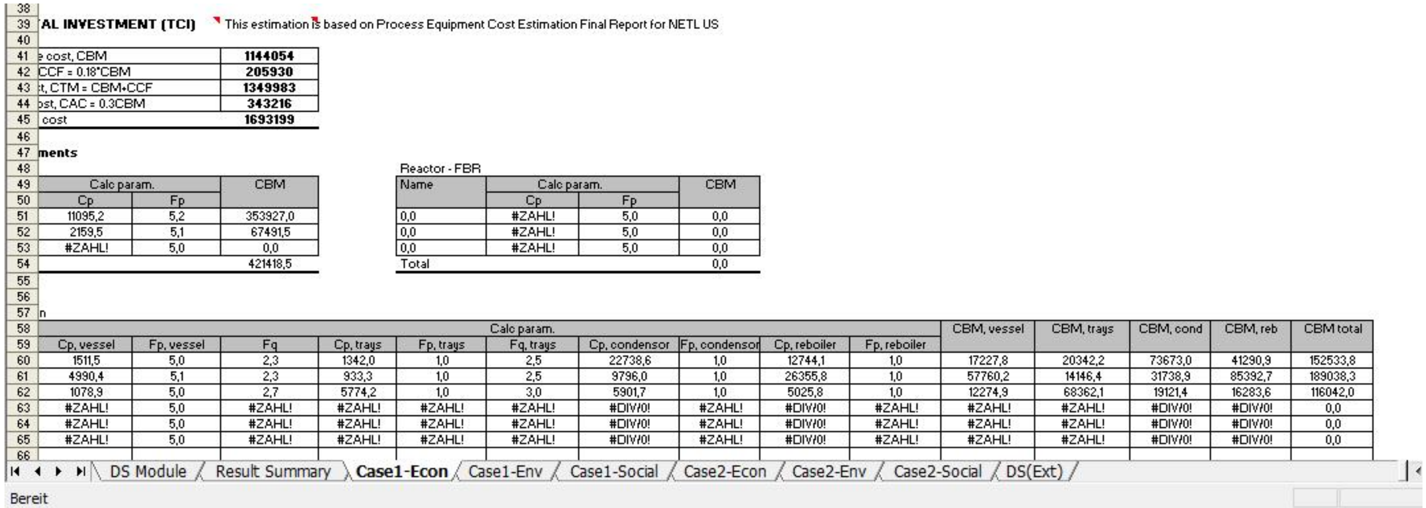


Figure 4.12: DS module - weights setting.



38		
39	AL INVESTMENT (TCI)	This estimation is based on Process Equipment Cost Estimation Final Report for NETL US
40		
41	e cost, CBM	1144054
42	CCF = 0.18*CBM	205930
43	t, CTM = CBM+CCF	1349983
44	ost, CAC = 0.3CBM	343216
45	cost	1693199
46		
47	ments	

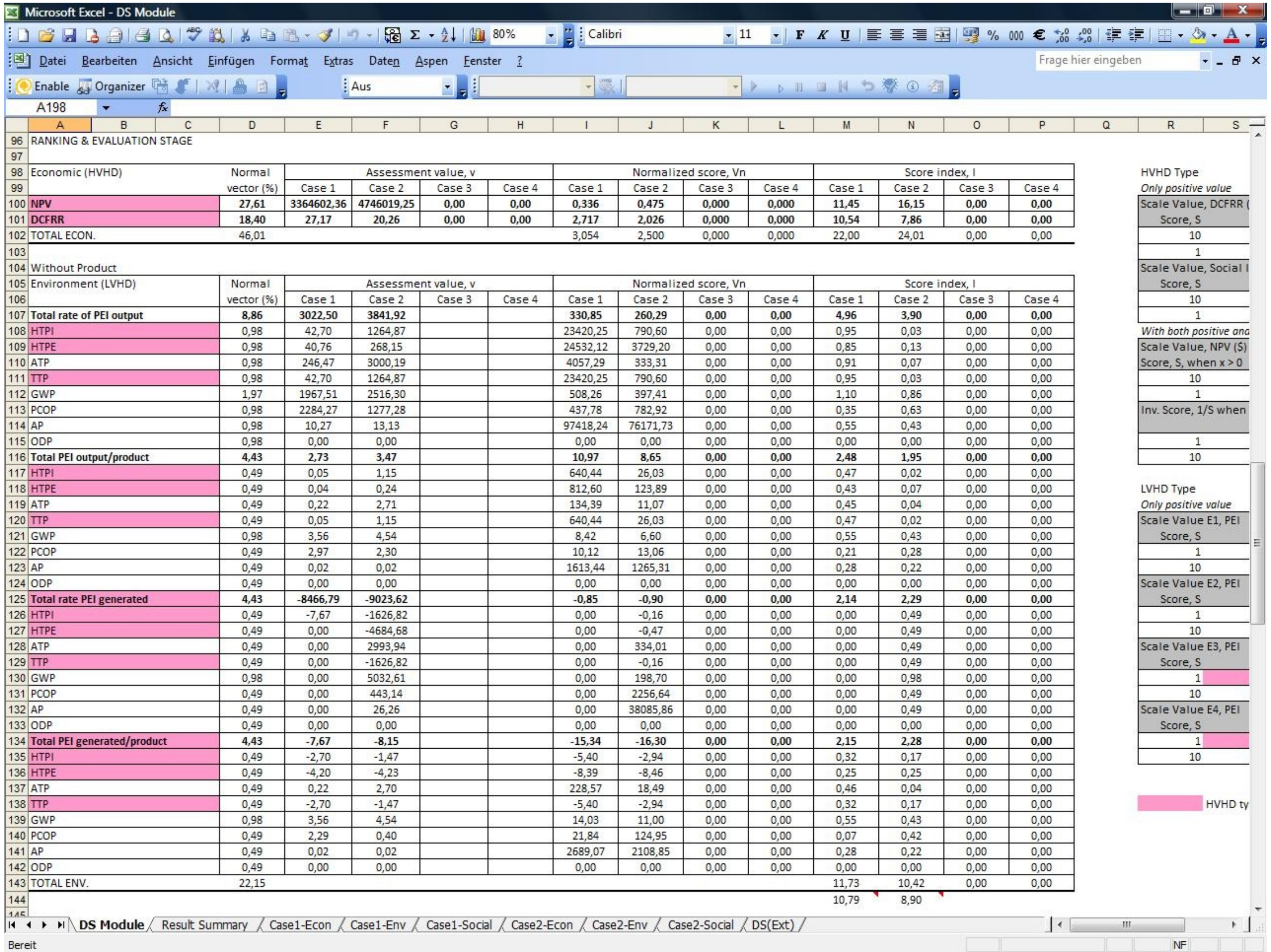
Row	Calc param. Cp	Calc param. Fp	CBM
51	11095,2	5,2	353927,0
52	2159,5	5,1	67491,5
53	#ZAHL!	5,0	0,0
54			421418,5

Reactor - FBR

Name	Calc param. Cp	Calc param. Fp	CBM
0,0	#ZAHL!	5,0	0,0
0,0	#ZAHL!	5,0	0,0
0,0	#ZAHL!	5,0	0,0
Total			0,0

Row	Cp, vessel	Fp, vessel	Fq	Cp, trays	Fp, trays	Fq, trays	Cp, condensor	Fp, condensor	Cp, reboiler	Fp, reboiler	CBM, vessel	CBM, trays	CBM, cond	CBM, reb	CBM total
60	1511,5	5,0	2,3	1342,0	1,0	2,5	22738,6	1,0	12744,1	1,0	17227,8	20342,2	73673,0	41290,9	152533,8
61	4990,4	5,1	2,3	933,3	1,0	2,5	9796,0	1,0	26355,8	1,0	57760,2	14146,4	31738,9	85392,7	189038,3
62	1078,9	5,0	2,7	5774,2	1,0	3,0	5901,7	1,0	5025,8	1,0	12274,9	68362,1	19121,4	16283,6	116042,0
63	#ZAHL!	5,0	#ZAHL!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#ZAHL!	#DIV/0!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#DIV/0!	0,0
64	#ZAHL!	5,0	#ZAHL!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#ZAHL!	#DIV/0!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#DIV/0!	0,0
65	#ZAHL!	5,0	#ZAHL!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#ZAHL!	#DIV/0!	#ZAHL!	#ZAHL!	#ZAHL!	#DIV/0!	#DIV/0!	0,0

Figure 4.13: Example of spreadsheet table created containing the sustainability assessment results of each cases.



Row	A–C	D	E	F	G	H	I	J	K	L	M	N	O	P	R
96	RANKING & EVALUATION STAGE														
97															
98	Economic (HVHD)	Normal	Assessment value, v				Normalized score, Vn				Score index, I				HVHD Type
99		vector (%)	Case 1	Case 2	Case 3	Case 4	Case 1	Case 2	Case 3	Case 4	Case 1	Case 2	Case 3	Case 4	Only positive value
100	NPV	27,61	3364602,36	4746019,25	0,00	0,00	0,336	0,475	0,000	0,000	11,45	16,15	0,00	0,00	Scale Value, DCFRR (
101	DCFRR	18,40	27,17	20,26	0,00	0,00	2,717	2,026	0,000	0,000	10,54	7,86	0,00	0,00	Score, S
102	TOTAL ECON.	46,01					3,054	2,500	0,000	0,000	22,00	24,01	0,00	0,00	10
103															1
104	Without Product														Scale Value, Social I
105	Environment (LVHD)	Normal	Assessment value, v				Normalized score, Vn				Score index, I				Score, S
106		vector (%)	Case 1	Case 2	Case 3	Case 4	Case 1	Case 2	Case 3	Case 4	Case 1	Case 2	Case 3	Case 4	10
107	Total rate of PEI output	8,86	3022,50	3841,92			330,85	260,29	0,00	0,00	4,96	3,90	0,00	0,00	1
108	HTPI	0,98	42,70	1264,87			23420,25	790,60	0,00	0,00	0,95	0,03	0,00	0,00	With both positive and
109	HTPE	0,98	40,76	268,15			24532,12	3729,20	0,00	0,00	0,85	0,13	0,00	0,00	Scale Value, NPV ($)
110	ATP	0,98	246,47	3000,19			4057,29	333,31	0,00	0,00	0,91	0,07	0,00	0,00	Score, S, when x > 0
111	TTP	0,98	42,70	1264,87			23420,25	790,60	0,00	0,00	0,95	0,03	0,00	0,00	10
112	GWP	1,97	1967,51	2516,30			508,26	397,41	0,00	0,00	1,10	0,86	0,00	0,00	1
113	PCOP	0,98	2284,27	1277,28			437,78	782,92	0,00	0,00	0,35	0,63	0,00	0,00	Inv. Score, 1/S when
114	AP	0,98	10,27	13,13			97418,24	76171,73	0,00	0,00	0,55	0,43	0,00	0,00	
115	ODP	0,98	0,00	0,00			0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1
116	Total PEI output/product	4,43	2,73	3,47			10,97	8,65	0,00	0,00	2,48	1,95	0,00	0,00	10
117	HTPI	0,49	0,05	1,15			640,44	26,03	0,00	0,00	0,47	0,02	0,00	0,00	
118	HTPE	0,49	0,04	0,24			812,60	123,89	0,00	0,00	0,43	0,07	0,00	0,00	LVHD Type
119	ATP	0,49	0,22	2,71			134,39	11,07	0,00	0,00	0,45	0,04	0,00	0,00	Only positive value
120	TTP	0,49	0,05	1,15			640,44	26,03	0,00	0,00	0,47	0,02	0,00	0,00	Scale Value E1, PEI
121	GWP	0,98	3,56	4,54			8,42	6,60	0,00	0,00	0,55	0,43	0,00	0,00	Score, S
122	PCOP	0,49	2,97	2,30			10,12	13,06	0,00	0,00	0,21	0,28	0,00	0,00	1
123	AP	0,49	0,02	0,02			1613,44	1265,31	0,00	0,00	0,28	0,22	0,00	0,00	10
124	ODP	0,49	0,00	0,00			0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	Scale Value E2, PEI
125	Total rate PEI generated	4,43	-8466,79	-9023,62			-0,85	-0,90	0,00	0,00	2,14	2,29	0,00	0,00	Score, S
126	HTPI	0,49	-7,67	-1626,82			0,00	-0,16	0,00	0,00	0,00	0,49	0,00	0,00	1
127	HTPE	0,49	0,00	-4684,68			0,00	-0,47	0,00	0,00	0,00	0,49	0,00	0,00	10
128	ATP	0,49	0,00	2993,94			0,00	334,01	0,00	0,00	0,00	0,49	0,00	0,00	Scale Value E3, PEI
129	TTP	0,49	0,00	-1626,82			0,00	-0,16	0,00	0,00	0,00	0,49	0,00	0,00	Score, S
130	GWP	0,98	0,00	5032,61			0,00	198,70	0,00	0,00	0,00	0,98	0,00	0,00	1
131	PCOP	0,49	0,00	443,14			0,00	2256,64	0,00	0,00	0,00	0,49	0,00	0,00	10
132	AP	0,49	0,00	26,26			0,00	38085,86	0,00	0,00	0,00	0,49	0,00	0,00	Scale Value E4, PEI
133	ODP	0,49	0,00	0,00			0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	Score, S
134	Total PEI generated/product	4,43	-7,67	-8,15			-15,34	-16,30	0,00	0,00	2,15	2,28	0,00	0,00	1
135	HTPI	0,49	-2,70	-1,47			-5,40	-2,94	0,00	0,00	0,32	0,17	0,00	0,00	10
136	HTPE	0,49	-4,20	-4,23			-8,39	-8,46	0,00	0,00	0,25	0,25	0,00	0,00	
137	ATP	0,49	0,22	2,70			228,57	18,49	0,00	0,00	0,46	0,04	0,00	0,00	
138	TTP	0,49	-2,70	-1,47			-5,40	-2,94	0,00	0,00	0,32	0,17	0,00	0,00	HVHD ty
139	GWP	0,98	3,56	4,54			14,03	11,00	0,00	0,00	0,55	0,43	0,00	0,00	
140	PCOP	0,49	2,29	0,40			21,84	124,95	0,00	0,00	0,07	0,42	0,00	0,00	
141	AP	0,49	0,02	0,02			2689,07	2108,85	0,00	0,00	0,28	0,22	0,00	0,00	
142	ODP	0,49	0,00	0,00			0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	
143	TOTAL ENV.	22,15									11,73	10,42	0,00	0,00	
144											10,79	8,90			

Figure 4.14: DS module - AHP score calculation.

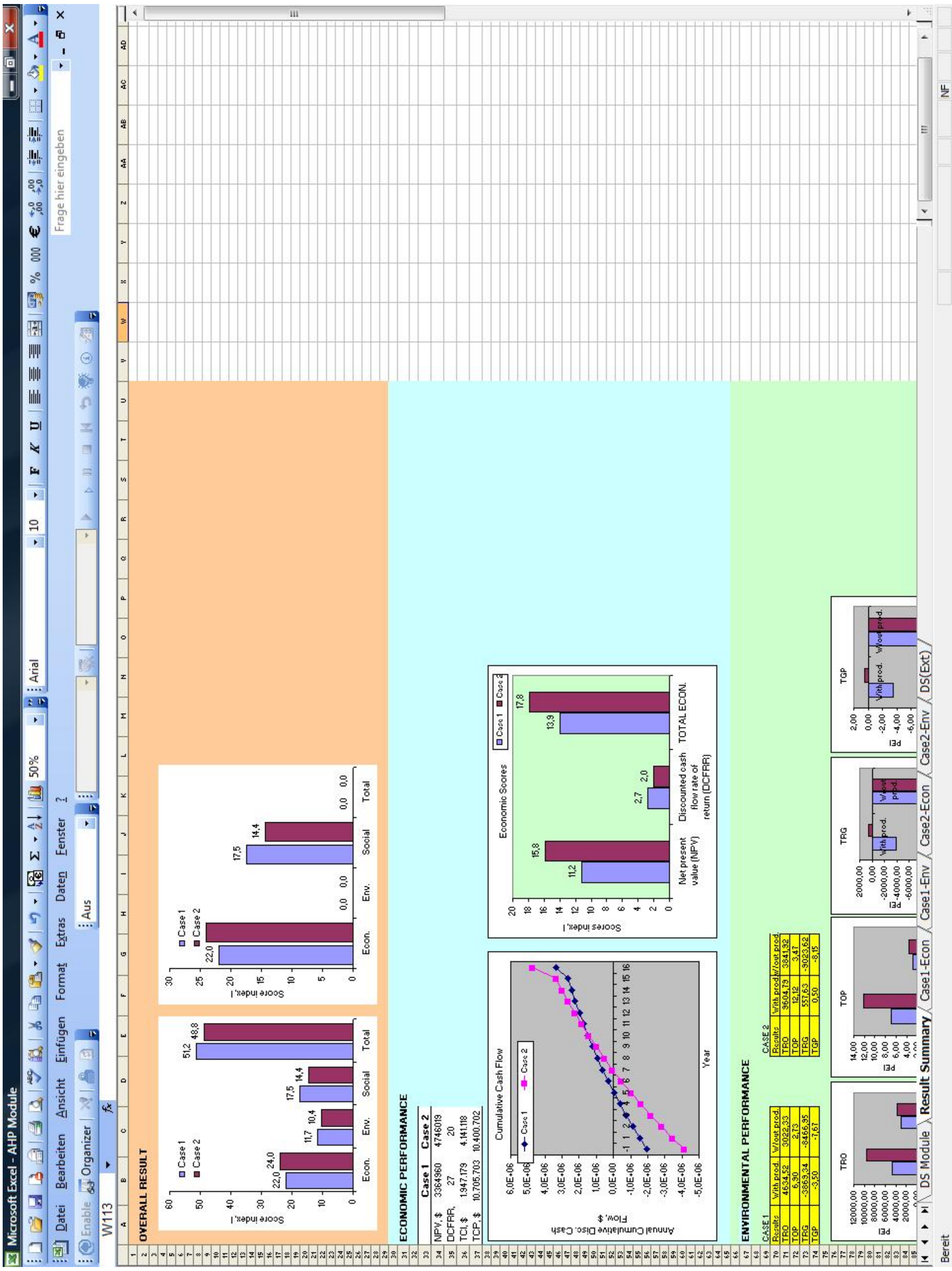


Figure 4.15: DS module - result summary.

4.2 m-SAS algorithm

The m-SAS algorithm is shown in Figure 4.16. The left hand side shows the flow diagram, while the right explains the details on how to execute a specific task block. It starts with a definition of the problem by providing a design flowsheet and the information on product type and quality. The production scale or the problem could also assess the feasibility of any intensification or modification on the existing design flowsheet. Once the problem is defined, the next step is to model each identified flowsheet in Aspen Plus. The modeling includes the definition of chemical components, the selection of thermodynamic models and methods, the flowsheet design setting and process specifications and the input parameters setting. Once modeling is completed, a process flowsheet is selected, and equipment and inventory acquisition are performed with the assistance of the EIA module. The user defined data, which includes the economic parameters and the component-specific potential environment impact, is provided by the users whereas simulation data is acquired using ASW. These data are then analyzed by the SA module to calculate the hard indicators, such as NPV, DCFRR and the four environmental indicators. This step is repeated for all modeled flowsheets. The next step involves group participation. A good blend of a decision group should involve members within the organization and also external partners, e.g., investors, top managers, engineers, technicians and government officers so that a holistic and in-depth evaluation can be conducted. Once the group is formed, it needs to assign weights to each level and its indicators. They are then grouped accordingly, based on their expertise, to either a single or combination of social indicators. With provided information concerning the design, they perform a thorough discussion to finally set the scores to the designated social indicators assigned to each specific group. Once the results are obtained, they are inserted into the DS module for elicitation of the final ranking and selection solution.

4.3 Concluding remarks

This chapter presents a modular based sustainability assessment and decision making tool called m-SAS (modular-Sustainability Assessment and Selection). The tool consists of four modules, namely the Process Simulator (PS) module, Equipment and Inventory Assessment (EIA) module, Sustainability Assessment (SA) module and Decision Support (DS) module. Its development fully utilizes the capability of the process simulator, Aspen Plus and Aspen Simulation Workbook (ASW), and the EXCEL spreadsheet that systematically integrates case model development, data acquisition and analysis, team contribution assessment and decision support process. The aim of m-SAS is to assist engineers and managers to systematically assessed sustainability performance of a design and also aiding them in performing process decision making for selection of a sustainable design option. To test the functionality of the tool, two potential biodiesel process designs will be used as case studies. The goal is to perform sustainability assessments on both cases and select the one that meets the sustainability criteria. Details will be given in the next chapter.

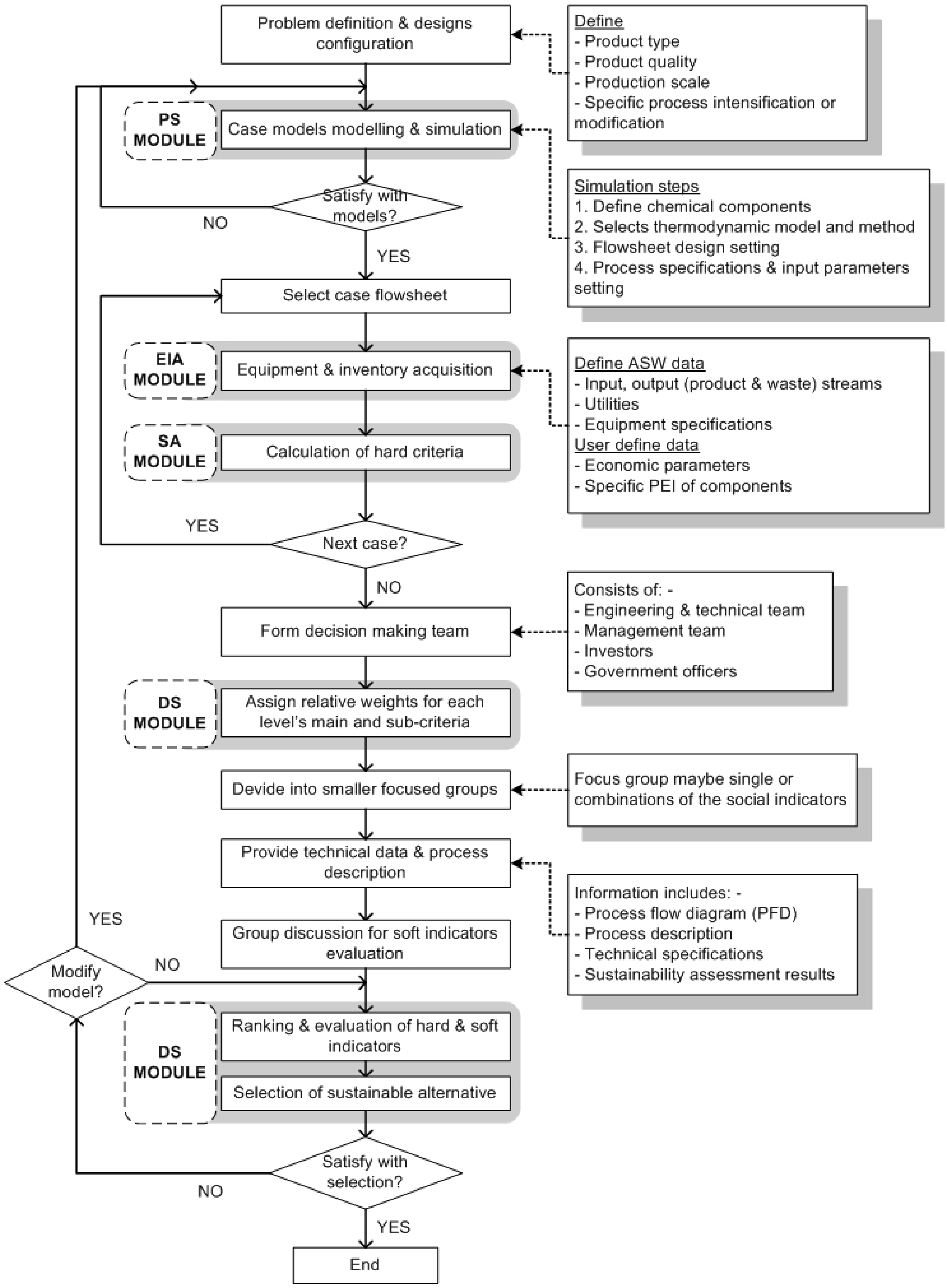


Figure 4.16: Flowchart of the m-SAS algorithm.

Chapter 5

Case Study: Biodiesel Process

5.1 Introduction

Biodiesel is a renewable energy synthesized by alcoholysis of natural triglycerides from vegetables oil or animal fats to short chain alkyl esters. The use of biodiesel as motor fuel was first demonstrated by Rudolf Diesel in 1893. In a 1912 speech Diesel said, *'The use of vegetable oils for engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time.'*

Nowadays, the global community is more concerned about the environment, particularly the impact of using fossil based fuels. In addition, the ever increasing petroleum price also urges people to find a suitable alternative. Hence, biodiesel seem to be a good alternative and today has become an important developing area of production and research. Germany has taken a step forward in utilizing the use of biodiesel in motor fuel. With its government policies, incentives, cooperation with car manufacturers, creative marketing strategies and others, it has contributed to the success story of biodiesel in Germany. Now Germany is the largest biodiesel producer in Europe with total production capacity in 2004 reaching to 1.060.000 tons, followed by France with 520.000 tons in the same year [54]. However, the cost of producing biodiesel is more than diesel fuel. The economic feasibility of biodiesel production is highly influenced by plant capacity, the price of feedstock and the price of biodiesel [55]. Rough projections of the cost of biodiesel production from vegetable oil and waste grease are, respectively, USD 0,54-0,62/l and USD 0,34-0,42/l. With pre-tax diesel priced at USD 0,18/l in the US and USD 0,20-0,24/l in some European countries, biodiesel is thus currently not economically feasible and thus needs more extensive research and technological development [56].

5.2 Process description

Most biodiesel plants today operate based on the alkali-catalyzed system. The schematic diagram of the processes involved is shown in Figure 5.1. The process includes transesterification reaction, ester/glycerol separation, biodiesel refining and glycerol refining. The raw materials for biodiesel production are naturally obtainable

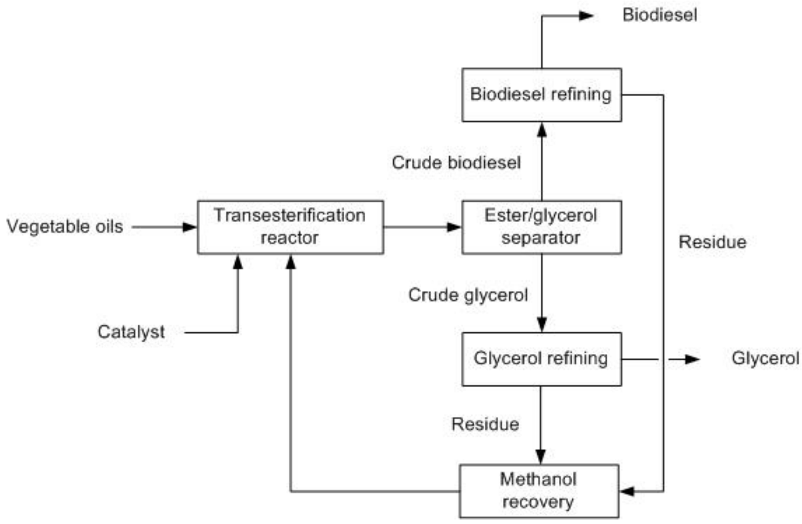


Figure 5.1: Basic scheme for biodiesel production.

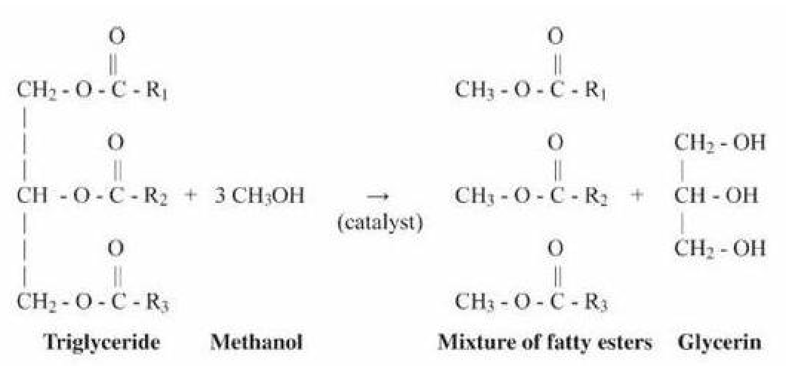


Figure 5.2: Biodiesel reaction.

and renewable. Refined or crude vegetable oil, waste cooking oil or microalgal oils are some examples of what can be used as the main feedstock.

5.2.1 Transesterification reaction

The general reaction for producing biodiesel is shown in Figure 5.2. In this reaction long hydrocarbon chains called fatty acid chains, R1, R2 and R3, react with an alcohol to produce esters and glycerine or glycerol with the help of a catalyst such as sodium hydroxide, potassium hydroxide and sodium methoxide. The reaction involves a sequence of three reversible consecutive steps (see Figure 5.3). In all these reactions esters are produced. The stoichiometric relation between alcohol and oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product [57]. There are five types of chain that are common in biodiesel raw materials, specifically in soybean and animal fat, that is oleic acid, palmatic acid, stearic acid, lenoleic acid and lenolenic acid. The typical fatty acid and oil composition of vegetable oils are given in Table 5.1 and Table 5.2, respectively. Whereas its chemical properties is given in Table 5.3.

$$\text{Triglycerides (TG)} + \text{R}'\text{OH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \text{Diglycerides (DG)} + \text{R}'\text{COOR}_1,$$

$$\text{Diglycerides (DG)} + \text{R}'\text{OH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \text{Monoglycerides (MG)} + \text{R}'\text{COOR}_2,$$

$$\text{Monoglycerides (MG)} + \text{R}'\text{OH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \text{Glycerin (GL)} + \text{R}'\text{COOR}_3.$$

Figure 5.3: Biodiesel reaction step.

Vegetable	Fatty acid composition % by weight									Acid	Phos	Peroxide
oil	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3	value	(ppm)	value
Corn	11,67	1,85	0,24	0,00	0,00	26,16	0,00	60,60	0,48	0,11	7	18,4
Cottonseed	28,33	0,89	0,00	0,00	0,00	13,27	0,00	57,51	0,00	0,07	8	64,8
Crambe	20,7	0,70	2,09	0,80	1,12	18,86	58,51	9,00	6,85	0,36	12	26,5
Peanut	11,38	2,39	1,32	2,52	1,23	48,28	0,00	31.95	0.93	0,20	9	82,7
Rapeseed	3,49	0,85	0,00	0,00	0,00	64,4	0,00	22,30	8,23	1,14	18	30,2

Table 5.1: Fatty acid composition for various feedstock [2].

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0,1	0,1	0,1	0,1	0,1	46,5
Myristic	0,1	0,7	1,0	1,4	2,8	19,2
Palmitic	10,2	20,1	42,8	23,6	23.3	9,8
Stearic	3,7	2,6	4,5	14,2	19,4	3,0
Oleic	22,8	19,2	40,5	44,2	42,4	6,9
Lonoleic	53,7	55,2	10,1	10,7	2,9	2,2
Linolenic	8.6	0,8	0,2	0,4	0,9	0,0

Table 5.2: Oil composition for various feedstock [2].

Vegetable oil	Kinematic viscosity (mm ^{2}/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4,9	54	5	-	176	0,883	33,6
Soya bean	4,5	45	1	-7	178	0,885	33,5
Babassu	3,6	63	4	-	127	0,875	31,8
Palm	5,7	62	13	-	164	0.880	33,5
Sunflower	4,6	49	1	-	183	0,860	33,5
Tallow	-	-	12	9	96	-	-

Table 5.3: Chemical properties of vegetables oils [3].

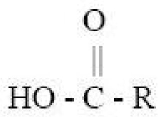


Figure 5.4: Carboxylic acid.

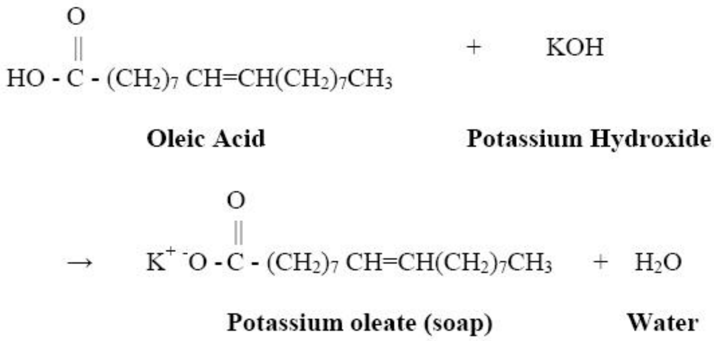


Figure 5.5: Soap formation.

In biodiesel production, in addition to using virgin vegetable oil, it is also possible to use used vegetable oil. However, whether new or used vegetable oil, it is common to contain contaminants such as free fatty acid (FFA) and water. Crude vegetable oil for example has 0,3 up to 0,7% FFA. The refined oil has less than 0,05% FFA. Restaurant waste grease has 2-7% FFA whereas animal fat and trap grease has 5-3% FFA and 40-100% FFA, respectively. The presence of these contaminants however, affects the production of esters.

FFA which are sometimes called carboxylic acids (see Figure 5.4) react with the alkali to form soap as shown in Figure 5.5. Such side reactions are undesirable because they bind the catalyst into a form that does not contribute to accelerating the reaction. Meanwhile, the presence of water in oil feedstock, at high temperatures, can hydrolyze the triglycerides to diglycerides and form a free fatty acid (see Figure 5.6). The FFA then reacts with the presence of alkali catalysts to form soap following the reactions given earlier. When water is present in the reaction it generally manifests itself through excessive soap production. The soaps of saturated fatty acids tend to solidify at ambient temperatures, so a reaction mixture with excessive soap may gel and form a semi-solid mass that is very difficult to recover. Furthermore, the production of soaps may allow emulsification that causes the separation of the glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap.

Generally, when the FFA level is less than 1% the FFAs can be ignored otherwise it needs to be pre-treated. It is especially important to make sure that the feedstock contains no water. 2-3% FFA may be the limit if traces of water are present. When working with feedstock that contains 5-30% FFA or even higher, it is important to convert the FFAs to biodiesel or the process yield will be low. There are at least four techniques for converting the FFAs to biodiesel which include enzymatic methods, glycerolysis, acid catalysis, as well as alkali catalysis [58].

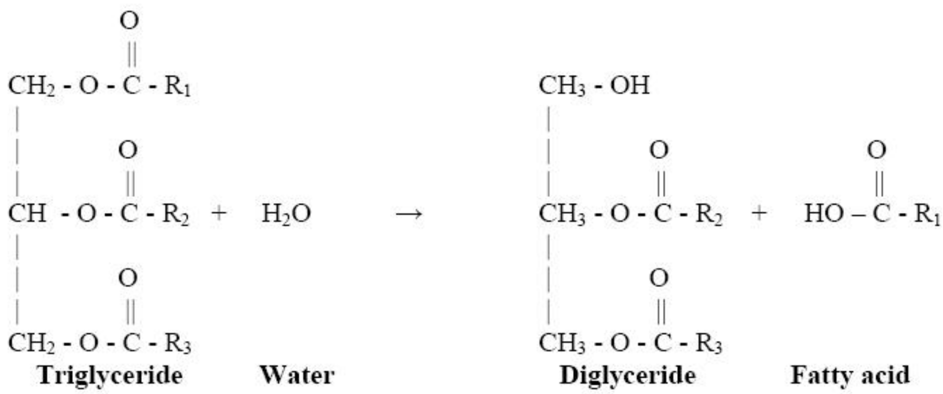


Figure 5.6: FFA formation with presence of water.

5.2.2 Ester/glycerol separation

The ester/glycerol separation is typically the next step after the transesterification reactor. The separation process is based on the difference in density between the ester and glycerol phases. This density difference is sufficient for the use of simple gravity separation techniques for the two phases. However, the rate of separation is affected by several factors. Most biodiesel processes use relatively intense mixing, at least at the beginning of the reaction, to incorporate the sparingly soluble alcohol into the oil phase. If this mixing continues for the entire reaction, the glycerol can be dispersed in very fine droplets throughout the mixture. This dispersion requires from one hour to several hours to allow the droplets to coalesce into a distinct glycerol phase. For this reason, mixing is generally slowed as the reaction begins to progress, to reduce the time required for phase separation. The more nearly neutral the pH, the quicker the glycerol phase will coalesce. This is one reason to minimize the total catalyst use. In some batch systems the reaction mixture is neutralized at the beginning of the glycerol/ester phase separation step.

Gerpen et al. [58] lists three categories of equipment used to separate the ester and glycerol phases. The first is by using decanter. Decanter systems rely solely on the density difference and residence time to achieve the separation. It may need one to eight hours for complete separation, depending of the production volume. For a production of almost 19.000.000 liters/year, a decanter with a volume of at least 2.700 L is needed for one hour residence time. The primary determinant for designing a decanter for biodiesel production is the desired residence time and the product mixture flowrate. Decanter units should be rather tall and narrow to allow physical separation between the ester and the glycerol withdrawal points. L/D ratios of 5 to 10 can work well. The temperature of the decanter also affects the separation. High temperature can cause residual alcohol to flash, potentially restricting the flow of the ester phase out of the tank. On the other hand, low temperature increases the viscosity in both phases. The presence of an emulsion layer is indicative of mono- and di-glycerides. The emulsion layer will form between the phases. In continuous operation, there must be a provision for removing the emulsion, so it does not fill the decanter.

Other than decanter, the use of a centrifuge system is also possible. Many of the continuous plants use a centrifuge for the phase separation since the separation can be completed rapidly and effectively. The disadvantage of the centrifuge is its initial cost, and the need for considerable and careful maintenance. Although centrifuges are relatively expensive, the use of multiple units to ensure on-line availability is advisable. At smaller capacities, either a batch or a continuous centrifuge can be used. The use of a batch centrifuge in a continuous process requires a surge tank to match the batch cycle time with the continuous processing rate.

An intriguing new device for use in the separation process is by using a hydrocyclone system. It is based on a density and has similar effect to a centrifuge, with the heavier material being forced towards the wall and downward, and the lighter material forced to the center and upward. It would appear that the presence of volatiles creates a problem in a hydrocyclone. The rapid reduction of pressure in the device will induce flashing of the volatile liquid (alcohol), disrupting or stopping the separation process. Excess methanol should be removed from the system before introducing the reaction mixture to a hydrocyclone.

5.2.3 Biodiesel refining

After the esters/glycerol separation process the next step is the biodiesel refining process. It involves water washing step before further refinement to produce the desired specification. The primary purpose of the ester washing step is the removal of any soaps formed during the transesterification reaction. In addition, the water provides a medium for addition of acid to neutralize the remaining catalyst and to remove the product salts. The residual methanol should be removed before the wash step. This prevents the addition of methanol to the wastewater effluent. However, some processes remove the methanol with the wash water and then remove it from the wash water. The use of warm water (49 to 60°C) prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes remaining base catalysts. Similarly, removal of iron and copper ions eliminates a source of catalysts that decrease fuel stability. Gentle washing prevents the formation of emulsions and results in a rapid and complete phase separation. There are absorbents on the market that selectively absorb hydrophilic materials such as glycerol and mono- and di-glycerides (i.e Magnesol from the Dallas Group). This treatment, followed by an appropriate filter, has been shown to be effective in lowering glycerides and total glycerol levels.

Ester washing using water produces about 3,8 liter of water per the same amount of ester per wash. All process water must be softened to eliminate calcium and magnesium salts and treated to remove iron and copper ions. The ester wash water will have a fairly high BOD from the residual fat/oil, ester, and glycerol. The glycerol ion exchange systems can produce large quantities of low salt waters as a result of the regeneration process. In addition, water softening, ion exchange and cooling water blowdown will contribute to a moderate dissolved salts burden. The aggregate process waste waters should meet local municipal waste treatment plant disposal requirements, if methanol is fully recovered in the plant and not present in the wastewater. In many areas, internal treatment and recycling of the process water may lead to cost savings and easier permitting of the process facility.

The phase separation between esters and water is typically very clean and complete. However, the equilibrium solubility of water in esters is higher than the specified water content for B100 (100% biodiesel). Therefore, after the washing step there will be more than the equilibrium amount of water present. Vacuum driers can either be batch or continuous devices for removing water. The system is operated at a highly reduced pressure, which allows the water to evaporate at much lower temperatures. A variation that also allows for rather high heating and evaporation rates is the falling film evaporator. This device operates at reduced pressure. As the esters pour down the inside wall of the evaporator the direct contact with the heated wall evaporates the water rapidly. Care should be taken with high temperature evaporators to avoid darkening the fuel which is a sign that the polyunsaturated methyl esters are polymerizing. Because the total water burden in the esters is low, molecular sieves, silica gels, etc. can also be used to remove the water. An advantage of these systems is that they are passive. However, a disadvantage is that these units must be periodically regenerated.

5.2.4 Side stream management

For biodiesel production there are basically three side streams that must be treated to optimize the profitability of a biodiesel plant which are excess methanol, glycerol byproduct and wastewater. These side streams must be treated properly to minimize the environmental impact to the surroundings, especially methanol, which is highly flammable and toxic, and also maximize the profit from recovering glycerol which has higher value than biodiesel. Wastewater constitutes an operating cost for the plant, both because of the water consumption and because of the water treatment costs to the plant.

Glycerol byproduct

The recovered glycerol from the transesterification reaction contains residual alcohol, catalyst residue, carry-over fat/oil and some esters. To increase plant profitability glycerol can be sold since it is widely use in the foods industry, pharmaceutical and personal care applications, botanical extracts, anti-freeze and chemical intermediates. There are several steps for glycerol refining which include chemical refining, physical refining and ion exchange purification.

In chemical refining steps there are several factors that are important. First, the catalyst tends to concentrate in the glycerol phase where it must be neutralized. The neutralization step leads to the precipitation of salts. Also, the soaps produced in the esterification must be removed by coagulation and precipitation with aluminum sulfate or ferric chloride. The removal may be supplemented by centrifuge separation. The control of the pH is very important because low pH leads to dehydration of the glycerol and high pH leads to polymerization of the glycerol. The glycerol may then be bleached using activated carbon or clay.

The first step in physical refining is to remove fatty, insoluble or precipitated solids by filtration and/or centrifugation. This removal may require pH adjustment.

Then the water is removed by evaporation. All physical processing is typically conducted at 65-93°C, where glycerol is less viscous, but still stable. The glycerol purification is completed using vacuum distillation with steam injection, followed by activated carbon bleaching. The advantages of this approach are that this is a well-established technology. The primary disadvantage is that the process is capital and energy intensive. Vacuum distillation of glycerol is best suited to operations >25 tons per day.

Another attractive option to this step is to use ion exchange purification of glycerol. The ion exchange system uses cation, anion, and mixed bed exchangers to remove catalyst and other impurities. The glycerol is first diluted with soft water to a 15 to 35 % glycerol-in-water solution. The ion exchange is followed by vacuum distillation or flash drying for water removal, often to an 85% partially refined glycerol. The advantage of this process is the fact that all purification takes place in the resin vessels so the system is suited to smaller capacity operations. The disadvantages are that the system is subject to fouling by fatty acids, oils and soaps. The system also requires regeneration of the beds producing large quantities of wastewater. Regeneration requires parallel systems to operate and regenerate simultaneously.

Methanol recovery

There are several physical parameters that are important to the recovery and recycling of methanol. Methanols relatively has low boiling point, 64.7°C, means that it is fairly volatile and can largely be removed from the oil, ester and aqueous streams by flash evaporation and re-condensation. The low boiling point, along with a low flash point, 8°C, also means the methanol is considered to be highly flammable. Methanol is fully miscible with water and with glycerol. However, it has a low solubility in fats and oils (approx. 10% wt/wt at 65°C in tallow). Methanol is more soluble in esters, but it is not fully miscible. The solubility in glycerol and water means that methanol will prefer these phases when there is a two-phase system present. The low solubility in fats and oils is the reason for the solubility-limited phase of the overall transesterification reaction. When the two phases present are esters and glycerol, the methanol will distribute between the phases. At 90:10% wt/wt ester and glycerol, the methanol distributes approximately 60:40 wt% between the phases. This fact is important, since the reaction is complete at 90:10 wt%. If the methanol is allowed to remain in the system during phase separation, the methanol acts as a phase stabilizer, retarding the rate of gravity separation. It is advantageous to remove the methanol before phase separation. Methanol can be recovered using distillation, either conventional or vacuum, or partially recovered in a single stage flash. An alternative to distillation is a falling-film evaporator. Residual methanol in the ester phase can be removed in the water wash step in ester post processing. Product esters are typically washed with warm (60°C), softened water to remove soaps and residual methanol.

5.3 Reaction kinetics

There are a number of studies on transesterification reaction kinetics. While most of them involve transesterification of esters and alcohol, a few studies deal with vegetables oils and fatty esters. Freedman et al. [5], for example, investigated both acid- and alkaline-catalyzed transesterification of soybean oil with butanol and methanol. Erciyes et al. [59], studied acidolysis of castor oil with oleic acid while Noureddini and Zhu [4] investigated transesterification kinetics of soybean oil with methanol in different mixing intensity. In general transesterification reaction is a reaction between 1 mol of triglyceride (TG) and 3 mol of alcohol (AL) to produce 1 mol glycerol (GL) and 3 mol esters (ES) as depicted in equation 5.1.

$$TG + 3AL \Leftrightarrow^{k_7}_{k_8}= 3ES + GL \tag{5.1}$$

This is a reversible reaction using either acid or a base catalyst and followed by the second order kinetics [4, 60]. Freedman and co-workers studied the kinetics of the acid- and alkaline catalyzed transesterification of soybean oil with 1-butanol and methanol at 30:1 and 6:1 molar ratios of alcohol to soybean oil. They proposed pseudo first-order kinetics at large molar excess of alcohol and second-order kinetics combined with a shunt-reaction scheme at the lower alcohol excess level. Noureddini and Zhu [4] conducted a study on a second-order reaction mechanism with and without shunt reaction using mathematical modeling. Initial stages of the reaction are not included since it is short and is minimized at realistic temperatures and mixing intensities. They performed a total of 15 sets of experimental data, which were evaluated with both kinetic schemes. Typical curve fitting of the experimental results without shunt reaction shows good fit of the lines in all cases. At the end of their work they concluded that inclusion of a shunt mechanism to describe the transesterification kinetics is not necessary.

The general transesterification reaction in equation 5.1 is further broken down into three stepwise reactions involving conversion of triglyceride (TG) to diglyceride (DG) and to monoglyceride (MG), as shown below:

$$TG + AL \Leftrightarrow^{k_1}_{k_2}= DG + ES + GL \tag{5.2}$$

$$TG + AL \Leftrightarrow^{k_3}_{k_4}= MG + ES + GL \tag{5.3}$$

$$TG + AL \Leftrightarrow^{k_5}_{k_6}= GL + ES + GL \tag{5.4}$$

where k_{1-8} are rate constants. The differential equation that describe the reaction steps are shown in equation 5.5 to 5.8.

$$\frac{d\,[TG]}{dt} = -k_1\,[TG]\,[AL] + k_2\,[DG]\,[AL] - k_7\,[TG]\,[AL]^3 + k_8\,[AL]\,[GL]^3 \tag{5.5}$$

$$\frac{d\,[DG]}{dt} = k_1\,[TG]\,[AL] - k_2\,[DG]\,[ES] - k_3\,[DG]\,[AL] + k_4\,[MG]\,[ES] \tag{5.6}$$

	N_{Re} = 6200		N_{Re} = 12400	
Reaction	Arrhenius[a]	Modified Arrhenius[b]	Arrhenius	Modified Arrhenius
TG → DG	13.145	11.707	13.600	12.130
DG → TG	9.932	8.482	9.783	8.313
DG → MG	19.860	18.439	18.769	16.767
MG → DG	14.639	13.433	11.177	9.710
MG → GL	6.421	7.937	5.182	8.036
GL → MG	9.588	10.992	9.873	11.365

TG = triglyceride, DG = diglyceride, MG = monoglyceride, GL = glycerol
N_{Re} = Reynolds number
[a]Arrhenius equation, $k = Ae^{-E^a/RT}$
[b]Modified Arrhenius equation, $k = ATe^{-E^a/RT}$

Table 5.4: Activation energy from Noureddini and Zhu [4].

$$\frac{d\,[MG]}{dt} = k_3\,[DG]\,[AL] - k_4\,[MG]\,[ES] - k_5\,[MG]\,[AL] + k_6\,[GLY]\,[ES] \tag{5.7}$$

$$\frac{d\,[ES]}{dt} = k_3\,[TG]\,[AL] - k_2\,[DG]\,[ES] + k_3\,[DG]\,[AL] - k_4\,[MG]\,[ES] + k_5\,[MG]\,[AL] \tag{5.8}$$

Noureddini and Zhu [4] proposed a modified Arrhenius equation (Equation 5.9) derived from the transition state theory. It shows the dependency of temperature to the reaction rate constant. If $m = 0$, then it will form the general Arrhenius equation (Equation 5.10).

$$k_n\,(T) = A_n T^m e^{-E_n/RT} \tag{5.9}$$

$$k_n = A_n e^{-E_n/RT} \tag{5.10}$$

where $R = 8314$ J kmol^{-1}K^{-1}, T is the reactor temperature (K), k_n is the specific reaction rate (s^{-1}) and E is the activation energy (J/kmol). The relationship between reaction rate constant, k, and temperature is given by the integrated form of the Arrhenius equation:

$$log_{10}k = \frac{(-E_o/2,303R)}{T} + C \tag{5.11}$$

where E_o is the energy of activation. R the gas constant in cal^{-1}degree^{-1}, T the absolute temperature and C a constant. From a plot of log k vs $1/T$, the slope can be determined. This slope is equal to $(-E_o/2,303R)$. Thus $E_o = -4,58$ (slope). Table 5.4 and 5.5 shows the energy activation from the work of Noureddini and Zhu [4] and Freedman et al. [5], respectively.

Effect of mixing

Previous research shows that transesterification reaction is limited by its mass transfer rate. This is due to the immiscibility between triglyceride and alcohol phases

	E_o(cal/mol): reaction conditions				
	BuOH/SBO, 30:1			BuOH/SBO, 6:1	MeOH/SBO, 6:1
	1% H_2SO_4	1%NaOBu	0,5% NaOBu	1% NaOBu	0,5% $NaOCH_3$
Rate Designation	77-117°C	20-60°C	20-80°C	20-60°C	20-60°C
TG → DG	14.922	15.360	15.662	17.092	16.062
DG → MG	16.435	11.199	13.053	12.187	17.247
MG → GL	15.067	11.621	13.395	10.693	-
DG → TG	19.895	17.195	15.587	15.925	15.843
MG → DG	16.885	-	13.336	15.816	13.571
GL → MG	12.196	-	13.110	8.181	-
TG → GL	-	-	-	-	20.022

TG = triglyceride, DG = diglyceride, MG = monoglyceride, GL = glycerol

Table 5.5: Activation energy from Freedman et al. [5].

that forms two layers upon contact. Because the catalyst is polar and mainly dissolved in the alcohol phase, only triglyceride that dissolved in the alcohol phase was converted via diglyceride and monoglyceride to form ester and glycerol. If not homogeneously mixed the reaction rate will be hindered by the effect of this limited mass transfer phenomena. Therefore, a proper mixing method is important to ensure large conversion of TG to ester. Several mixing method were proposed by researchers which include mechanical stirrer [4], ultrasonic mixing [61], co-solvent [62, 60] and hydrodynamic cavitation [63]. However in this work, the mechanical stirrer is selected as the default mixing method since the kinetics data was very widely published.

The effect of mechanical stirring causes the transport of triglyceride into the methanol phase, where most of the catalysts are, and rapidly converted triglyceride into ester and glycerol. Study by Noureddini and Zhu as depicted in Figure 5.7 fully support the mass transfer controlled phenomena and the effect of mixing towards ester conversion. Figure 5.7 also shows that there were delays or slow rate region at the beginning of the reaction. As oil and alcohol is initially immiscible, slow rate region occurs when there is poor diffusion between phases, but it will eventually form a single phase as esters concentration started to build up where it acts as a mutual solvent for the reactants. This phenomenon observed at a time where the sudden surge of esters shown in Figure 5.7. This delay, however, decreased as the mixing intensities increases and after N_{Re} greater than 10 000 this slow rate region reduced to a constant value from 1 to 2 minutes. When single phases are formed, mixing becomes insignificant and the reaction is then temperature dependent. The reason being is that at elevated temperatures it provides a higher energy state of the molecules and also promotes higher solubility, thus resulting in more effective collisions.

Effect of time and temperature

Figure 5.8 shows the effect of using different catalyst on the reaction time. Ester formation of BuOH with soybean oil at a molar ratio 30:1 catalyzed by 1% H_2SO_4 is essentially completed in 3 hours at 117°C. The reaction time will increase to 20

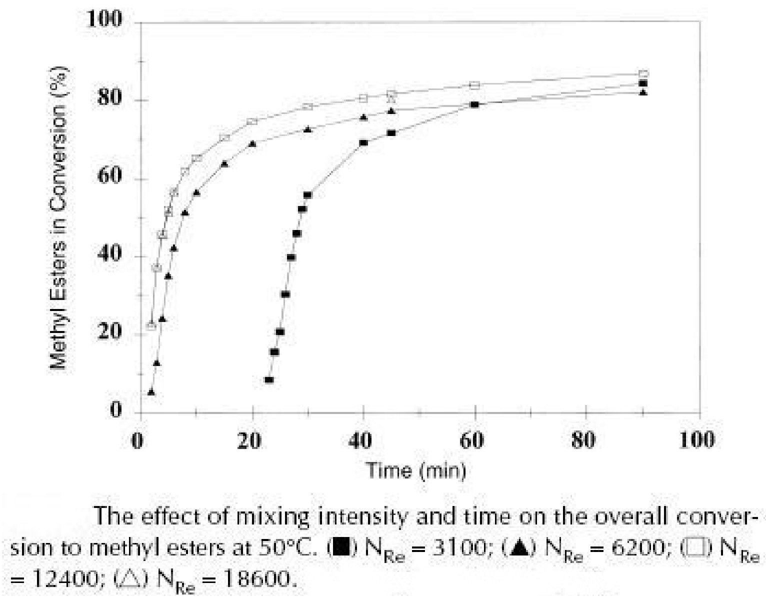


Figure 5.7: Effect of mixing [4].

hours at 77°C. Compared with ester formation for a molar ratio BuOH : soybean oil (6:1) catalyzed by 1% NaOBu it takes approximately 12 min, 10 times faster than using acid based catalyst. This clearly shows the advantage of using alkali based catalyst for large scale production.

Temperature dependency of the overall reaction rate is presented in Figure 5.9 at two different mixing intensities. As shown in the figure, the time for the mass transfer region is shortened as temperature is increased which may be due to the higher energy state of the molecules resulting in more effective collisions. Higher solubility of the reactants at elevated temperatures may also be partially responsible for this behavior. Mass transfer region is reduced from 55 minutes to about 20 minutes, as temperature is increased from 30 to 60°C at N_{Re}=3100. At higher mixing intensities N_{Re}=6200, the mass transfer region is short and this effect is not significant.

In general, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy. Table 5.4 and 5.5 lists the calculated activation energies for the three reversible reactions involved in the transesterification reactions. In the first two reactions (TG↔DG and DG↔MG) the energy of activation is higher for the forward reactions. Thus, higher temperatures should favor these reactions, and higher concentrations of MG are expected. However, for the third reaction (MG↔GL), the forward reaction has a lower activation energy than the reverse reaction. Theoretically, this implies a more favorable reverse reaction at higher temperatures but, apparently, higher concentrations of MG offset this effect and the kinetic-controlled region for the combined transesterification reactions is more favorable at higher temperatures. This effect becomes minimal as temperature is increased and the overall conversion reaches an asymptotic value at about the boiling temperature of the

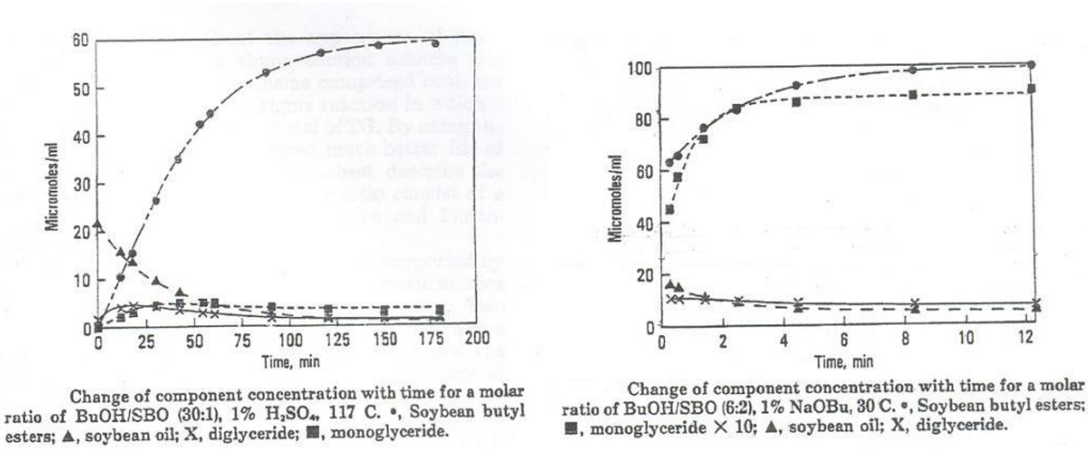


Figure 5.8: Effect of time [4].

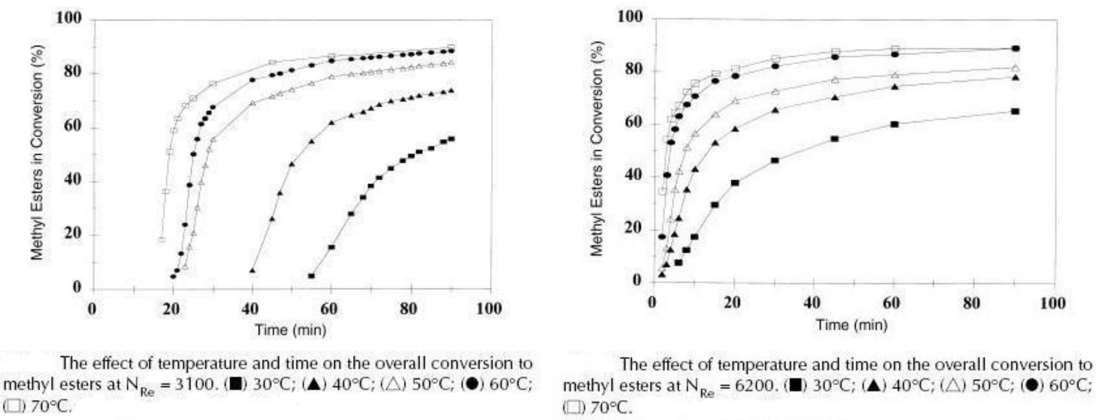


Figure 5.9: Effect of temperature [4].

alcohol [4].

5.4 Technological option for biodiesel production

The research and development in biodiesel production centers around the factors that influence its economic feasibility, such as raw material utilization, process design, price of feedstock, waste management. Most of the large scale biodiesel plants were based on alkali-catalyzed system because of its high efficiency, low operating conditions and less corrosive. However, the process is very sensitive to purity of reactants e.g., water and FFA content. Because of that, refined vegetable oil with less than 2,0 wt% FFA was often used but with a higher feedstock price. To reduce raw material cost, feedstock with high FFA such as waste cooking oil is sometimes used. To ensure good conversion, acid catalyst provides an excellent alternative for feedstock with such high FFA. Generally the esterification reaction is independent from FFA, and an advantage when using used cooking oil. The process gives very high yield in esters. However, the drawback is the slow reaction rate which requires almost more than one day to complete. Despite that, its corrosivity also makes it less preferable.

There are also attempts to use supercritical method for biodiesel production [64, 65]. Experimentally, it shows higher reaction rates which show the FFA in the oils transformed completely into the fuel. The method also water tolerable and can be used with wide variety of feedstock. But handling with such high temperatures and pressures has huge safety and cost constraints, thus making it commercially less preferable.

Another interesting approach is by introducing various mixing methods. Beside the typical mixing using stirrers some researchers suggest using ultrasonic reactor. Based on alkali-catalyzed using KOH such an approach can increase productivity (with or without catalyst) and improved quality and color of the product without high temperature treatment [61]. On lab scale, it is proven one can achieve higher yield with reduced reaction time. Note that higher microwave amplitude does not mean a higher conversion, in fact, it decreases yield drastically due to cracking followed by oxidation. Higher input energies also decreases yield mainly due to cracking and degradation [61].

Another similar approach to ultrasonic is by using hydrodynamic cavitation [63]. An experimental works for biodiesel production with, the help of ultrasonic and hydrodynamic cavitation, was done by Jianbing et al. [63]. Their result shows that the equilibrium reaction time was shortened in order of ultrasonic > hydrodynamic cavitation > mechanical stirring. For energy consumption the efficiency is in order of hydrodynamic cavitation > pulse ultrasonic > mechanical stirring. However, scale up of hydrodynamic cavitation had better opportunities than the ultrasonic reactor because of its easier generation and less sensitivity to the geometric details.

Other than using chemical-based catalyst, it is also reported that the use of enzyme such as lipase for biodiesel production [66, 67, 68]. Using enzyme has the advantage that it has the possibility for regeneration and reuse, longer activation of the lipase and bigger thermal stability. Other than that, it protects solvents to be used in reaction and prevent enzyme particles getting together and ease of separation of product. However, the disadvantages are loss of initial activity due to volume of the oil molecule, the number of support enzyme is not uniform, and the cost is more expensive.

With regards to raw material issue, Chisti [69] introduced a potentially new raw material using microalgae. He claimed that only small areas are needed for huge amounts of oil yield. However, microalgae oil has high content in polyunsaturated fatty acids with four or more double bonds, and is based on its compositions of many microalgal oils, most of them unlikely to comply with the European standards. Nevertheless, the extent of unsaturation of microalgal oils and its content of fatty acids with more than four double bonds can be reduced easily by partial catalytic hydrogenation of the oil as commonly used in making margarine [70, 71].

The potential of using heterogeneous catalyst for biodiesel production is extensively studied by various researchers. In 2004, Furuta et al. [72] studied the production of biodiesel with the use of solid superacid catalysis; tungstated zirconia (WO_3/ZrO_2), sulfated tin oxide (SO_4/SnO_2) and sulfated zirconia (SO_4/ZrO_2). Although all three catalyst are possible to use, their finding concluded that tungstated zirconia is a more promising catalyst for the production of biodiesel because of its activity for both transesterification process and esterification process. Marchetti et al. [73] conducted an experiment by using basic resin to perform esterification reaction into biodiesel. Overall heterogeneous catalyst is a good alternative to the current process and they achieved final conversion around 80%. Research by Park et al. [74] focuses on the esterification of FFA to biodiesel. Their finding concluded that powder-type catalyst performed better than the pellet-type because of large surface area and higher pore size distribution. They also investigate the regeneration effect of catalyst to the esterification process. Using heterogeneous catalyst has the advantage of eliminating the use of homogeneous catalyst, having no catalyst recovery process, no aqueous treatment steps, no neutralization process, and it can avoid side reactions between FFA and alkali catalyst. This is a huge advantage as most of the plants are equipped with additional equipment to compensate the problems that occur when using alkali-catalyzed system, thus contributing to the increased cost of biodiesel production. Meanwhile, using heterogeneous catalyst enables one to comprehend this problem and possibly reduce the cost of biodiesel production. Axens had developed a heterogeneous catalyzed process for biodiesel production process known as The Esterfip-H process that requires neither catalyst recovery nor aqueous treatment steps, which are drawbacks from the current homogeneous catalytic processes. Esterfip-H exhibits very high FAME yields and directly produces salt-free glycerol at purities exceeding 98%.

In 2008, McNeff et al. [75] revealed a revolutionary method in the biodiesel manufacturing process. Based on a paper discussed esterification catalyzed by solid strong acids to manufacture biodiesel, they built and tested a column that mixed oil and alcohol with the catalyst, zirconia, under supercritical conditions. Under the right conditions in the column, the oil and alcohol were converted into biodiesel in six seconds. The column allows for continuous production of biodiesel. It is suggested that a column about 10 cm in diameter and 61 cm long will be able to produce 11,4 million liters of biodiesel per year. The process can also convert glycerin into dimethyl ether, which is more valuable in the current market. It is also tested for wide ranges of feedstocks and poses no problems. McNeff has formed the company, Ever Cat Fuels LLC, to build a commercial-sized 11,4 million liters per year facility in Isanti, Minnesota, scheduled to be in operation by October. The plant will use hydrous ethanol, rather than methanol, and corn oil extracted from distillers grains as the feedstock. The plant can compensate the feedstock up to 20% free fatty acids. At the end of the process, the finished biodiesel does not need to be washed.

Table 5.8 summarizes the applicability of the biodiesel process technology reviewed in this chapter.

Catalyst	Process Condition	Advantage	Disadvantage
Alkali (NaOH, KOH)	Include:- • 0.5%-1% w/w (Barnwal and Sharma, 2005, Srivastava and Prasad, 2001) or 0.005% - 0.35% w/w [2]. • Use hot water washing, 50°C to get high purity (99%) and yield (86%). • Reaction time can be shortened to 2-4 hrs at 105°F and 1-2 hrs at 140°F & High conversion yield. • Higher temperatures decrease reaction time but need a pressure vessel because methanol boils at 65°C. • High shear mixing and use of co solvents, tetrahyfrofuran (THF), have been proposed to accelerate reaction [62].	Include:- • More efficient and less corrosive. • Temperature: 25°C-120°C & Low temperature and pressure. • If free fatty acid >2% it is recommended to use a pre-treatment via esterification with alcohol using sulphuric acid [5]. • Most preferable to be used for large scale.	Include:- • Sensitive to purity of reactants e.g. water content and FFA. • Too much water may lead to formation of emulsion.
Acid, (H_2SO_4, Sulfonic acid	Include:- • Molar ratio 30:1 • Amount of catalyst varies from 0,5 to 1 mol% • Temperature: 55°C-80°C • Molar ratio of 245:1 methanol to oil can result 99% conversion [76]. But increase in the size of equipment.	Include:- • Gives very high yield in esters • Excellent way to make biodiesel if it has relatively high free fatty acid content [76].	Include:- • The reaction is slow, requiring almost more than one day to finish. • Not suitable for commercialization purpose. • The reaction is independent from FFA and an advantage when using used cooking oil.

Table 5.6: Summary of technological applicability.

Catalyst	Process Condition	Advantage	Disadvantage
Lipase (M. Mieh, C. Antarctica)	Include:- • Methanol/fatty acid (mole/mole) larger than 0,5 than the product becomes insoluble in alcohol and reduces the lipase activation [77]. • Temperature: 30°C-40°C	Include:- • Possibility of regeneration and reuse. • Longer activation of the lipase. • Bigger thermal stability. • Protect solvent to be used in reaction and prevent enzyme particles getting together. • Ease of separation of product [78].	Include:- • Lose some initial activity due to volume of the oil molecules. • Number of support enzyme is not uniform. • Expensive [78].
Ultrasonic reactor method (KOH)	Include:- • Recommended operation is at 24 kHz frequency, combination of 5 min/75%, 5 min/100% and 15 min/24%, reaction time/amplitude, respectively, gave yields that met ASTM D6751 standard [61]. • Input energy should be between 125 and 215 kJ for production yield >97% [61]. • Factors that affected FAMEs yield by order are substrate molar ratio >temperature >pulse frequency [63]. • Large ultrasonic does not mean lower reaction time as it create mass bubbles that reduce methanol content in the liquid phase and interface area [63].	Include:- • Increased productivity (with or without catalyst) and improved quality and colour of the product without high temperature treatment [61]. • High yield with reduce reaction time • Estimate that the cost is between 0,002/l - 0,015/l for commercial scale depending on the flow rate.	Include:- • Higher amplitude, decrease yield drastically due to cracking followed by oxidation [61]. • Higher input energies decrease yield mainly due to cracking and degradation [61].

Table 5.7: Summary of technological applicability (cont.).

Catalyst	Process Condition	Advantage	Disadvantage
Supercritical methanol	Include:- • The reaction is perform using excess methanol. • The reactor temperature in operate with temperature of over 300°C and pressure above 300 bar.	Include:- • Offers non-catalyst process. • Insensitive to reactants impurities. • Perform simultaneous esterification & transesterification reaction. • The reaction will take only few minutes with yield of 95% (Lim et al. [79]).	Include:- • Require high operating temperature and pressure thus affect the operating cost and equipment cost.
Microalgae	Include:- • Can be produced using raceway ponds and photobireactors. More economically feasible using photobioreactors because it produces much more oil yield per hectare and higher biomass productivity. • Biomass concentration in photobioreactors is nearly 30 times the biomass concentration in raceway ponds with the same volume.	Include:- • Potential new raw material. • Small area needed for huge amount of oil yield.	Include:- • High content in polyunsaturated fatty acids with four or more double bonds. • Based on compositions of many microalgal oils, most of them unlikely to comply with the European standards. • The extent of unsaturation of microalgal oils and its content of fatty acids with more than 4 double bonds can be reduced easily by partial catalytic hydrogenation of the oil [70, 71] as commonly used in making margarine.

Table 5.8: Summary of technological applicability (cont.).

5.5 Biodiesel production issues

There are several issues involving biodiesel production. First is the feedstock requirement. Since biodiesel depends on vegetable oil, the price for crop feedstock is very high. Dependability on edible oil also affects its consumption for dietary usage, especially in food industries. Used vegetable could be an alternative for cheaper feedstock but the presence of high percentage of water and FFA could increase its overall production cost as it needs additional pre-treatment. In latest developments, many researchers are trying to find an alternative feedstock which is non-edible. Some researchers suggest the use of microalgae [69] and jatropha.

Another issue related to biodiesel production involves the process design. When comparing between continuous and batch processing one must consider its feasibility. Batch process is suitable for smaller plants, simpler and less complicated and easier to control/operate. Continuous process on the other hand, although difficult to operate, allows use of high-volume separation system. Hybrid systems are also a possible option. In presence, there are several methods available for shortening the reaction time such as supercritical methanol and McNeff processes. Ultrasonic and hydrodynamic cavitation has also been investigated to fasten reaction time. But this development however needs more assessment on its application and economic part, especially for large scale production. Some researchers have developed new process options. These include using heterogeneous catalyst which eliminates the need for biodiesel washing as the solid catalyst is not consumed during transesterification.

Increasing the profitability of biodiesel production should not solely depend on the product itself but on efficient utilization of the byproducts and side streams could be an advantage, since glycerol is a very valuable byproduct. Pharmaceutical grade glycerol can be sold at a high price, but needs additional treatment. The development of processes to convert crude glycerol into higher value products is both an urgent need and a target of opportunity for the development of biorefineries. Such technologies could be readily integrated into existing biodiesel facilities, thus establishing true biorefineries and revolutionizing the biodiesel industry by dramatically improving its economics.

Methanol management is also an important aspect. Since methanol is used in excess, recycling could optimize the methanol consumption. Recycling also helps to prevent methanol, at certain amounts, from retarding the rate of gravity separation, and also to make sure of allowable amounts of methanol in waste streams. Properly managed, wastewaters can be treated in a municipal sewer system, but internal treatment and recycling should be considered.

Biodiesel research and development is becoming an interesting area. As shown in previous chapters, researchers have done extensive research on biodiesel. Many efforts have been done to find potential process technology either by finding a new sustainable feedstock or developing a new process design. Eventually, this leads to several options for biodiesel production. Therefore, introduction of sustainability assessment and decision making in chemical industries is significantly relevant and crucial. It is our hope that by this PDM approach, it could help decision makers to make meaningful decisions for future generations. In the next chapter we will show the applicability of the approach and the use of the m-SAS tool for assessing and selecting two potential biodiesel process designs.

5.6 Sustainability assessment and selection using m-SAS

To demonstrate the applicability of the proposed approach, two biodiesel processes will be investigated. The first process (Case 1) in Figure 5.10a, is using a conventional method to produce biodiesel using alkali-based catalyst, whiles the second process (Case 2), in Figure 5.10b, is using supercritical methanol. Alkali-based catalyst for producing biodiesel is mostly preferred in the industry. One limitation of alkali-catalyzed process, however, is its sensitivity to the purity of reactants, e.g., water content and free fatty acid (FFA).

In recent years, researchers began to investigate producing biodiesel at supercritical condition. Applying such conditions offers several advantages, including non-catalyst process, insensitive to both water and FFA, and simultaneous esterification of FFA in oil [80]. Recent studies shows that it is technologically and economically promising [81, 79]. Therefore, supercritical methanol can be an alternative to the conventional method of producing biodiesel. Although it can compensate problems associated with the alkali-based process, it requires a high operating cost due to its high operating temperature and pressure. Consequently, a consumption of too much energy leads to more pollutants resulting from high consumption of energy resources. No research thus far has assessed and selected these cases from the sustainability point of view, although there is an effort that focuses solely on the environment impact [82]. Thus, it will be interesting to assess and compare these two cases based on economic, environmental and social criteria and finally select a sustainable option.

5.7 Process modeling

Process modeling is done using process simulators. Generally, process simulators are used to mimic real processes. Equipped with advanced computation techniques, comprehensive thermodynamic packages and large component libraries, process simulators today provide reliable information of process design and operations. In this work, both cases are modeled using Aspen Plus. Basic steps to process modeling and simulation using process simulators include defining chemical components, selecting thermodynamic model and method, designing process flowsheet by choosing proper operating units, determining plant capacity and setting up input parameters. Detailed descriptions of each step will be discussed in the preceding chapter.

5.7.1 Chemical components

Table 5.9 below shows the chemical compounds used in the simulation work. Simulating an actual content of vegetable oil is complex because of its mixture of oils with fat content. In this work, rapeseed oil is used as the feedstock. Since oleic acid is a major fatty acid in rapeseed oil with a composition of 64,4% [2], triolein

Compound	Component name	Component ID	Formula
TG	Triolein	TRIOLEIN	$C_{57}H_{104}O_6$
Glycerol	Glycerol	GLYCE-01	$C_3H_8O_3$
Methanol	Methanol	METHA-01	CH_4O
Methyl oleate	Methyl-oleate	METHY-01	$C_{19}H_{36}O_2$
Softwater	Water	SOFTH2O	H_2O
Water	Water	H2O	H_2O
NaOH	Water	NAOH	H_2O

Table 5.9: Compounds defined in Aspen Plus.

is chosen to represent rapeseed oil. Methyl oleate is taken as the resulting biodiesel product. In real application, however, new vegetable oil actually contains 0,05 wt% FFA [83], but this is not considered in this work. Today most large scale plants prefer base-catalyst. For that reason, sodium hydroxide is chosen as the catalyst and softwater (contain 37% hydrochloric acid) is used to neutralize any remaining catalyst.

5.7.2 Thermodynamic model and method

In biodiesel production, both methanol and glycerol are highly polar components. Therefore, both NRTL and UNIQUAC models are recommended for predicting the activity coefficients of the components in a liquid phase [76]. In this simulation, NRTL is used as the main thermodynamic method. For the modeling of decanter and mixer, the Redlich-Kwong-Soave (RKS) thermodynamic properties are used following the approach by Myint and El-Halwagi [83]. Electrolyte chemistry is not modeled in detail here and because sodium hydroxide and softwater are both electrolyte chemistry, they are modeled using physical property data for water, but with their correct molecular weight.

Most of the compounds properties are available in the Aspen Plus component library. Nevertheless, some of them have to be estimated. For example, coefficients for the extended antoine vapor pressure equation for the adjusted sodium hydroxide and softwater are estimated using Aspen Properties and their results are inserted into the flowsheet. In another example, although triolein is in the Aspen chemical database, some of the properties such as coefficients for ideal gas heat capacity equation, Watson heat of vaporization equation coefficients and OMEGA value have to be estimated using Aspen Properties for the model to converge properly.

5.7.3 Process flowsheet design

The simulated capacity of both cases is 8000 ton/yr with oil feed input of 1050 kg/hr. The biodiesel purity of more than 99.6 wt% is assumed according to the ASTM specification. Additionally, to optimize the plant profitability, glycerol is further refined to meet the pharmaceutical standard of more than 92 wt%. Since the economic feasibility of the biodiesel industry is much more affected by plant capacity, vegetable oil price, and price of biodiesel, it requires government subsidy for positive net profit [55]. In this work, the total biodiesel selling price is assumed to be \$1,30/kg, with inclusion of government subsidy.

Case 1 - Alkali-based process

The modelling for Case 1 is based on the work of several researchers [81, 83, 76]. The flowsheet configuration is shown in Figure 5.10a. The reaction is carried out with a 100% excess of methanol to oil or 6:1 molar ratio with 1 wt% sodium hydroxide based on oil. The catalyst and methanol feed flowrates are 10 kg/hr and 110 kg/hr, respectively. The reaction yield is assumed 95%, the temperature is set at 60°C, and the pressure is at 1 bar. The reaction product then enters a methanol recovery unit with 6 theoretical stages and the reflux ratio of 0,05. The distillation column is kept below the atmospheric pressure in order to maintain the bottom product temperature under 250°C, which will prevent a decomposition of biodiesel and glycerol. The bottom product is then sent to a water washing column. It is mixed with 10 kg/hr water before being settled down in a decanter to separate the main products, i.e., biodiesel and glycerol. Based on the component density, the upper part which contains 97% biodiesel is sent to a biodiesel purification column. Using six theoretical stages with a reflux ratio of two and being operated under vacuum to maintain product temperature below 250°C, biodiesel is further purified to meet the product specifications of 99,6wt%. The bottom stream of the decanter contains 82% glycerol and the rest is a mixture of methanol, water and sodium hydroxide. To further purify glycerol, the stream is first passed to a catalyst neutralization reactor. Phosphoric acid at 8,33 kg/hr is added to neutralize the sodium hydroxide. The output stream is then sent to a filter to separate the solid sodium phosphate salt. The liquid stream is then sent to a glycerol purification column. Using four theoretical stages, at the reflux ratio of one and being operated under vacuum, the bottom product stream is able to achieve glycerol purification of above 92wt%. Summary of the main unit operation specifications for Case 1 is listed in Table 5.10 and Table 5.11 gives the simulation results of the input and output streams. Full results of each stream can be viewed in Appendix B.

Case 2 - Supercritical methanol

Modeling of Case 2 is based on the work of several researchers [80, 81, 79]. The flowsheet configuration is shown in Figure 5.10b. Setting the reaction condition varies from the literature, but generally it uses excess methanol with temperature of over 300°C and pressure above 300 bar. In this work, the reaction condition with 42:1 methanol to oil molar ratio, temperature of 350°C and pressure of 430 bar are used. According to Lim et al. [79], at this condition, the reaction takes only four minutes with the yield of 95%. Because of the high temperature of the reactor output stream, the heat is utilized to preheat the reactor input stream using heat exchanger while maintaining the product below 250°C. The reaction product then enters the methanol recovery distillation column with 12 theoretical stages and the reflux ratio of 0,5. Nearly 99,6% of the excess methanol can be recovered with the purity nearly 99,9%. This recycled methanol is mixed with the fresh methanol feed of 114 kg/hr before being fed again, together with oil, to the reactor. The bottom stream of the column is then cooled down before being sent to a decanter. Based on the component density, the upper part contains 94,7% biodiesel and the rest is unreacted oil and other impurities. The bottom stream contains over 92% of glycerol

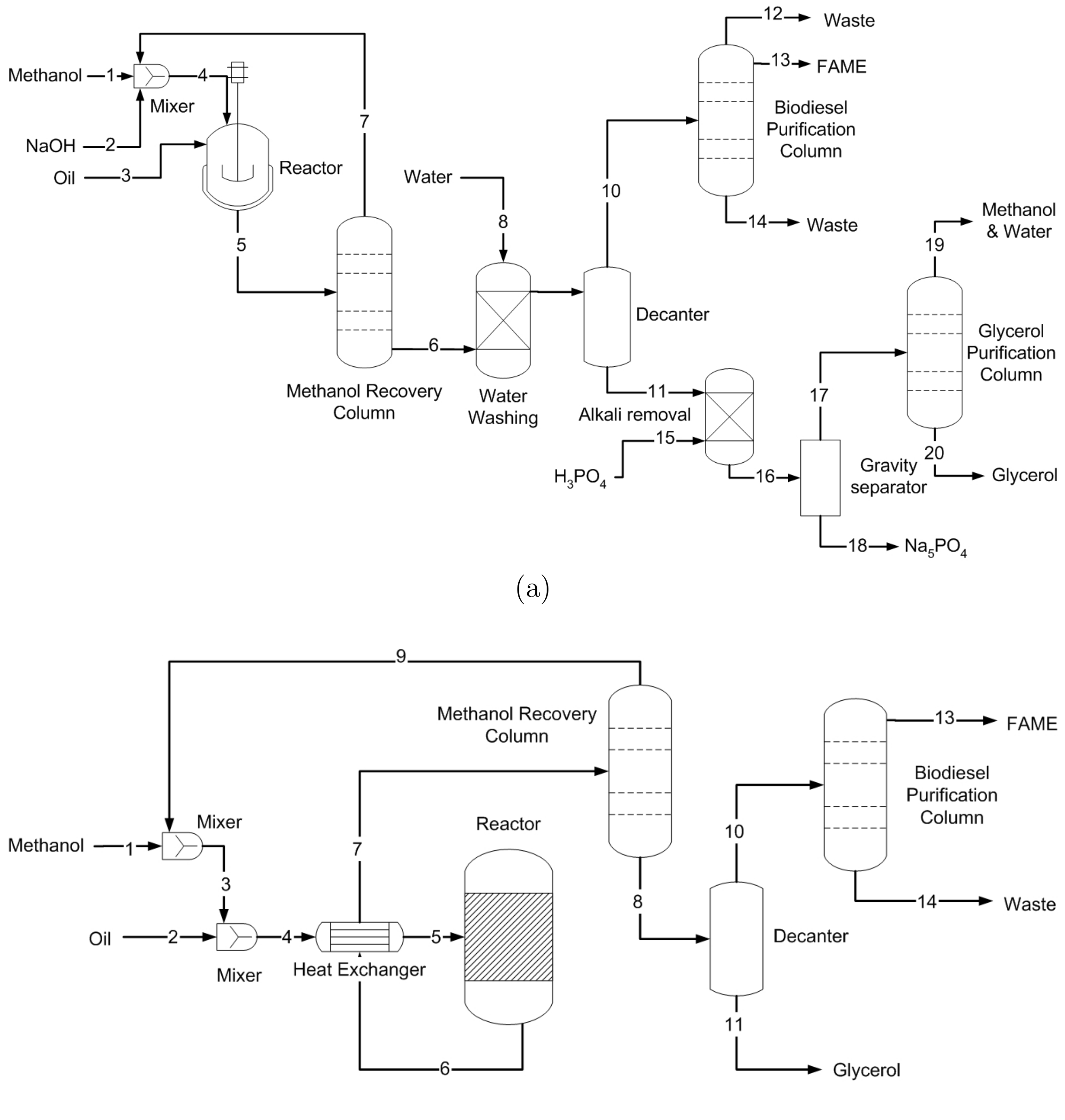


Figure 5.10: Biodiesel process flowsheet (a) Case 1: alkali-based (b) Case 2: supercritical methanol

Operating specifications	Case 1	Case 2
Transesterification reactor		
Catalysts	NaOH	N/A
Reactor type	CSTR	CSTR
Temperature, °C	60	350
Pressure, bar	1	430
Alcohol:oil molar ratio	6:1	42:1
Residence time, min	60	4
Conversion, %	95	95
Volume, m^3	9,72	2,10
Bare module cost, \$ x 10^3	354	960
Neutralization reactor		
Reactor type	CSTR	N/A
Temperature, °C	30	
Pressure, bar	1	
H_3PO_4 flowrate, kg/hr	8,33	
Conversion, %	100	
Volume, m^3	0.40	
Bare module cost, \$ x 10^3	67,5	
Methanol recovery column		
Reflux ratio, mass	0,05	0,5
Number of stages	6	12
Distillate/Bottom temperature, °C	32,8/176,0	64,5/158,3
Condensor/Reboiler pressure, kPa	25/30	101,3/105,3
Condensor/Reboiler duty, MJ/hr	181,5/462,4	2552,7/1354,2
Recovery, %	99,6	99,6
Distillate flowrate, kg/hr	148,9	1487,7
Distillate purity, wt%	99,9	99,9
Size (Diameter x Height), m	0,23 x 2,93	0,61 x 7,32
Bare module cost, \$ x 10^3	153	324
Biodiesel purification column		
Reflux ratio, mass	2	0,05
Number of stages	6	8
Distillate/Bottom temperature, °C	194,0/329,7	49,8/356,4
Condensor/Reboiler pressure, kPa	15/20	Okt 15
Condensor/Reboiler duty, MJ/hr	1382,9/1781,4	846,0/876,6
Recovery, %	99,5	99,6
Distillate flowrate, kg/hr	1000,6	1002,0
Distillate purity, wt%	>99,6	>99,7
Size (Diameter x Height), m	1,05 x 2,93	0,85 x 4,39
Bare module cost, \$ x 10^3	189	171
Glycerol purification column		
Reflux ratio, mass	1	N/A
Number of stages	4	
Distillate/Bottom temperature, °C	71,1/221,9	
Condensor/Reboiler pressure, kPa	40/50	
Condensor/Reboiler duty, MJ/hr	64,1/105,6	
Recovery, %	99,9	
Bottom flowrate, kg/hr	103,6	
Bottom purity, wt%	>92	
Size (Diameter x Height), m	0,10 x 1,46	
Bare module cost, \$ x 10^3	116	
Pumps		
Total energy requirement, kW	0,112	211,251
Total bare module cost, \$ x 10^3	31,8	657

Table 5.10: Summary of main unit operation specifications.

	Input stream					Output stream					
	1	2	3	8	15	12	13	14	18	19	20
Temp., °C	30	30	30	30	30	194	194	329,7	60,5	71,1	221.9
Pres., bar	1	1	1	1	1	0,15	0,15	0,2	1	0,4	0,5
Moleflow, kmol/hr	1,19	0,25	3,43	0,56	0,09	0,03	3,40	0,07	0,08	0,75	1.17
Massflow, kg/hr	1050	10	110	10	8,33	1,47	1001	55,07	13,66	13,99	103,6
Mass fraction											
TG	1,00	0,00	0,00	0,00	0,00	0,00	0,00	0,92	0,00	0,00	0,00
MeOH	0,00	0,00	1,00	0,00	0,00	0,45	0,00	0,00	0,00	0,06	0,00
NaOH	0,00	1,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Glycerol	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,99
FAME	0,00	0,00	0,00	0,00	0,00	0,40	1,00	0,08	0,00	0,00	0,00
Water	0,00	0,00	0,00	1,00	0,00	0,15	0,00	0,00	0,00	0,93	0,01
H_3PO_4	0,00	0,00	0,00	0,00	1,00	0,00	0,00	0,00	0,00	0,01	0,00
Na_3PO_4	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,00	0,00	0,00

Table 5.11: Input and output streams results for Case 1.

	Input stream		Output stream		
	1	2	11	13	14
Temp., °C	30	30	49,85	30	356,35
Pres., bar	1	1	0,1	1	0,15
Moleflow, kmol/hr	1,19	3,56	3,47	1,20	0,07
Massflow, kg/hr	1050	114	1002	105,42	56,58
Mass fraction					
TG	1,00	0,00	0,00	0,00	0,93
MeOH	0,00	1,00	0,00	0,03	0,00
FAME	0,00	0,00	0,00	0,97	0,00
Glycerol	0,00	0,00	0,99	0,00	0,07
Water	0,00	0,00	0,00	0,00	0,00

Table 5.12: Input and output streams results for Case 2.

and the rest is mostly methanol. As the purity of glycerol meets the commercial standard, no further purification step is needed. The biodiesel rich stream still needs to undergo further purification. The stream is fed to a biodiesel purification column using eight theoretical stages with the reflux ratio of 0,05 and under vacuum. The biodiesel purity at the distillate stream achieves the product specifications of more than 99,6wt%. Summary of the main unit operation specifications for Case 2 is listed in Table 5.10 and Table 5.12 summarizes the simulation results of the input and output streams. Full results of each stream can be viewed in Appendix B.

5.7.4 Data acquisition

As previously describe the economic and environmental data are provided by the users and the process simulator. Tables 5.13 and 5.14 show, respectively, the economics parameters and the component-specific potential environment impact (PEI). The values for the latter are obtained from the MSDS datasheet and classification factor published in Heijung et al. [39]. The (-) value in Table 5.14 denotes either non-applicable or non-determined data. The data from the process simulator is exported to the EIA module using ASW. These include stream flowrates, compositions, process utilities parameters such as heat duty and utility type, mass of cooling

Specifications	Value
Feed input price, \$/kg	
Soy oil (crude, degummed)[a]	0,5
Methanol (99,85%)[a]	0,18
NaOH[a]	0,34
H_3PO_4[a]	4
Product price, \$/kg	
Biodiesel (with subsidy)	1,3
Glycerol (92wt%)[a]	1,2
Utilities price, \$/kg	
Electricity, \$/kWh[a]	0,062
LP steam (5 barg, 160°C)[b]	0,00608
MP steam (10 barg, 184°C)[b]	0,0068
HP steam (41 barg, 400°C)	0,1164
Process water[b]	$6{,}7 \times 10^{-53}$
Disposal cost, \$/kg	
Solid waste[a]	0,15
Liquid waste[a]	0,037
Discount factor, %	10
Annual depreciation, %	10
Tax, %	34
Salvage value recovery %	5
Plant life cycle, yrs	15
Construction duration, yrs	1
Working weeks/yr	49
Working hours/yr	8000

[a] Value from Zhang et al. [76]
[b] Value from Turton et al. [28]

Table 5.13: Economic parameters.

water and steam, and operating temperature, pressure and design specifications of unit operations and equipments. Once defined, any modification to the designated process model is automatically updated in the EIA module.

Comp.	HTPI[a] (mg/kg)	HTPE[b] (ppm)	ATP[c] (ppm)	TTP[a] (mg/kg)	GWP[d]	PCOP[d]	AP[d]	ODP[d]	EF
TG	-[e]	-	-	-	-	-	-	-	-
MeOH	5628	200	29400	5628	-	0,123	-	-	-
NaOH	-	2	-	-	-	-	-	-	-
Glycerol	12600	10	58,5[f]	12600	-	-	-	-	-
FAME	-	-	-	-	-	0,223	-	-	-
Water	-	-	-	-	-	-	-	-	-
H_3PO_4	1530	1	-	1530	-	-	-	-	-
Na_3PO_4	4150	15	220[g]	4150	-	-	-	-	-
SO_x	1,2	-	-	1,2	-	-	1	-	0,00272
NO_x	0,78	-	-	0,78	-	-	1,77	-	0,001814
CO_2	-	-	-	-	1	-	-	-	0,3719
HCl	-	-	-	-	-	-	0,88	-	0,00009
Methane	-	-	-	-	35	0,007	-	-	0,4763
Mercury	-	0,025	500	-	-	-	-	-	$4{,}90 \times 10^{-9}$

[a]LD50 (Oral-Rat)
[b]TWA-TLV (CGIH)
[c]LC50 (Fathead Minnow)
[d]Classification factors published by Heijungs et al. [39]
[e]Denotes either nonapplicable or nondetermined data
[f]LC50 (Trout)
[g]LC50 (Bluegill Sunfish)

Table 5.14: Score value of the PEI of components.

5.7.5 Assessment results

Table 5.15 shows the economic performance of both cases. Case 1 has a lower total capital investment (TCI) value as compared to Case 2. Since Case 2 is operated at an extremely high pressure and temperature, the equipment cost increases especially for the transesterification reactor and methanol recovery column, because of expensive material and a huge heat transfer area for heat exchangers, reboilers and condensers. Furthermore, the huge requirements for recirculation of large amounts of methanol into the process increases the pump load, thus increasing its price due to expensive material and high energy consumption. On the other hand, Case 2 has a lower total production cost (TPC). Because Case 2 requires no catalyst, acid and also water, it manages to cut down the overall production costs despite of a high demand of utility. For the plant life cycle of 15 years, Case 1 has a shorter payback period than Case 2 with a higher percentage of DCFRR. However, since Case 2 has a lower production cost, it is able to compensate a high initial investment and obtained a higher NPV at the end of the plant life cycle. In a long run, Case 2 is economically feasible. This economic trend agrees with the work by West et al. [81]. It seems that in the economic point of view, supercritical methanol is a promising alternative. But when it comes to sustainability, this criterion alone is not enough for a process design decision.

In this paragraph, the results on environmental and social aspects will be discussed. The environmental assessment results for both cases are shown in Figure 5.11. Figure 5.11a gives the potential environmental impact for the process material input streams. It is found that Case 1 has a higher PEI input value than Case 2, which is caused by the presence of catalyst for the transesterification reaction and acid for neutralization of the catalyst. Although Case 2 does not use any other components besides the reactants, it does consume 9% more methanol than Case 1. This increases significantly the PEI value, but it is still lower than Case 2. Apparently, this result seems to influence the PEI value of the process material output streams. Note that the output stream assessment excluded the biodiesel and glycerol product streams so as to avoid unnecessary penalization for producing chemicals with high demands. As indicated in Figure 5.11b, the PEI for the output stream of Case 2 is more environmentally friendly than Case 1. Given that Case 2 requires no catalyst and acid, and water washing step, the amount and type of raw materials is reduced, and so is the amount of effluents and wastes generated. Overall, as far as the process material is concerned, Case 2 performs better than Case 1. However, a contrary result is found when energy usage is taken into consideration. Figure 5.11c shows the PEI output energy of both processes, which indicates that Case 2 has a higher value. This result is expected, since Case 2 operates at a very high pressure and temperature, and thus it consumes a large amount of energy. Furthermore, the requirement for recirculation of a large amount of methanol to the process also contributes significantly to energy consumption. This finding agrees with the study conducted by Kiwjaroun et al. [82].

For the social criteria, the evaluation of both processes is heuristic based, due to the soft type indicators whose score is indicated in Table 5.16. Justification for each indicator is also provided in the table.

	Case 1	Case 2
NPV, \$ x 10^3	3.365	4.073
DCFRR, %	27	18
Payback period, yr	5,5	8,2
Total capital investment (TCI), \$ x 10^3	1.947	4.141
Total production cost (TPC), \$ x 10^3	10.706	10.525

Table 5.15: Economic performance.

Soft indicators	Score		Justifications
	Case 1	Case 2	
Safety during operation	5	3.5	Case 2 operates at very high pressure and temperature thus exposes a higher risk to workers.
Operability of the plant	5	6	Case 2 involves integrated equipment e.g. heat exchanger and reactor. This may impose difficulty to process control because of influence of disturbances from other equipments. On the other hand, Case 2 is able to compensate high amount of FFA in the feedstock. Therefore enable the use of used cooking oil as feedstock. Furthermore, exclusion of water and catalyst eliminate saponification and soap formation effect.
Safe start-up and shut-down	5	3	Operation at very high pressure and temperature usually requires tedious and complicated start-up and shut-down procedure.
Design should meet location specific demands	10	10	Criteria meet.

Table 5.16: Social criteria assessment results.

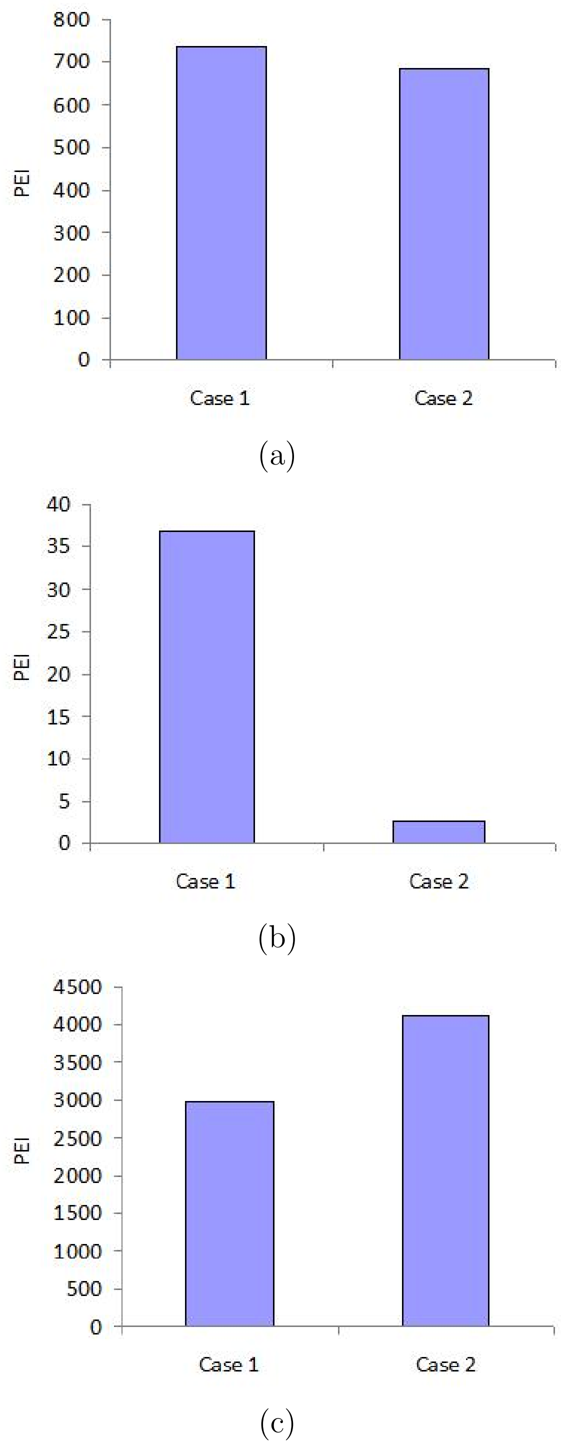


Figure 5.11: Total rate of PEI for (a) input material stream (b) output material stream (without product streams) and (c) energy consumption.

5.7.6 Decision making

Weight assignment and ranking of indicators

Table 5.17 shows the weights assignment and corresponding priority value. Since weight assignment is subjective justification for such a decision is important. As previously mentioned, the economic feasibility of the biodiesel industry is vital for its survival. Although there has been increasing awareness regarding the environment, biodiesel production generally uses and produces non-toxic and non-pollutant materials. Therefore, in general, economic consideration is more important than environmental concern. On the other hand, social aspects are also important. Since environmental issues are a non-determinant sustainability factor of biodiesel production, social-related criteria such as safety and operability should be emphasis for producing quality products in a timely manner. Overall for the second level, the economy and social criteria influence 46% and 32% of the total decision, respectively, whilst the environmental influence is 22%. The remaining weights assignment and priority value for the third and fourth levels are shown in Table 5.17. Note that the weights assigned to the normalized vectors indicate the percentage importance of the criteria in the overall decision of its parent level.

Evaluation

Performing evaluation in AHP needs the assessors to be aware of the contradictory behavior between the value desirability of the indicators that are sometimes overlooked namely higher-value-higher-desirability (HVHD) and lower-value-higher-desirability (LVHD). While the HVHD is obvious, such as profits, the LVHD refers to the inverse behavior which prefers a lower value. This type of behavior is closely related to the environmental indicators, such as CO_2 emission and the PEI. Such proportional and inverse value desirability behavior could create confusion, especially for the ranking purpose. Therefore, in order to make the evaluation consistent, a score-based approach is proposed. The approach works by converting the indicator value into a score of 1 to 10. For indicators with the HVHD behavior, a high value is assigned to a high score. Inversely, for a LVHD indicator, a low value is assigned to a high score. Detailed discussion on this approach is presented in Chapter 3. Once the corresponding score has been defined, the procedure for calculation of the normalized value remains the same and variation of the value margin does not affect the normalization value.

Scoring

Figure 5.12 illustrates the scores index for all criteria and the final solution. The score index for the economic criteria in Figure 5.12a shows that Case 2 has its advantage over Case 1. As previously mentioned, Case 2 has a lower production cost, which contributes to a long term profit, despite having a higher initial investment cost. However, for the environmental criterion, Case 1 is environmentally more friendly than Case 2 (see in Figure 5.12b), which is due to its large energy consumption. Note than the environmental score is an inverse of the indicators value. Figure 5.12c depicts the score index for the social indicators. Case 1 has the advantage

2nd level

Goal	Economy	Environment	Social	PV
Economy	1,00	2,00	1,50	0,46
Environment	0,50	1,00	0,67	0,22
Social	0,67	1,49	1,00	0,32

3rd level

Economy	NPV	DCFRR	PV		
NPV	1,00	1,50	0,60		
DCFRR	0,67	1,00	0,40		
Environment	TRO	TOP	TRG	TGP	PV
TRO	1,00	2,00	2,00	2,00	0,40
TOP	0,50	1,00	1,00	1,00	0,20
TRG	0,50	1,00	1,00	1,00	0,20
TGP	0,50	1,00	1,00	1,00	0,20
Social	SO	OP	SSS	DMLSD	PV
SO	1,00	2,00	3,00	4,00	0,47
OP	0,50	1,00	2,00	3,00	0,28
SSS	0,33	0,50	1,00	2,00	0,16
DMLSD	0,25	0,33	0,50	1,00	0,09

4th level

TRO	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP	PV
HTPI	1	1	1	1	0,5	1	1	1	0,11
HTPE	1,00	1	1	1	0,5	1	1	1	0,11
ATP	1,00	1,00	1	1	0,5	1	1	1	0,11
TTP	1,00	1,00	1,00	1	0,5	1	1	1	0,11
GWP	2,00	2,00	2,00	2,00	1	2	2	2	0,22
PCOP	1,00	1,00	1,00	1,00	0,50	1	1	1	0,11
AP	1,00	1,00	1,00	1,00	0,50	1,00	1	1	0,11
ODP	1,00	1,00	1,00	1,00	0,50	1,00	1,00	1	0,11
TOP	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP	PV
HTPI	1	1	1	1	0,5	1	1	1	0,11
HTPE	1,00	1	1	1	0,5	1	1	1	0,11
ATP	1,00	1,00	1	1	0,5	1	1	1	0,11
TTP	1,00	1,00	1,00	1	0,5	1	1	1	0,11
GWP	2,00	2,00	2,00	2,00	1	2	2	2	0,22
PCOP	1,00	1,00	1,00	1,00	0,50	1	1	1	0,11
AP	1,00	1,00	1,00	1,00	0,50	1,00	1	1	0,11
ODP	1,00	1,00	1,00	1,00	0,50	1,00	1,00	1	0,11
TRG	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP	PV
HTPI	1	1	1	1	0,5	1	1	1	0,11
HTPE	1,00	1	1	1	0,5	1	1	1	0,11
ATP	1,00	1,00	1	1	0,5	1	1	1	0,11
TTP	1,00	1,00	1,00	1	0,5	1	1	1	0,11
GWP	2,00	2,00	2,00	2,00	1	2	2	2	0,22
PCOP	1,00	1,00	1,00	1,00	0,50	1	1	1	0,11
AP	1,00	1,00	1,00	1,00	0,50	1,00	1	1	0,11
ODP	1,00	1,00	1,00	1,00	0,50	1,00	1,00	1	0,11
TGP	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP	PV
HTPI	1	1	1	1	0,5	1	1	1	0,11
HTPE	1,00	1	1	1	0,5	1	1	1	0,11
ATP	1,00	1,00	1	1	0,5	1	1	1	0,11
TTP	1,00	1,00	1,00	1	0,5	1	1	1	0,11
GWP	2,00	2,00	2,00	2,00	1	2	2	2	0,22
PCOP	1,00	1,00	1,00	1,00	0,50	1	1	1	0,11
AP	1,00	1,00	1,00	1,00	0,50	1,00	1	1	0,11
ODP	1,00	1,00	1,00	1,00	0,50	1,00	1,00	1	0,11

Table 5.17: Weights assignment and priority value.

over Case 2, as reflected by a larger area. Mainly, a process that is operated at a lower temperature and a lower pressure is more preferable due to safety concerns and the simplicity of operation, start-up and shut down procedures. But the main advantage of Case 2, however, is the capability of processing oil feed materials with a high content of FFA. Thus, it is able to provide better plant operability despite the variation in oil FFA content. This crucial attribute manages to close up the social advantage gap between these two processes.

Overall, the total score index of all criteria is summarized in Figure 5.12d. It is found that Case 2 is more economically desirable, but the other two criteria prefer Case 1. Unlike any other decision-making methodology, AHP considers not only the quantitative evaluation of indicators but also the trade-off between the elements in the decision environment which make the decisions more justified. Adding all the scores for the criteria, the final result prefers Case 1 with 16,9% higher preferability compared to Case 2. This difference is very much influenced by the modifications made to the process models and also the weights in the AHP procedure.

5.8 Concluding remarks

In this work, we present a systematic and modularized framework for sustainability assessment and selection of chemical process design alternatives. The framework of the assessment methodology utilizes specifically defined indicators that consider both 'hard' and 'soft' performance of process design. It does not only offer a quantitative evaluation, but also imparts knowledge-based solutions, thereby providing the decision makers with important and holistic information for achieving sustainable design. A multi-criterion decision hierarchy is also established to embed the indicators, and the AHP methodology is adopted for performing trade-offs between the economic-environment-social criteria in solution derivation. The assessment and decision support methodology is built in four modules with an integrated function utilizing the integration capabilities of process simulators and spreadsheet. With its structured form, the assessors are able to focus on the real issues involving process design development. Furthermore, it allows the involvement of a multi-disciplinary team in process design evaluation. The case study on biodiesel process evaluation shows the methodological effectiveness in assessing sustainable conscious process design and supporting persuasive decision making thus shows its pre-eminence over commonly practiced techno-economy evaluation approaches.

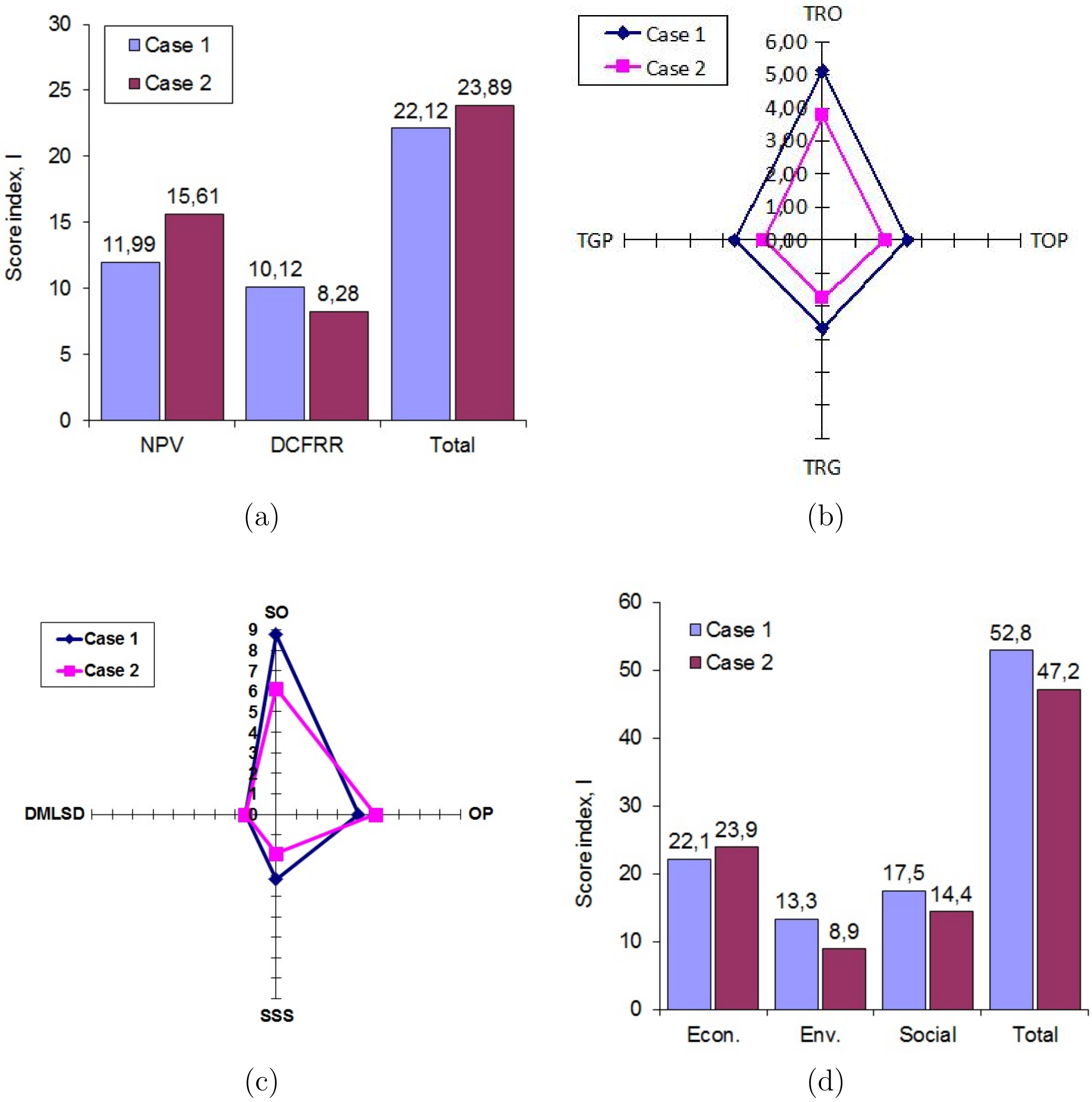


Figure 5.12: Score index for (a) economic criteria, (b) environmental criteria, (c) social criteria, and (d) overall final result.

Chapter 6

Effect of Indicators Definition

6.1 Introduction

Evaluation of the sustainable design option requires identification of specifically defined indicators that represent the economic, environmental and social performance of a design. In recent years there are many new sustainability measurements using different indicators proposed by individuals, groups of researchers or organizations, to measure sustainability performance of a plant [84, 9, 8]. Commonly, these indicators are evaluated in parallel whereby each indicator that represents each criterion is assessed separately. To come up with an overall result, weights might be introduced to each indicator or criteria.

In recent development, there are efforts to use a single indicator such as emergy. In general, emergy is the available energy of one kind previously required, directly and indirectly, to make products or services. Using a single indicator able to simultaneously represent the sustainability of industrial systems, especially the environment and economic criteria [37] and make it less dependable towards weights effect. The drawback is however, a single value could create confusion and difficulty particularly when analyzing the direct effect of individual criteria to the overall design evaluation, especially when changes occur to the initial design.

When relating sustainability measurement to decision making, indicators are used to represent the decision problem hierarchy. Obviously, different sustainability measurements elucidate different decision hierarchies. The method used in our work for example consists of ten indicators whereas if we take the IChemE sustainability metric, it consists of 49 different indicators. Comparing these two examples, IChemE provides a very comprehensive but rather complex sustainability assessment. While each method is useful in assessing sustainability, it will be interesting to compare these different methods toward decision making. In this chapter, we study the effect of using different sustainability measurements towards decision preferability. In doing so, we compare our assessment methodology to that of IChemE sustainability metrics [8]. Our aim is basically to observe the effect of different sustainability measurements on the overall decision making preferability.

6.2 Assessment method

In Chapter 2 we proposed two types of indicators; hard and soft. The former gives quantitative assessment while the latter gives qualitative assessment. While hard indicators are based on sets of equations, soft indicators depend on the assessors knowledge and experience. The hard indicators were applied to economic and environmental criteria. Net present value (NPV) and discounted cash flow rate of return (DCFRR) represent the economic performance while the environmental criteria are assessed using a waste reduction (WAR) algorithm [31]. In the WAR algorithm, it defines four indicators that assess the potential environmental impact (PEI) of a particular design. For all indicators, lower PEI values are preferred. The social indicators, on the other hand are soft based. It was based on the criteria of good quality design proposed by Herder & Weijnen [45]. Because of the heuristics behavior of the criteria, it is converted into numbers using scaling systems, as was commonly used in safety and operability related analysis. Although very subjective, it plays an important role in obtaining a rapid assessment without the need for extensive data search. The IChemE sustainability metrics was introduced in 2002 by a group of academia, consultants and industrialists after three years of intensive work. It introduced a set of indicators as a practical tool for practicing engineers using, as far as possible information readily available to measure the sustainability performance of a process system. When adopting IChemE's approach, it is important to define the system boundaries as they could range from resource extraction to final disposal. It also important to note that all indicators suggested, however, may not be applicable in all cases. Therefore, assessors should carefully review that each indicator is fully compatible with the case being reviewed for a more meaningful evaluation.

Figure 6.1 and 6.2 show the problem decomposition for the two sustainability measurements namely Othman et al. [84] and IChemE Sustainability Metrics [8], respectively. Othmans approach consists of four levels of decision hierarchies. The first level is the decision objective which is to select a sustainable process design. It is then expanded into the second level that consists of the three pillars of sustainability. Each of these criteria is then expanded into the third level in which each criterion is represented by specifically defined indicators. The fourth level is the alternative to be assessed. IChemE sustainability metrics, on the other hand, is divided into six levels of decision hierarchies. The first and second levels are the same as in Othman and remaining levels of evaluation indicators are shown in Figure 6.2. Note that the sixth layer is the alternative to be assessed but is not shown in the figure. As one can see from these figures, IChemE indicators offers a substantial detail evaluation of a sustainable industrial system compared to our measurement indicators.

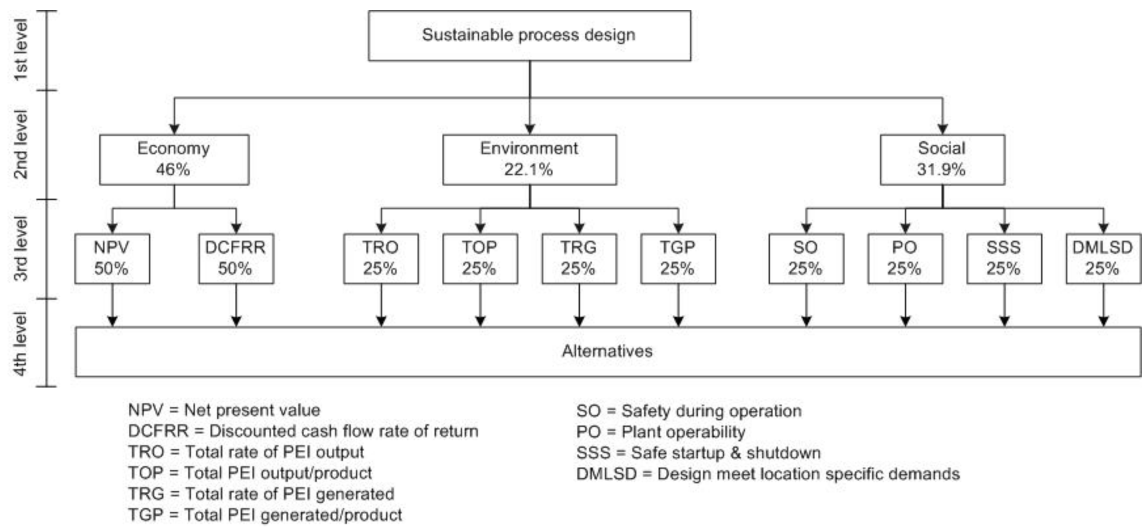


Figure 6.1: Problem decomposition from our work and its priority value.

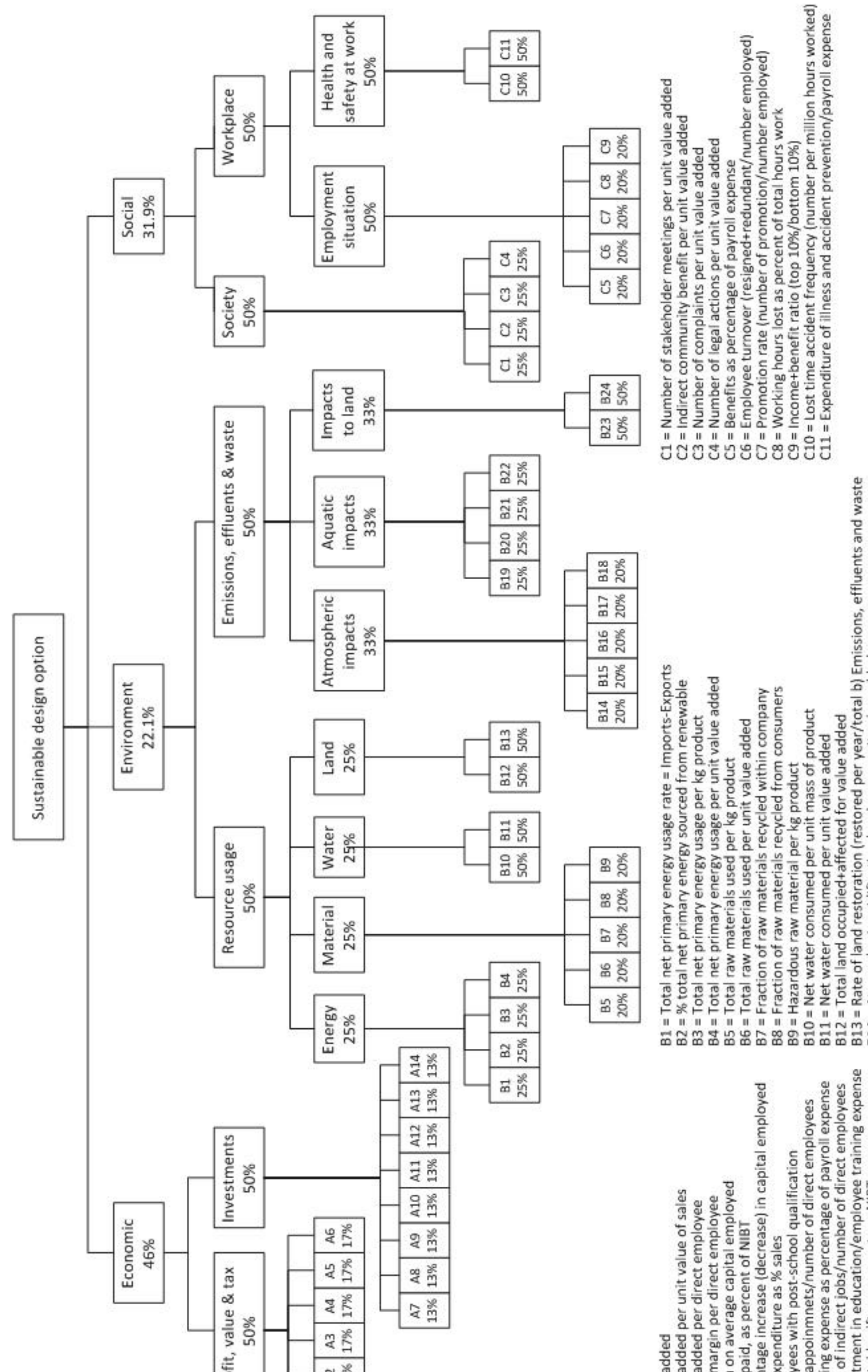


Figure 6.2: Problem decomposition based on IChemE sustainability metrics [8] and its priority value.

6.3 Case study: Biodiesel process

To demonstrate the effect of using different sustainability assessments to process decision making, two biodiesel processes; alkali-based catalyst (Case 1) and supercritical methanol (Case 2), will be used. Details on these two processes have been presented in the previous chapter. In summary, Case 1 is mostly preferred because of its efficiency, less corrosive, and operated at low temperature and pressure with a high conversion yield. However, it is sensitivity to the purity of reactants, e.g., water content and free fatty acid (FFA) that could lead to formation of emulsion and soap which consume the catalyst, and hinders the transesterification reaction. Moreover, the formation of emulsions can cause difficulties in downstream recovery and biodiesel purification. In recent years, researchers began to investigate producing biodiesel at supercritical conditions. It offers several advantages, including non-catalyst process, insensitive to both water and FFA, and simultaneous esterification of FFA in oil. Recent studies on supercritical methanol show that it is technologically and economically promising [81, 79]. However, high operating temperature and pressure may hinder it from being commercially feasible since it requires large energy demand and indirectly leads to release of more pollutants resulted from a high consumption of energy resource.

6.3.1 Assessment result

The assessment results based on our methods have been presented in detail in Chapter Five. In this chapter only the results of the IChemE method will be discussed. As depicted in Figure 6.2, the IChemE approach offers 49 indicators. Some of the indicators can be obtained through modeling efforts while others depend on historical data. The historical data are only obtainable either from an already operating plant or from other similar existing plants. This back-driven assessment requires extensive data and may not be available particularly for a newly developed process. Examples such as lost time accident frequency, expenditure of illness and accident prevention/payroll expense, number of stakeholder meetings per unit value added, indirect community benefit per unit value added, number of complaints per unit value added, number of legal actions per unit value added, etc., are all back driven assessments which are subjected to already existing and operating plants with a few years of operation history. To overcome this, there are some indicators which we have to assume. In particular to the socially related indicators we set both processes with the equal assessment value. In reality however, this might not be true. It is suggested to conduct a more comprehensive investigation for a more realistic result.

6.4 Decison making

6.4.1 Weights setting and value-desirability classification

As mentioned earlier, weights setting is subjective. For a fair comparison we decided to only set different weights to the second level decision hierarchy while the others were set with equal weights as depicted in Figure 6.1 and 6.2. Note that the priority value assigned to each indicator indicates the percentage importance of the element corresponding group level. For example, in the second level, the economy and social criteria influence is 46,1% and 31,9% of the total decision, respectively, whilst the environmental influence is 22,1%.

Another important step to be conducted is the classification of indicators value-desirability behavior. Such classification depends heavily on the indicators characteristics. Generally, economic indicators are the HVHD type while environmental indicators are LVHD type. Social indicators on the other hand might be HVHD or LVHD. Table 6.1 shows the behavior classification of the indicators for both methods.

6.4.2 Decision results and discussions

Figures 6.3(a) and (b) show the overall decision results of our approach and IChemE, respectively. From both methods, it is found that Case 2 is more economically desirable. The fact that Case 2 manages to cut down the overall production costs despite the high utility demand contributes to its higher profitability at the end of its plant life cycle. The environmental criteria assessment however resulted with a contradictory result. Our approach prefers Case 1 whereas IChemEs prefers Case 2. In our approach the environmental impact is based on the direct effect of the material streams and the indirect effect of energy usage. On the other hand, the IChemE approach only focuses on the effect of material streams, and the indirect potential harm by energy usage is neglected. This assumption has lead the IChemE approach to assess Case 2 to be environmental friendlier, since it only measures the environmental impact associated with raw materials usage.

For the social criteria, Othmans approach is heuristic based, due its soft type indicators. It assesses other aspects of a quality design that includes safety, operability, safe start-up and shutdown and design meet location specific demands. Based on this indicator it prefers Case 1. Generally a process that operates at a lower temperature is preferable due to safety concerns and also simplicity of operating, start-up and shut down procedures. On the other hand, the IChemE approach is more quantitative. It reflects the company's attitude towards the treatment of its own employees, suppliers, contractors and customers, and also its impact on society at large. Although these indicators give a holistic assessment, at early design stages the data needed for indicator calculation are often limited or unavailable. Because of these limitations, both cases are assumed to have the same social performance. However, if applicable, historical data from previous plant experience or internal company information can be used as a basis of calculation. Overall summation of each criterion value shows that Othmans approach prefers Case 1 whereas for the IChemE approach however, elucidates contradictory result whereby Case 2 is preferred over Case 1. From these findings several important points can be extruded. First, defining appropriate and relevant indicators to measure sustainability is of utmost importance. While each method involves specific sets of indicators, in contexts of decision making, selection preferability may differ. In the two methods studied above both of them particularly show the same result for economic feasibility, but not to the other two criteria. This result is quite interesting. We believe that since

Criteria	Indicator	HVHD	LVHD
Economy	*NPV	x	
	*DCFRR	x	
	Value added	x	
	Value added per unit value of sales		x
	Value added per direct employee	x	
	Gross margin per direct employee	x	
	Return on average capital employed	x	
	Taxes paid	x	
	Percentage increase (decrease) in capital employed	x	
	R&D expenditure as % sales	x	
	Employees with post-school qualification	x	
	New appointments/number of direct employees	x	
	Training expense as percentage of payroll expense	x	
	Ratio of indirect jobs/number of direct employees		x
	Investment in education/employee training expense	x	
	Charitable gifts as percentage of NIBT	x	
Environment	*Total rate PEI output		x
	*Total PEI output/product		x
	*Total rate PEI generation		x
	*Total PEI generation/product		x
	Total Net Primary Energy Usage rate		x
	% Total Net Primary Energy sourced from renewable	x	
	Total Net Primary Energy Usage per kg product		x
	Total Net Primary Energy Usage per unit value added		x
	Total raw materials used per kg product		x
	Total raw materials used per unit value added		x
	Fraction of raw materials recycled within company	x	
	Fraction of raw materials recycled from consumers	x	
	Hazardous raw material per kg product		x
	Net water consumed per unit mass of product		x
	Net water consumed per unit value added		x
	Total land occupied + affected for value added		x
	Rate of land restoration (restored per year/total)	x	
	Atmospheric acidification burden per unit value added		x
	Global warming burden per unit value added		x
	Human Health burden per unit value added		x
	Ozone depletion burden per unit value added		x
	Photochemical ozone burden per unit value added		x
	Aquatic acidification per unit value added		x
	Aquatic oxygen demand per unit value added		x
	Ecotoxicity to aquatic life per unit value added		x
	Eutrophication per unit value added		x
	Hazardous solid waste per unit value added		x
	Non-hazardous solid waste per unit value added		x
Social	*Safety during operation	x	
	*Operability of the plant	x	
	*Safe start-up and shutdown	x	
	*Design should meet location specific demands	x	
	Benefits as percentage of payroll expense	x	
	Employee turnover		x
	Promotion rate	x	
	Working hours lost as percent of total hours worked		x
	Income + benefit ratio (top 10%/bottom 10%)	x	
	Lost time accident frequency		x
	Expenditure on illness and accident prevention/payroll expense		x
	Number of stakeholder meetings per unit value added	x	
	Indirect community benefit per unit value added	x	
	Number of complaints per unit value added		x
	Number of legal actions per unit value added		x

* based on our work

Table 6.1: Classification of indicators value-desirability behavior.

the measurement of economic performance is very well established, assessors tend to use the same or similar method, i.e., NPV as a standard assessment methodology. As such, both methods elucidate the same preference. On the other hand, the indicators to measure environment and social criteria are still debatable. Even though there are some internationally known methods to assess them such as Eco99 and LCA, there is still some organizations or individual adopt different methods to measure the environmental and social performance. We think that because the awareness of environmental importance is beginning to rise in the last few decades, research is still being conducted to find the best approach to measure them. Thus, it is very important for the chemical engineering community to establish a standardized approach to assess environmental and social aspects. When this is likely to happen, chemical industries practitioners still have the opportunity to define their own methods and select one that would help create good image for their company.

Besides that, it is suggested that for assessment and decision making at early design stages, the indicators should be less data-extensive but on the other hand should also not be under justified. Nevertheless, to give a balanced and meaningful analysis, a standard and common definition of each criteria, especially the environment and social, should specifically characterize the sustainability performance of a process system that is based on the assessment and decision making objective. In addition, it is also important that the assessors are capable of evaluating the performance of the process system with sound knowledge and experience.

6.5 Concluding remarks

In this work, we present a process decision making based methodology for the selection of a sustainable process design option. AHP is adopted for performing trade-off between the economic-environment-social criteria in solution derivation. Using the methodology, we compare our approach to that of IChemE sustainability metrics aiming to study the effect of different assessment methodology toward the overall decision making results. Case studies on two biodiesel processes are chosen to demonstrate the applicability of the approach. From our observation, we found that the elucidation of the final result preferability is affected among others by:-

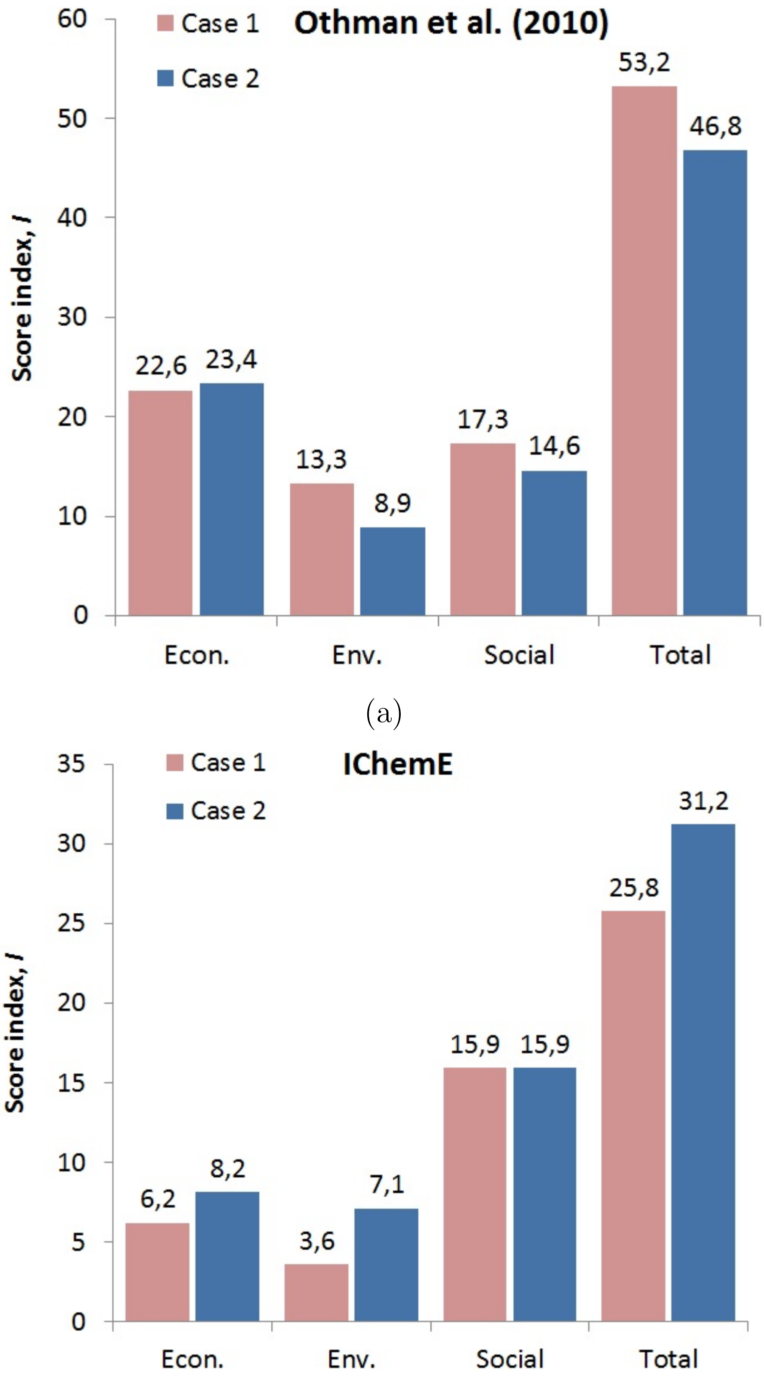
1. Design modifications

2. Definition of the selected indicators

3. Assessors competency

4. Weights setting in AHP

It is suggested that for assessment and decision making at early design stage the indicators should not be too data-extensive, but on the other hand should not also to be under justified. In addition, it is also important that the assessors are capable of evaluating the performance of the process system with sound knowledge and experience. Overall, the PDM methodology is effective in assessing sustainable



(b)

Figure 6.3: AHP selection result from (a) our proposed indicators (b) IChemE.

conscious process design over commonly practiced techno-economy evaluation approaches, and could assists engineers, designers and also students for selection of a sustainable chemical process design option.

Chapter 7

Incorporating Negative Values in AHP

7.1 Introduction

Various indicators have been proposed in the past by various researchers and organizations. Normally, decision making using AHP involves indicators with positive value without realizing few indicators are constrained to be non-positive such as debts, assets, loss and expression of undesirability [85]. Some of the indicators mentioned above, despite having positive value, may span over into negative value. Calculating profitability, for instance, could result in negative value, which indicates losses. Other than that, social indicators could also have negative preferences to express undesirability. In addition, the decision indicators may also have different or contradictable value-desirability behavior. As previously mentioned this can be categorized as either higher-value-higher-desirability (HVHD) or lower-value-higher-desirability (LVHD). While HVHD behavior is obvious for example in measuring profitability, LVHD refers to decision indicators which prefer lower value for example environmental indicators, i.e., potential environment indicator (PEI) value, CO2 emission, etc.

Applying conventional AHP in presence of the above mentioned conditions will become challenging and could elicit spurious and inconsistent results unless some modifications are made to the AHP process. Millet and Schoner [85] mentioned two typical approaches to handle positive and negative values in the AHP. The first is to handle positive and negative value separately and to calculate a benefit to cost ratio. The second approach, which is a standard method, involves inverting negative values into positive preferences. They then proposed a new approach called Bipolar AHP (BAHP) that introduces modifications to the AHP software user interface, and also its computational process. It provides a simple solution to accommodating negative preferences while maintaining a true zero reference point. The approach however is highly software dependable and it does not consider the value-desirability behavior of the indicators.

To overcome this, a new approach is proposed using a rule-based scoring methodology. This approach requires several simple modifications to the ranking and evaluation step of AHP. The first step involves defining each indicator according to its value-desirability behavior. Using specific conversion factors, the indicators value is converted into a credit-penalize score reflecting desirability-undesirability. In the evaluation step, treating both positive and negative value simultaneously, however, may create scenarios which can pose numerical inconsistencies. Therefore, a rule-based approach is proposed to accordingly treat each scenario to elicit the final solution.

7.2 Overview of the methodology

Figure 7.1 shows the overall modified AHP process incorporating the proposed methodology. The modifications introduced are shown in the ranking and evaluation step (step 3 and 4 of the figure). As previously mentioned decision indicators may span to positive-negative values and in addition may also have contradictable value-desirability behavior. The idea is to convert the initial indicators value to a scoring system with a credit-penalize concept reflecting the accommodation of both HVHD and LVHD behavior. Through this concept any desirable value is credited with a positive score, while undesirability is penalized with a negative score. Such concepts will ensure that negative preferences are taken into consideration in the overall score instead of positively making it to a lower preferable value.

The conversion of the assessment value v, into its corresponding score V, depends on its behavior which can be categorized as follows:-

Category 1: Credit score with HVHD behaviour for $v_{0\to\infty}$ and $T_{x\to y} > 0$

$$V^{ij} = \frac{v^{ij}}{T_x^{ij}}\left(V_x^{ij}\right), V_x^{ij} > V_y^{ij}, T_x^{ij} > T_y^{ij} \tag{7.1}$$

Category 2: Penalize score with HVHD behaviour for $v_{0\to-\infty}$ and $T_{x\to y} < 0$

$$V^{ij} = \frac{v^{ij}}{T_y^{ij}}\left(V_y^{ij}\right), V_x^{ij} < V_y^{ij}, T_x^{ij} < T_y^{ij} \tag{7.2}$$

Category 3: Credit score with LVHD behaviour for $v_{0\to\infty}$ and $T_{x\to y} > 0$

$$V^{ij} = V_x^{ij} - \left[\frac{v^{ij}}{T_x^{ij}}\left(V_x^{ij}\right)\right], V_x^{ij} < V_y^{ij}, T_x^{ij} < T_y^{ij} \tag{7.3}$$

Category 4: Penalize score with LVHD behaviour for $v_{0\to\infty}$ and $T_{x\to y} > 0$

$$V^{ij} = \left[\frac{v^{ij}}{T_x^{ij}}\left(V_x^{ij}\right)\right], -V_x^{ij} < -V_y^{ij}, T_x^{ij} > T_y^{ij} \tag{7.4}$$

Category 5:Credit score with LVHD behaviour for $v_{0\to-\infty}$ and $T_{x\to y} < 0$

$$V^{ij} = \left[\frac{v^{ij}}{T_x^{ij}}\left(V_y^{ij}\right)\right], V_x^{ij} < V_y^{ij}, T_x^{ij} < T_y^{ij} \tag{7.5}$$

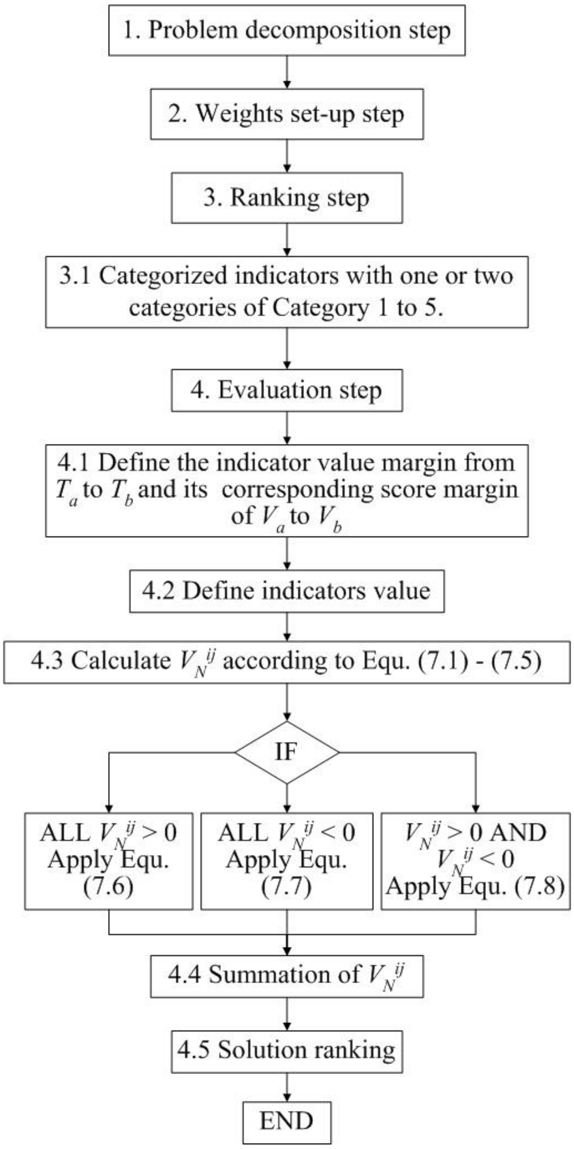


Figure 7.1: Modified flow diagram of the AHP steps

where v_{ij} is the assessment value of i-th criteria for j-th indicator. The indicators value margin, $T_{a \to b}$ is set from the highest to the lowest value that corresponds to a score margin of $V_{x \to y}$. The ranking stage (step 3.1) requires the assessor to define each indicator as either one or two of the Category 1 to 5, reflecting the indicator's value-desirability behavior. This is important so that the indicators are evaluated to accordingly reflect its true behavior.

The evaluation step (step 4) involves firstly determining the range of $T_{x \to y}$ and its corresponding score margin of $V_{x \to y}$. Note that setting the score margin $V_{x \to y}$ however, depends on its value-desirability behavior. For HVHD high value is assigned with high a score while LVHD assigns low scores to high values. It is also important to note that a negative score is given to negative preferences as a penalization for its undesirability. After the indicators value has been defined (step 4.2), step 4.3 involve converting this value into its corresponding score using equation (1) to (5). The next step involves calculation of the normalized score using the weighting vectors determined in the weights set-up step and the score determined previously. The calculation is however not straight forward since the score spans over negative and positive values, and this creates contradicting scenarios that could affect the overall result. In order to correctly respond to each scenario, a rule-based approach is proposed. It consists of sets of rules to handle specific scenarios as follows,

Rule 1: IF $V^{ij} > 0$ THEN

$$V_{N,a}^{ij} = \frac{V^{ij}}{\sum_{a=1}^{k} V^{ij}} \left(n^{ij}\right) \tag{7.6}$$

Rule 2: IF $V^{ij} < 0$ THEN

$$V_{N,a}^{ij} = \frac{V^{ij}}{\sum_{a=1}^{k} V^{ij}} \left(-n^{ij}\right) \tag{7.7}$$

Rule 3: IF $V^{ij} < 0$ AND $V^{ij} > 0$ THEN

$$V_{N,a}^{ij} = \frac{V^{ij}}{\sum_{a=1}^{k} V_{pos}^{ij} - \sum_{a=1}^{k} V_{neg}^{ij}} \left(n^{ij}\right) \tag{7.8}$$

where $V_{N,a}^{ij}$ is the normalized score for the j-th indicator in the i-th criteria of an alternative a, k is the number of alternatives, n^{ij} is the normalized priority value, PV of the j-th indicator of criteria i and V_{pos} and V_{neg} are the positive and negative assessment score, respectively. Applying these rules helps to properly handle various situations of mixed positive and negative scores for correct and consistent solution rankings. Adopting the rule-based scoring methodology offers the opportunity for automated decision support using computer programs, i.e., spreadsheet, Visual Basic etc.

7.3 Application of the methodology

In 2003, Zhang et al. [76, 55] conducted a good techno-economic assessment on four simulated biodiesel processes, namely alkali-catalyzed systems using virgin oil

(Case 1), an alkali-catalyzed system using waste cooking oil (Case 2), acid-catalyzed process using waste cooking oil (Case 3) and an acid-catalyzed system using hexane extraction (Case 4). The process flowsheet and the simulated result from Zhang's work can be found in the Appendix C. Their simulation results concluded that all of these processes are proved to be technically and economically feasible but each had its limitations. Their conclusions however are limited to only techno-economic criteria, and furthermore, no selection and ranking of alternative methodologies were applied. To test the functionality of the proposed methodology the four biodiesel processes will be used as case studies in this work. As the work focuses only towards techno-economic assessment, additional work on environment and social assessment have been performed utilizing the data and reviews included in their work. To have varieties of scenarios, the environmental assessment will focus on the material usage. The lists of indicators and its categorical behavior are shown in Table 7.1. This table also includes the range of indicators value and its corresponding score used in this work. A spreadsheet program has been developed embedding all the equations mentioned earlier to assist decision making. The user only needs to provide the data or parameters as in Table 1 into the spreadsheet.

The results are shown in Figure 7.2. The proposed rule-based scoring methodology was able to recognize the positive-negative values and perform overall ranking of alternatives according to the normalized score priorities. Figure 7.2a shows the segregation of the results according to the three sustainability criteria. In economic evaluation Case 3 and 4 are the most promising. All options have negative net annual profit, but based on an after-tax rate of return and break-even price of biodiesel, the acid-catalyzed processes (Case 3 and 4) were economically competitive alternatives compared to the alkali process systems. These results are consistent with the work from Zhang [76, 55]. Environmental assessment shows a significant difference of environmental performance between different design systems whereby the alkali-catalyzed processes is environmentally friendlier than the acid-catalyzed systems. This result is contributed mostly by the large amount of methanol used by the acid-catalyzed system for transesterification reaction. The high amounts of calcium sulphate deposited also contribute to the high impact on the environment. Among cases in each system however, the difference is small.

Social criteria show almost similar scores for Case 1, 3 and 4. The fact that Case 2 was the most complex process with the greatest number of equipment because of the addition of a pretreatment unit for free fatty acid removal, make it the least preferable. The overall ranking of the four biodiesel processes is shown in Figure 7.2b. Introduction of penalization concepts makes alkali-catalyzed processes less preferable than the acid-catalyzed systems mainly because of its huge economic disadvantage. The most sustainable feasible design option is Case 3. Although environmentally unattractive, but taking into consideration the trade-off between the two other criteria, it perform better than others. However, it is important to note that the decision results using AHP are very sensitive. Any modifications made either to the process models or weights in the AHP weights set-up step could significantly affect the decision outcome. Overall, from the results obtained it shows the proposed methodology is able to successfully consider both desirability and undesirability in design assessment, which cannot be done in the conventional AHP.

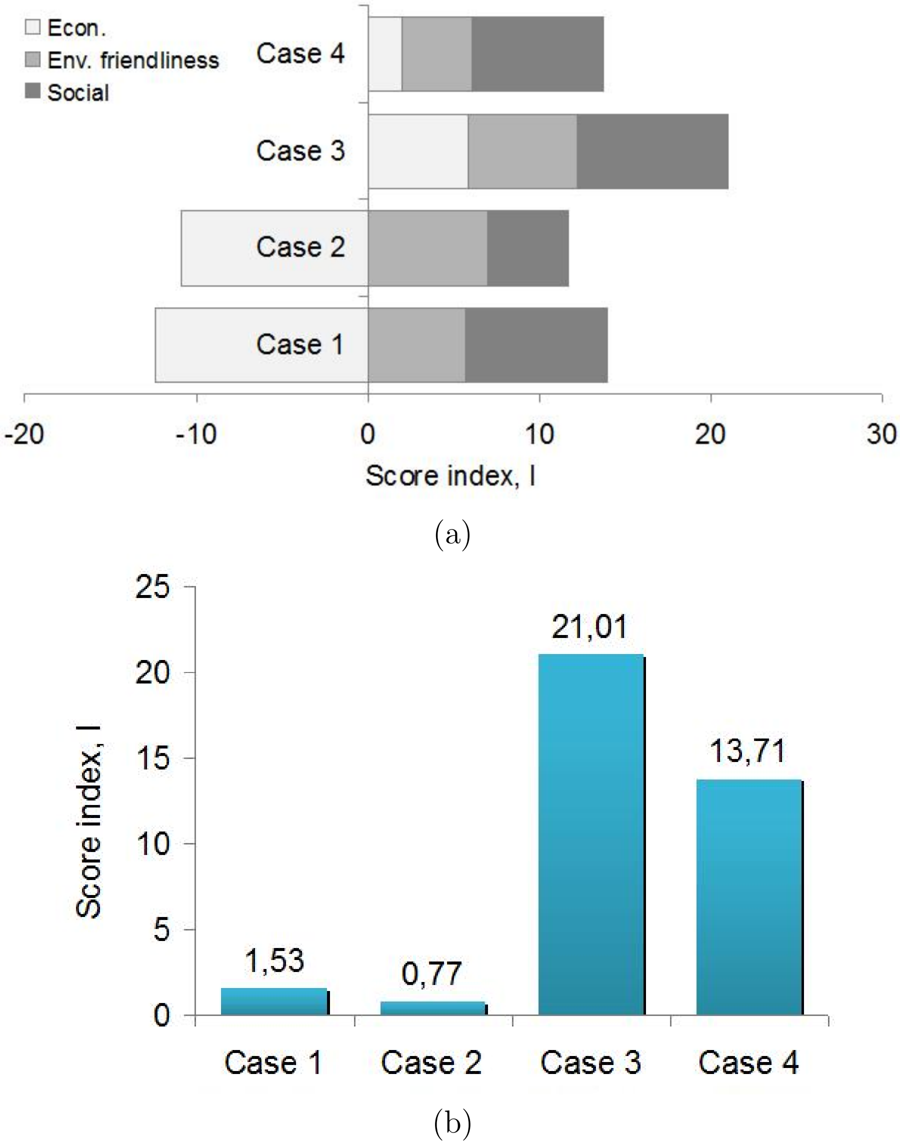


Figure 7.2: AHP (a) score for each criteria (b) overall ranking result

Indicators	Cat.	Case 1	Case 2	Case 3	Case 4	T_a	T_b	V_a	V_b
Economy									
Net annual profit, \$x10^{-6}	1,2	-2,06	-2,28	-0,35	-0,82	10	-2,28	10	-10
After tax rate of return, %	1	-85,27	-51,18	-15,63	-21,48	100	-100	10	-10
Break even price, \$	3	857	884	644	702	885	0	1	10
Env.friendliness									
Total rate of PEI output	3	224,04	100,40	271,05	589,72	600	0	1	10
Total PEI output/product	3	0,2	0,09	0,24	0,52	0,6	0	1	10
Total rate PEI generated	5	-2142	-2297	-3175	-3561	0	-4000	1	10
Total PEI gen./product	5	-1,92	-2,06	-2,81	-3,14	0	-4	1	10
Societal									
Safety during operation	1,2	3	2	3	2	10	-10	10	-10
Operability of the plant	1,2	3	-1	3	3	10	-10	10	-10
Safe start-up and shut-down	1,2	5	3	5	5	10	-10	10	-10
Fit for purpose	1,2	10	10	10	10	10	-10	10	-10
Design should meet location specific demands	1,2	10	10	10	10	10	-10	10	-10
Control of quality and quantity	1,2	-1	5	5	5	10	-10	10	-10
Maintenance	1,2	5	3	4	4	10	-10	10	-10

Table 7.1: Summary of the indicators values and the score conversion specification

7.4 Concluding remarks

A rule-based scoring methodology has been proposed to handle positive and negative preferences in process design selection and ranking. The functionality of the approach has been successfully demonstrated through the use of four biodiesel design options. It is able to correctly evaluate the credit-penalize score and provide consistent result despite the presence of various contradicting scenarios. The useful feature of this methodology is that the modification took place at the numerical calculation step of AHP, specifically at the ranking and evaluation step, thus enabling decision makers to focus more on the real issues in process design development. Potentially, such approach offers the opportunity for automated decision support, e.g., using spreadsheets.

Chapter 8

Decision Making Using ANP

8.1 Introduction

The design for sustainability in chemical process design considers the three pillars of sustainability namely, economic feasibility, environmental friendliness and social benefits. In reality however, agreeability among the criteria are not easily obtained, especially when dependencies exist between them. The decision will be more complex when conflict of interest between the decision makers; engineers and managers, are included in the decision making environment. While AHP has been very popular for solving MCDM problem, analytic network process (ANP) is less prominent in the literature. ANP, a more generalized approach, is an attractive multicriteria decision making tool because it allows for the consideration of interdependencies among and between levels of attributes [86]. It is a more accurate approach for modeling complex decisions, especially when interactions exist in the problem environment.

Since the introduction of AHP/ANP, there are bundles of engineering based research dedicated to its application. The implementation in process system engineering (PSE), specifically in chemical process design, is however uncommon. The objective of this chapter is twofold. The first is to discuss the various elements that influence the decision of sustainable chemical design option. The element not only considers the factors which are important to the technologist, e.g., engineers, but also factors that are important at the management level as well. The second objective is to adopt the ANP for selection of the sustainable chemical process design option which considers the interdependencies among the multi-elements within the problem decomposition. Four biodiesel process design options based on the work by Zhang et al. [76, 55] will be used to show the applicability of the proposed approach.

8.2 Decision framework

In selection of process design, the task must not be championed or made solely on what the engineers feel is important but also must take into account the reflection of other organizational functions such as managers. Omitting them from the decision making process can have detrimental organizational effects, but including them, increases the complexity and difficulty, as sometimes-conflicting agendas and objectives must somehow be resolved [87]. Considering this, there is a need to reconcile and integrate the needs and desires of different stakeholders in the decision environment. Herder and Weijnen [45] from their industrial and academic observation concluded top ten quality indicators. These qualitative indicators are suitable as the guideline to assess a good quality design since they utilize the heuristics knowledge of assessors in process design evaluation.

In this work, a decision framework combining quantitative and qualitative indicators to measure the system sustainability performance at early design stage is proposed. The approach utilizes the capability of process simulators for quantitative evaluation and human heuristics for qualitative evaluation. The approach provides a good tool to support decision making but the decision framework however is only focused within an engineers perspective.

In 2002, Meade & Presley [87] provided a decision framework for selection of R&D projects from management, marketing and technologist perspectives. It is in a generalized form but can be extended or adapted to meet a particular application. To take advantage of all of these works, we embed and integrate the relevant elements and come out with a new set of decision frameworks. The framework not only combines the technical and management requirements of a good design, it also introduces quantitative and qualitative evaluation. Also, the objective of the assessment is to evaluate a specific type of process with a few design options. But on the other hand, it is also useful to assess the performance of any modified or intensified basic design.

The decision framework is illustrated in Figure 8.1. The framework does involve representing relationships hierarchically, but does not have a strict structure as does AHP. It does include a system-with-feedback where a level may both dominate and be dominated, directly or indirectly, by other decision attributes and levels [86]. In general, the sustainability indicators are divided into two categories; hard and soft. Hard indicators give a quantitative evaluation of process using numerical information and formulas whilst soft indicators give qualitative evaluation which depends heavily on expert judgments that are mostly heuristic. The economic and environmental criteria and its indicators are associated with the hard category since there are quantitative methodologies to measure these indicators. On the other hand, the social and technical criteria are represented by soft-based qualitative indicators. These ill-defined indicators are very subjective because of different interpretations, and are often represented by specific scales as widely used in process safety engineering. In the end however, they play important roles in obtaining agreeable solutions.

To test the functionality of the proposed methodology, four biodiesel process options from Zhang's [76, 55], as describe in previous chapter, will be used as the case study.

8.3 Selection of sustainable option: ANP approach

8.3.1 Problem decomposition

The decomposed model in ANP is shown in Figure 8.1. The main goal of the assessment is to select the most sustainable chemical process design option that meets

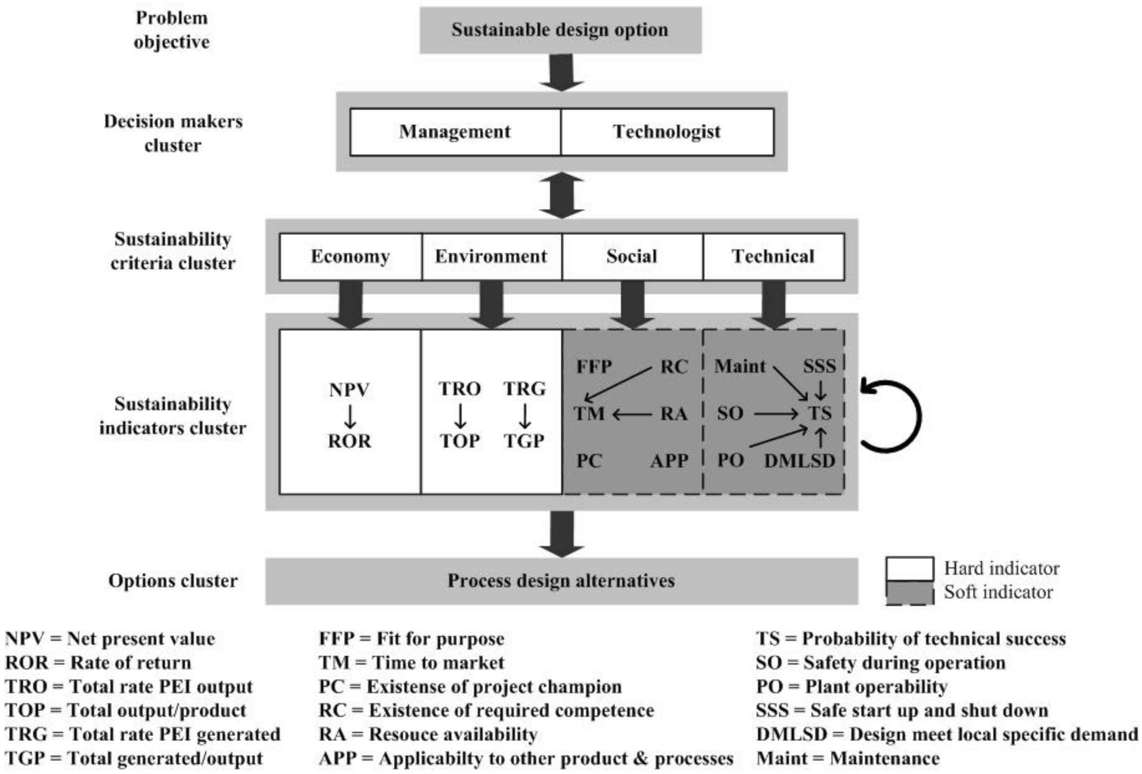


Figure 8.1: Decision framework based on ANP.

the sustainability criteria. The framework also contains interdependency between clusters in particular, between the decision makers cluster and sustainability criteria cluster. Other than that, the framework also includes inner dependencies among the elements within the sustainability indicator cluster. It is important for the decision makers when considering interdependencies in ANP to carefully analyze the feedback effect of the elements in each criteria cluster. This is because they may interact or have impact or influences by some or all of the elements of that cluster or another cluster with respect to a property governing the interaction of the entire system, such as energy or capital. Taking care of this agenda is crucial to ensure that the model resembles the problem being addressed and thus, elucidate significant and convincing results.

8.3.2 Pairwise comparisons and priority vectors

Performing pairwise comparison and calculating priority vectors follows the typical procedure. However, it is important to note that assigning weights to indicators is subjective. Therefore, decision makers knowledge, experience, and judgment ability are critical in weight assignment. Generally, in the biodiesel industry the economic feasibility is vital for its survival. Although there is increasing awareness towards environment, biodiesel production generally uses and produces non-toxic and non-pollutant materials, thus its impact is relatively low. When comparing environment to social aspects, for the biodiesel case, it is more important to focus on the socially related issues such as safety or operability. Such consideration is necessary to ensure

Criteria	Indicators	Assessment value, v				Norm. assessment score, V_N			
		C1	C2	C3	C4	C1	C2	C3	C4
Economy	NPV, $\$x10^{-6}$	-2,06	-2,28	-0,35	-0,82	0,10	0,09	0,57	0,24
	ROR, %	-8,27	-51,18	-15,63	-21,48	0,08	0,14	0,45	0,33
Environment	TRO	2563	4384	11855	12277	0,50	0,29	0,11	0,10
	TOP	2,31	3,94	10,52	10,86	0,50	0,29	0,11	0,10
	TRG	197	1987	8410	8126	0,87	0,09	0,02	0,02
	TGP	0,18	1,18	7,45	7,18	0,83	0,13	0,02	0,02
Societal	FFP	10	10	10	10	0,25	0,25	0,25	0,25
	TM	6	3	5	4	0,33	0,17	0,28	0,22
	PC	5	5	5	5	0,25	0,25	0,25	0,25
	RC	10	10	10	10	0,25	0,25	0,25	0,25
	RA	4	6	6	6	0,18	0,27	0,27	0,27
	APP	7	7	5	5	0,29	0,29	0,21	0,21
Technical	DMLSD	10	10	10	10	0,25	0,25	0,25	0,25
	TS	10	10	10	10	0,25	0,25	0,25	0,25
	SO	3	2	3	2	0,30	0,20	0,30	0,20
	OP	5	1	5	3	0,36	0,07	0,36	0,21
	SSS	5	3	5	5	0,28	0,17	0,28	0,28
	Maint	6	3	5	4	0,33	0,17	0,28	0,22

Table 8.1: Assessment results.

that the plant operates smoothly and manages to deliver timely products without jeopardizing the product quality.

8.3.3 Process alternatives evaluation

The assessment results of the four biodiesel process alternatives are shown in Table 8.1. The data for quantitative evaluations were obtained from Zhang's [76, 55] article whereas the social and technical evaluations were based on our experience using specific scales as presented in Chapter 2. It is important to note that since the unit of measurements is different, it is essential that the assessment values be transformed into a score index. Then the index of each indicator for each case is normalized to get a normalized score index, as shown in Table 8.1. Note that the transformation also takes into account the value-desirability behavior of the indicators namely, higher-value-higher-desirability (HVHD) and the lower-value-higher-desirability (LVHD). Direct comparison of the score attained by each case indicates that Case 3 is the most economically feasible while Case 2 is the least preferred. Environmental performance, on the other hand, shows that the alkali based process (Case 1 and 2) performed better than the acid base system (case 3 and 4).

For the social and technical criteria, Case 1 is assessed as the most preferred with Case 2 being the least preferred. Direct summation of the total score shows that Case 3 is the most sustainable, followed by Case 1, Case 2 and Case 4. This result however is a linear comparison that does not reflect the decision makers preferability and interactions between the elements and could elucidate spurious and under justified answers. This is where ANP plays an important role in decision making.

8.3.4 Supermatrix formation and analysis

The next step is the formation of a supermatrix. The supermatrix has a similar concept to the Markov chain process where it allows for a resolution of the effects of interdependence that exists between the elements of the system [86]. To obtain global priorities in a system with interdependent influences, the local priority vectors are entered into the appropriate columns of a matrix, known as a supermatrix. As a result, a supermatrix, $\boldsymbol{M}$ is actually a partitioned matrix, where each matrix segment represents a relationship between two nodes (components or clusters) in a system [86]. All the pairwise comparisons priority vectors, PV and the normalized score performed before, were arranged with respect to its control criteria to form the supermatrix as shown in Table 8.2. Because of the presence of interdependencies, this unweighted supermatrix must be transformed to make it stochastic. This makes each column of the matrix sums to unity. A recommended approach by Saaty [88] is to determine the relative importance of the clusters in the supermatrix with the column cluster (block) as the controlling component [86]. The clusters comparison is performed and the eigenvalue obtained is used to form weighted supermatrix which is column stochastic. Raising the weighted supermatrix to powers gives the long-term relative influences of the elements to each other. The so called limit supermatrix has the same form as the weighted supermatrix, but all the columns of the limit supermatrix are the same as shown in Table 8.3.

The supermatrix is raised to its limit and reaches it convergence at $\boldsymbol{M}^{30}$. The limit supermatrix with its stable weighted values is shown in Table 8.4. The result of the alternative assessment using ANP is obtained from the alternatives block matrixes located at the bottom left of the limit supermatrix table. The alternative with the largest overall priority should be the one selected. According to Chung et al. [47] since the supermatrix formed covers the whole network, the priority weights of alternatives can be found in the column of alternatives in the normalized supermatrix. On the other hand, if a supermatrix only comprises of components that are interrelated, additional calculations must be made to obtain the overall priorities of the alternatives.

The results form Table 8.4 show that the most sustainable design option is found in Case 3 mainly influenced by its huge economic advantage. Follow by Case 1, Case 4 and finally Case 2. Although the acid-catalyzed systems (Case 3 and 4) have a huge economic advantage, Case 1 which is an alkali-catalyzed system, however, manage to get in the top two because of its very low environmental impact since it use and release less toxic materials. As a whole, the results obtained show that the ANP is able to successfully select and rank the preferability of several design alternatives embedding the interdependencies that exist among the elements which cannot be conducted in the conventional AHP method.

	Goal	Man.	Eng.	Econ.	Env.	Social	Techn.	NPV	ROR	TRO	TOP	TRG	TGP	FFP	TM	PC	RC	RA	APP	DMLSD	TS	SO	OP	SSS	Maint	Case 1	Case 2	Case 3	Case 4
Goal	1																												
Man.	0,50			0,75	0,25	0,67	0,20																						
Eng.	0,50			0,25	0,75	0,33	0,80																						
Econ.		0,46	0,18																										
Env.		0,15	0,14																										
Social		0,29	0,19																										
Techn.		0,11	0,50																										
NPV				0,75																									
ROR				0,25				1																					
TRO					0,18																								
TOP					0,14					1																			
TRG					0,19																								
TGP					0,50							1																	
FFP						0,10																							
TM						0,07											1	1											
PC						0,08																							
RC						0,24																							
RA						0,28																							
APP						0,22																							
DMLSD							0,10																						
TS							0,07													1		1	1	1	1				
SO							0,08																						
OP							0,24																						
SSS							0,28																						
Maint							0,22																						
Case 1								0,10	0,08	0,50	0,50	0,87	0,83	0,25	0,33	0,25	0,25	0,18	0,29	0,25	0,25	0,30	0,36	0,28	0,33	1			
Case 2								0,09	0,14	0,29	0,29	0,09	0,13	0,25	0,17	0,25	0,25	0,27	0,29	0,25	0,25	0,20	0,07	0,17	0,17		1		
Case 3								0,57	0,45	0,11	0,11	0,02	0,02	0,25	0,28	0,25	0,25	0,27	0,21	0,25	0,25	0,30	0,36	0,28	0,28			1	
Case 4								0,24	0,33	0,10	0,11	0,02	0,02	0,25	0,22	0,25	0,25	0,27	0,21	0,25	0,25	0,20	0,21	0,28	0,22				1

Table 8.2: Supermatrix.

	Goal	Man.	Eng.	Econ.	Env.	Social	Techn.	NPV	ROR	TRO	TOP	TRG	TGP	FFP	TM	PC	RC	RA	APP	DMLSD	TS	SO	OP	SSS	Maint	Case 1	Case 2	Case 3	Case 4
Goal	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Man.	0,25	0,00	0,00	0,38	0,12	0,33	0,10	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Eng.	0,25	0,00	0,00	0,13	0,38	0,17	0,40	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Econ.	0,00	0,46	0,18	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Env.	0,00	0,15	0,14	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Social	0,00	0,29	0,19	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Techn.	0,00	0,11	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
NPV	0,00	0,00	0,00	0,38	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
ROR	0,00	0,00	0,00	0,13	0,00	0,00	0,00	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TRO	0,00	0,00	0,00	0,00	0,09	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TOP	0,00	0,00	0,00	0,00	0,07	0,00	0,00	0,00	0,00	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TRG	0,00	0,00	0,00	0,00	0,09	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TGP	0,00	0,00	0,00	0,00	0,25	0,00	0,00	0,00	0,00	0,00	0,00	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FFP	0,00	0,00	0,00	0,00	0,00	0,05	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TM	0,00	0,00	0,00	0,00	0,00	0,04	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,50	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
PC	0,00	0,00	0,00	0,00	0,00	0,04	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
RC	0,00	0,00	0,00	0,00	0,00	0,12	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
RA	0,00	0,00	0,00	0,00	0,00	0,14	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
APP	0,00	0,00	0,00	0,00	0,00	0,11	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
DMLSD	0,00	0,00	0,00	0,00	0,00	0,00	0,05	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TS	0,00	0,00	0,00	0,00	0,00	0,00	0,04	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,50	0,00	0,50	0,50	0,50	0,50	0,00	0,00	0,00	0,00
SO	0,00	0,00	0,00	0,00	0,00	0,00	0,04	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
OP	0,00	0,00	0,00	0,00	0,00	0,00	0,12	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
SSS	0,00	0,00	0,00	0,00	0,00	0,00	0,14	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Maint	0,00	0,00	0,00	0,00	0,00	0,00	0,11	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Case 1	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,05	0,08	0,25	0,50	0,44	0,83	0,25	0,33	0,25	0,13	0,09	0,29	0,13	0,25	0,15	0,18	0,14	0,17	1,00	0,00	0,00	0,00
Case 2	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,04	0,14	0,15	0,29	0,04	0,13	0,25	0,17	0,25	0,13	0,14	0,29	0,13	0,25	0,10	0,04	0,08	0,08	0,00	1,00	0,00	0,00
Case 3	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,29	0,45	0,05	0,11	0,01	0,02	0,25	0,28	0,25	0,13	0,14	0,21	0,13	0,25	0,15	0,18	0,14	0,14	0,00	0,00	1,00	0,00
Case 4	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,12	0,33	0,05	0,11	0,01	0,02	0,25	0,22	0,25	0,13	0,14	0,21	0,13	0,25	0,10	0,11	0,14	0,11	0,00	0,00	0,00	1,00

Table 8.3: Weighted supermatrix.

	Goal	Man.	Eng.	Econ.	Env.	Social	Techn.	NPV	ROR	TRO	TOP	TRG	TGP	FFP	TM	PC	RC	RA	APP	DMLSD	TS	SO	OP	SSS	Maint	Case 1	Case 2	Case 3	Case 4
Goal	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Man.	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Eng.	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Econ.	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Env.	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Social	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Techn.	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
NPV	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
ROR	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TRO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TOP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TRG	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TGP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FFP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TM	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
PC	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
RC	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
RA	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
APP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
DMLSD	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TS	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
SO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
OP	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
SSS	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Maint	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C1	0,29	0,28	0,30	0,19	0,51	0,28	0,29	0,09	0,08	0,50	0,50	0,86	0,83	0,25	0,33	0,25	0,30	0,26	0,29	0,26	0,25	0,28	0,31	0,27	0,30	1,00	0,00	0,00	0,00
C2	0,19	0,18	0,19	0,15	0,18	0,21	0,20	0,11	0,14	0,30	0,29	0,11	0,13	0,25	0,17	0,25	0,22	0,23	0,29	0,26	0,25	0,23	0,17	0,21	0,21	0,00	1,00	0,00	0,00
C3	0,32	0,34	0,30	0,42	0,18	0,29	0,29	0,52	0,45	0,11	0,11	0,02	0,02	0,25	0,28	0,25	0,27	0,28	0,21	0,26	0,25	0,28	0,31	0,27	0,27	0,00	0,00	1,00	0,00
C4	0,24	0,24	0,24	0,27	0,14	0,24	0,24	0,29	0,33	0,11	0,11	0,02	0,02	0,25	0,22	0,25	0,24	0,25	0,21	0,26	0,25	0,23	0,24	0,27	0,24	0,00	0,00	0,00	1,00

Table 8.4: Results of the limit supermatrix at $\boldsymbol{M}^{30}$.

8.4 Concluding remarks

In this work, we proposed a holistic ANP-based decision framework for selection of sustainable chemical process design option that include quantitative and qualitative factors which are determinants for both engineers and managers perspectives. The framework however can be extended or modified depending on the specific process or decision problem environments. Other possible interdependencies can also be added depending on the decision makers intuition. The advantages of ANP rely on its structured and systematic approach. But more importantly, it account for the interdependencies among its elements. As such, ANP is capable of dealing with uncertainty and complexity in the problem environment. The approach is successfully tested to four biodiesel process technology. Compared to AHP, using ANP in cases where the elements are interacting among each other offers a more insightful and persuasive decisions. However, one drawback of ANP is the larger number of pairwise comparisons that need to be conducted compared to AHP. This number will increase with increasing complexity and interdependency. Overall, the approach is an effective decision tool for industrialists to support the selection of sustainable design options in a complex and interdependent problem environment.

Chapter 9

SAS in Chemical Engineering Education

9.1 Introduction

Sustainability aims at meeting the needs of the present generation without compromising the ability of future generations to meet their needs. Many efforts have been made from different perspectives, from industrial systems to national policies. Another important aspect to further enlighten public awareness towards sustainability is through education. Realizing its significance and importance, the United Nations in 2002 declared the years 2005 to 2014 the world decade on 'Education for Sustainable Development' which aims to anchor the ideal of sustainable development in all areas of education. The Decade seeks to provide education opportunities to all people, enabling them to acquire knowledge and values and learn about behavior and lifestyles which are needed to ensure a livable future and develop a future-oriented society [89]. The German Bundestag have taken an early initiative before the launch of the UN Decade by unanimously called for the development of a national plan 'Education for Sustainable Development on 1 July 2004 [90]'. Coordinated by the Bundesministerium für Bildung und Foschung (BMBF) it appointed a National Committee consisting of the Federal Ministries, the Bundestag, the Länder, NGOs, the media, industry and scientists to draft strategies to implement the Decade in Germany. This plan states the strategic aims for the Decade and currently includes over 60 far-reaching education policy measures which are to contribute to integrating the ideal of sustainable development into the education system in the long term.

In engineering, incorporating sustainability into products, technology systems, and services generally means including environmental and social performance in the evaluation of designs [91]. Chemical engineers in particular have much to offer in achieving sustainability goals through the very nature of their education, skills and outlook [92]. Recognizing its potential, several organizations such as the Accreditation Board for Engineering and Technology (ABET), Institute of Engineers Australia (IEAust) and The American Chemistry Society (ACS) recognized sustainability as a key element for future engineering and engineering education paradigms. ABET for example in its 2005-2006 accreditation criteria, states that *'Engineering programs must demonstrate that their students attain an ability to design a system, compo-*

nent, or process to meet desired needs within realistic constraints such as economic, environmental, social, political, ethical, health and safety, manufacturability, and sustainability.' On the other hand, ACS delivered a 'Statement on Sustainability of the Chemical Enterprise' which suggests the role of industry, trade associations and educational and professional organizations in sustainable development [92].

Incorporating sustainability into the chemical engineering curricula content is a challenge. With its already cramped fundamentals and application, it is a perceived dilemma by many engineering educators about how to incorporate sustainability. However, Favre et al. [93] proposed three options to solve this, which include:

- No change in the curriculum as it is relevant despite significant changes in the industry.
- In-depth overhaul of the curriculum.
- Adaptive approach which aims to preserve the fundamentals of the existing curriculum.

For the last five years, the department in which Favre and his co-workers [93] are adopting the last approach in introducing process, product and sustainability concepts to their students. In 2009, Allen et al. [91] conducted a survey of over 1300 academic department chairs and program heads from 366 engineering collages in the U.S., and also additional individuals, to identify who are active in incorporating sustainability into their teaching and research. Their survey found out that there are four ways of incorporating sustainability into the engineering curriculum. The first is with a dedicated sustainable-engineering course. Nearly 48% of the courses comes under this theme. Another approach is to integrate it into traditional engineering course with the aim to broaden the students' awareness and skills. The third way is through emphasizing the technologies expected to be important for sustainability such as carbon capture or solar power. The last approaches were described as some combination of the others, or as interdisciplinary courses given in conjunction with a non-engineering department. These approaches are mostly stand-alone courses and offered to upper-division undergraduate or graduate students. Overall, these efforts show that sustainability is gaining importance in the engineering education field.

Sustainability always revolves around the three pillars. Sometimes, it is difficult to have the same preference in all three criteria. Most of the time, there are contradictions and finding solutions that satisfy all criteria is often difficult. Engineers, researchers, managers or even us often encounter such multi-criteria problems. Situations like deciding on the best process design, suppliers, supply chain, etc., needs a practical and justifiable solution. As explained before, in general there are two known ways to derive an answer [20]. The latter is more preferred since the former has the lack of information on how to bring the different conclusions into an integrated outcome which could elucidate inaccurate and under justified conclusions. Regardless of which method to use, it is important for us to realize that what we decide today shapes future generations. Nevertheless, an effective and systematic decision making methodology could help in making a concrete and justifiable decision. Realizing the importance of decision making, it is of great significance for students to learn how to make an effective decision particularly in deciding a sustainable option.

For that purpose, our goal is to introduce the sustainability assessment and selection (SAS) concept into chemical engineering education curriculum. Based on this concept, we offer a 1-day lecture on sustainability assessment and decision making to Computer Aided Process Design (CAPD) students at TU Berlin. At the end of the lecture we distribute an evaluation form. The response from the students will be evaluated and presented in further detail. We believe through this, it would add an extra edge to the students especially in adopting sustainability assessment to process design and the systematic solving of multi optional problems that they may encounter during their career.

9.2 Class overview

The CAPD course was offered to chemical process engineering students at TU Berlin. It was a small class consists of 10 to 15 students. The students ranged from final year undergraduate students to master students, whom some already had working experience. The students worked in pairs for discussions and exercises. Doing this also promote team working.

In this lecture there were a few objectives to be met. First was to expose the students to the concept of sustainability particularly in chemical industries, and various methods to assess them. Apart from that, the students also learned to apply WAR algorithms to assess the environmental performance of a process design. They also learned and understood the steps to make decisions using AHP for solving multi criteria problems. In addition, they applied the assessment and decision methodologies for selection of a sustainable process design option.

To meet the underlined objectives, the lecture layout was divided into several parts. The first part provides some overview on sustainability in chemical industries, specifically in process design and issues surrounding it such as the assessment criteria and indicators. We then exposed the students to WAR algorithm and gave an exercise to develop spreadsheets for calculating the environmental impact. In the second part, we introduced AHP for MCDM. Introductory lectures were given on AHP, and also the steps to perform decision making. The students were also demonstrated on utilizing spreadsheets for aiding the decision process. At the end, we gave an exercise to assess the sustainability performance of two n-butane isomerization process designs and to perform decision making using AHP. At the end of the lecture, evaluation forms were distributed and the response from the students will be analyzed and presented in further details.

9.3 Case study - $n\mathrm{C}_4$ isomerization

The case study that was chosen was the n-butane isomerization process. The commercial n-butane isomerization process was originally developed by UOP. Known as the UOP butamer process, over 70 UOP butamer units have been commissioned with plant capacities ranging from 800 to more than 30.000 BPSD (barrel per stream

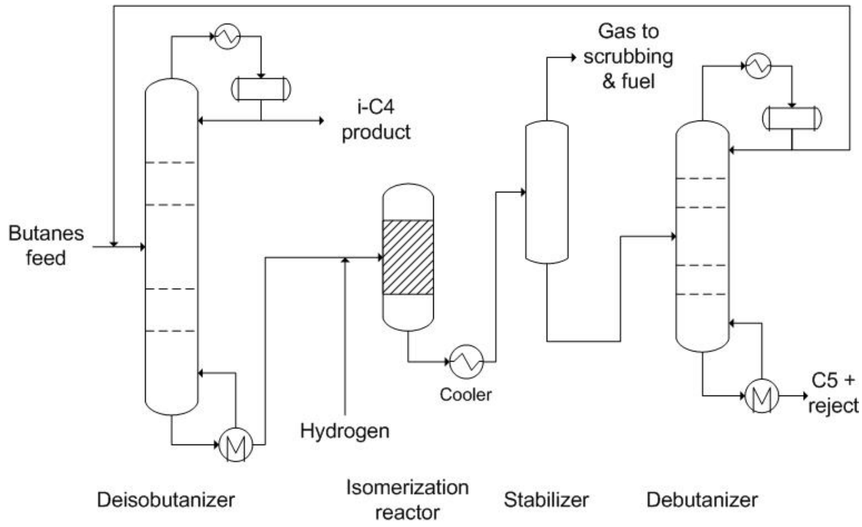


Figure 9.1: UOP butamer process flow diagram.

day) [94]. In UOP butamer process (see Figure 9.1), a feed stream of mixed butane enters a deisobutanizer column where $i\mathrm{C}_4$ is produced as an overhead product. The bottom stream, which is rich in $n\mathrm{C}_4$, is charged directly to the reactor section, where it is combined with makeup hydrogen. Reactor effluent is cooled and flows to a stabilizer for removal of the small amount of light gas co-product. The bottom stream of the stabilizer then enters a debutanizer column where higher hydrocarbons ($>\mathrm{C}_5$) are rejected as bottoms. The overhead which mainly consists of $i\mathrm{C}_4$ and unreacted $n\mathrm{C}_4$ are returned to the deisobutanizer. Any $i\mathrm{C}_4$ present in the feed stream or produced in the isomerization reactor is recovered overhead. Unconverted $n\mathrm{C}_4$ is recycled back to the reactor.

On the other hand, BP also proposed an alternative design shown in Figure 9.2. The design used the same raw materials and process technology as the UOP but the main difference is in the equipment layout. In BP n-butane isomerization process design, a feed stream enters a deisobutanizer column, where $i\mathrm{C}_4$ is produced as an overhead product. Instead of being directly charged to the reactor, the bottom product is fed to a debutanizer column where higher hydrocarbons ($>\mathrm{C}_5$) are withdrawn from the system as bottom product. Doing this will significantly reduce the total amount of mass flow downstream especially to the reactor and stabilizer. The overhead product then charged to the isomerization reactor combined with makeup hydrogen. Effluent from reactor is then cooled and enters the stabilizer where small amount of light gas is withdrawn from the overhead. The bottom stream, which consists mainly of $n\mathrm{C}_4$ and $i\mathrm{C}_4$, is returned to the deisobutanizer.

Because of time constraint, both designs have been modeled beforehand and only the streams and utilities results were given to the students. Despite that, the economic performance; NPV and DCFRR values also have been calculated and given to the students. The last exercise is basically the climax of this 1-day lecture. Using all the knowledge and spreadsheet prior to this last exercise, they will perform sustainability assessment and selection of the two process designs. In this exercise first they need to decompose the problem into a hierarchical decision model. Then,

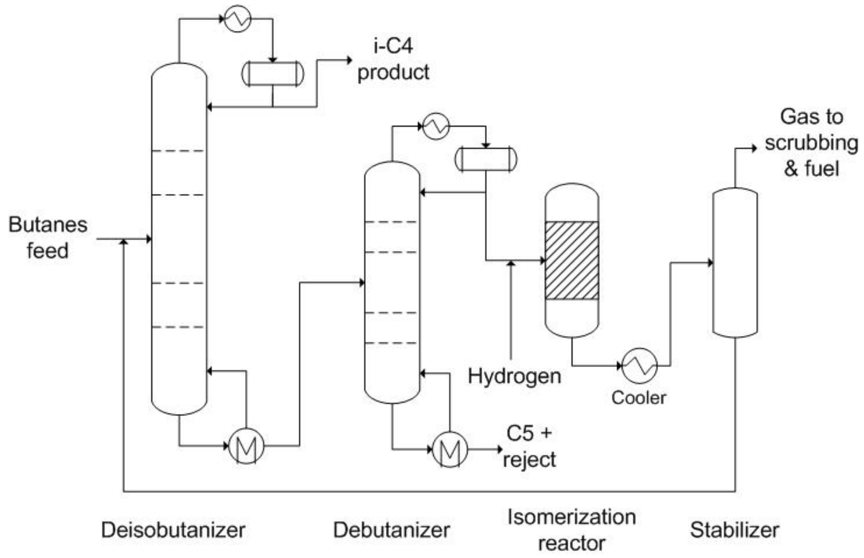


Figure 9.2: BP n-butane isomerization process flow diagram.

based on the given streams and utilities profile, they need to calculate the four environmental indicators utilizing the spreadsheet they have developed before. Next, based on their experience, they assessed the social-related indicators, namely safety during operation, plant operability, safe startup and shutdown, and design meet local specific demand of the two designs. At the end, after all the assessment values have been obtained, they then apply AHP procedure, which included weights setting, ranking and evaluation to finally elucidate the final answer. Examples of the results are given in Figure 9.3. It is important to note that the final answer differs between groups since the weights selection and also the qualitative assessment for social criteria influence the overall decision preferability.

9.4 Evaluation form

At the end of the session, an evaluation form was distributed to the students. With this form the students had the opportunity to give their feedback or response to this 1-day lecture. The evaluation form consisted of four parts, with three to five sub-points under each part. It evaluated not only the effectiveness of the lecture layout and activities, but also the extent of their understanding of the outlined objectives. Details on the questionnaire are given in Table 9.1. For each point the student set a rank between one and five. One indicated the lowest rating and five indicated highest rating. The evaluation results are presented next.

9.5 Evaluation results

The first part of the evaluation form focuses primarily on the layout and activities during the class. Belonging to this section are activities such as lectures, discussion, hands-on projects, group work and exercises. The questions aimed to find out to what extent these activities help the student to learn. The result of students'

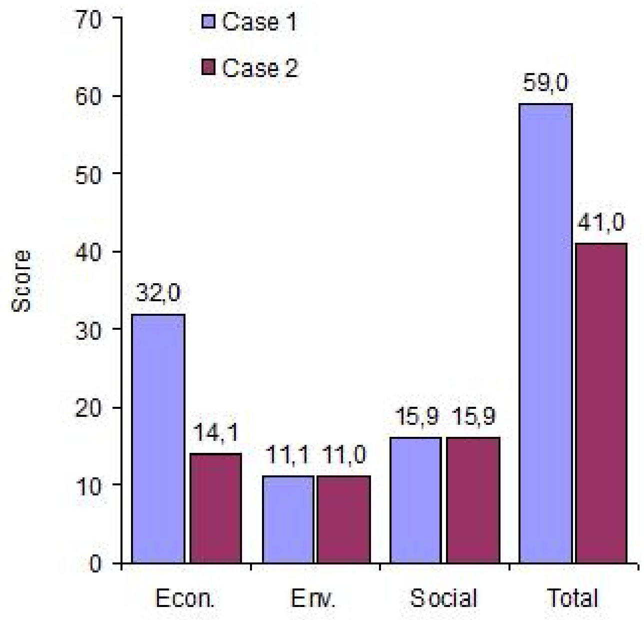


Figure 9.3: Example of the assessment and selection result

Part	Descriptions
A	HOW MUCH did each of the following aspects of the class HELP YOUR LEARNING?
A1	Lectures
A2	Discussion in class
A3	Hands on activities
A4	Group work in class
A5	Exercises in class
B	As a result of your work in this class, how well do you think that you now UNDERSTAND each of the following?
B1	The concept of Design for Sustainability in PSE
B2	WAR algorithm as an indicator to assess environmental impact of a process design
B3	Qualitative indicators to assess social related criteria of a process design
B4	The procedure for performing AHP (problem decomposition, pairwise comparison, ranking, evaluation)
C	To what extent did you MAKE GAINS in any of the following as a result of attending this class?
C1	Understanding the concept of Design for Sustainability
C2	Calculating the environmental impact using WAR algorithm
C3	Performing qualitative assessment for social-related criteria
C4	Understanding and adopting AHP as MCDM tools for selecting sustainable process design
D	How much of what you have learned in this class do you think you will REMEMBER and CARRY WITH YOU into other classes or other aspects of your life (i.e. daily, career etc.)?
D1	Concept of Design for Sustainability
D2	The criteria and indicators to assess sustainability of a process design
D3	Decision making using AHP

Table 9.1: Evaluation form parts and their sub-points.

evaluations are depicted in Figure 9.4. Overall, observing the results in general, the students were satisfied with all the class activities. Among those activities, exercises seem to have the highest rating where 40% of the students thinks that they helped in a great deal during the class lecture. However, around 30% of the students thought that the lectures only helped them a little during the class. Among other activities, there were the lowest rated activities that helped them during the class. In our opinion, oral presentations such as lectures were difficult to assess objectively. Many factors influenced an effective presentation, such as experience, capability, regularity, language, etc., and these are subjected to the speakers and personal preferences of the audience. Nevertheless, since this is the first time such a lecture was conducted, we believe with time the presentation can be improved.

The second part of the assessment focused on how much they understood the concept and purpose of the learning material. The learning material emphasized on the concept of Design for Sustainability (B1), WAR algorithm as indicator to assess environmental impact (B2), qualitative indicators to assess social related criteria of a process design (B3) and procedure for performing AHP to solve multi criteria problems (B4). The result is shown in Figure 9.5. From the figure, we can see that out of the four learning materials, B2 and B4 are the most understandable materials with 80% saying they at least understand a lot. This is due to the fact that these two materials involve exercises, and students were able to appreciate their application and usefulness. For material B1, 20% and 40% of the students say that they understand just a little or somewhat understand the learning materials, respectively. This trend was also found for material B3, where 44% says, 'somewhat understand'. We suspect that since these learning materials do not involve any exercises and mostly are presented orally, the extent of their understanding differs compared to material that included exercises. Nevertheless, overall the students were able to grasp most of the important points emphasized in each learning material.

In the third part, we asked the students to what extent they made gains based on the learning material as a result of attending the class. In previous parts, the questions were more focused on measuring the students' understanding of the general concepts and purposes of the learning material. In this part, we tried to find out how much they made gains in applying those concepts for sustainability assessment and decision making. This part included questions on understanding the concept of Design for Sustainability (C1), calculating environmental impact (C2), performing qualitative assessment (C3) and applying AHP for decision making (C4). The result is shown in Figure 9.6. From this figure we observed that 30% of correspondents say that they made a great deal of improvements in understanding and adopting AHP as a tool for selection of sustainable design. This is the highest rating given compared to other attributes. C2 also received good response from the students whereby 80% say they learned a lot from the learning material. Despite that, C1 and C3 did receive some cold responses from students. 20% and 10% of students say that they learned a little from C1 and C3 learning materials, respectively. Nevertheless, overall the students did improve in understanding and adopting the learning materials compared to their previous knowledge.

In the last part of the evaluation form we ask the students how much they will remember and apply or carry the learning materials into other classes or other

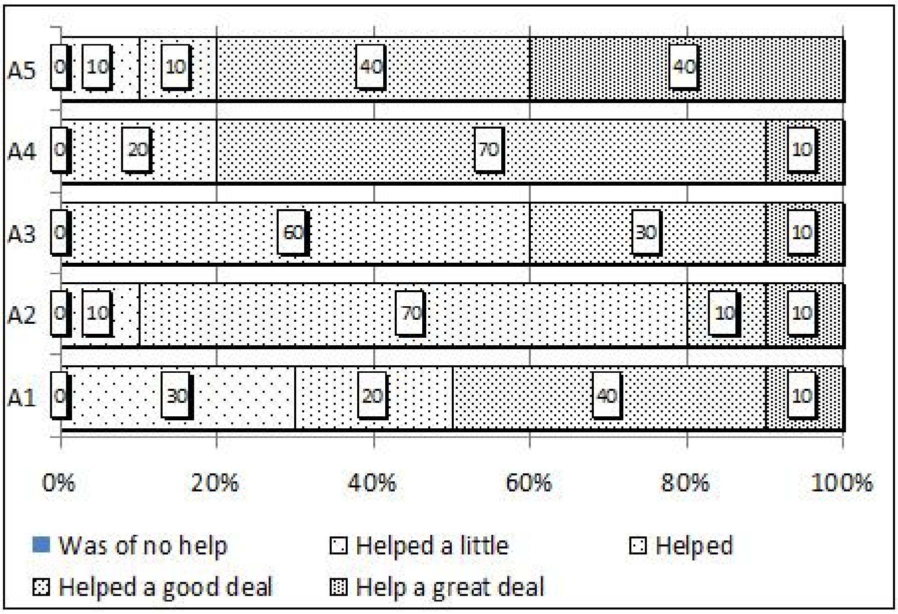


Figure 9.4: Results of the Part A question on 'HOW MUCH did each of the following aspects of the class HELP YOUR LEARNING? '

aspects of their life such as daily life, careers etc. This question is the most important and significant throughout this research. It reflects not only the effectiveness of the class in fulfilling the course objectives but also its attractiveness. Our hope is that such methodologies could trigger the interests of future engineers or managers in applying sustainability assessment and decision making methodology. We divided this last part into three sections. In the first section we stress the concept of Design for Sustainability (D1). Second section we stress on the criteria and indicators to assess sustainability of a process design (D2) and the last section on decision making using AHP (D3). The result is shown in Figure 9.7. For section D1, more than half of the students, 60%, will remember and apply the learning materials in a moderate amount. 20% did give cold responses with 'just a little'. Nevertheless, there were also students that gave very good responds. In total 20% of them actually will remember a lot, or a great deal (10%) towards the concept of design for sustainability. For section D2, the same pattern occurs but with slight improvements. Instead of the total of 20% in the previous section for remembering a lot and a great deal, a 10% increase was found in this section whereby 20% of the students gave 'a great deal' response and the remaining gave 'a lot' response. The third section shows even more interesting feedback. It was found that 30% of the respondents will remember and apply AHP in a great deal. Another 20% will remember and apply it a lot. Only 10% on the students gave the response of 'just a little'. The remaining 40% gave a 'somewhat' feedback. From these results, overall the students did give positive feedback towards the learning materials. Especially the AHP methodology for process design decision making received very good response from the students.

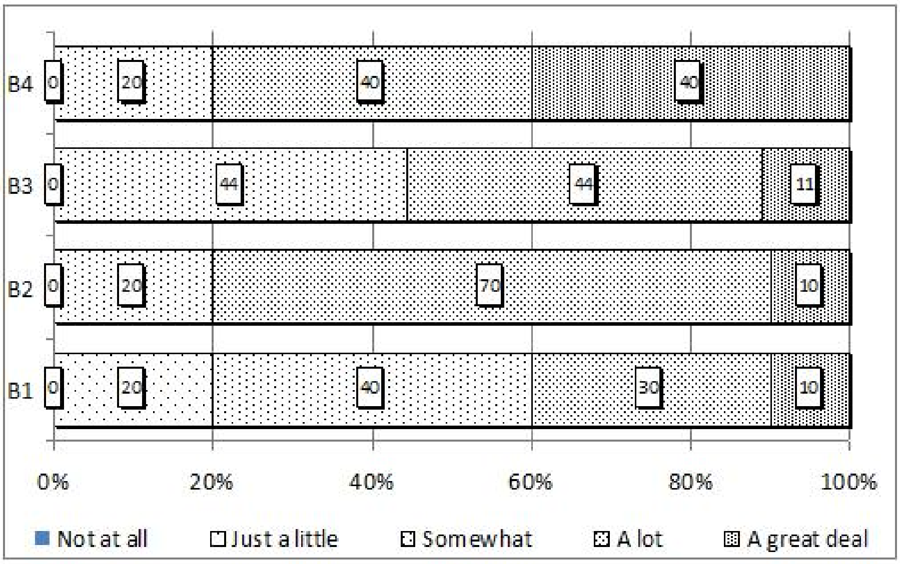


Figure 9.5: Results of the Part B question on 'As a result of your work in this class, how well do you think that you now UNDERSTAND each of the following?'

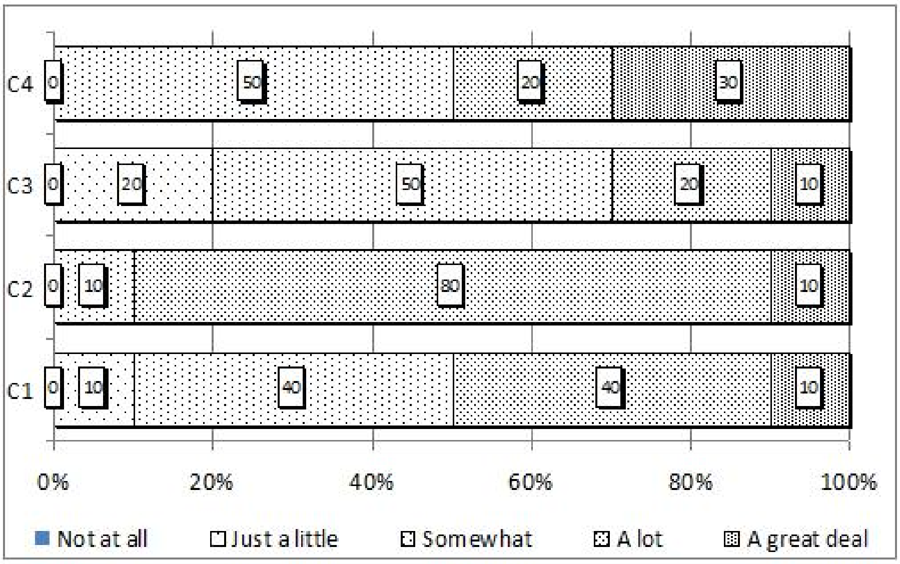


Figure 9.6: Results of the Part C question on 'To what extent did you MAKE GAINS in any of the following as a result of attending this class?'

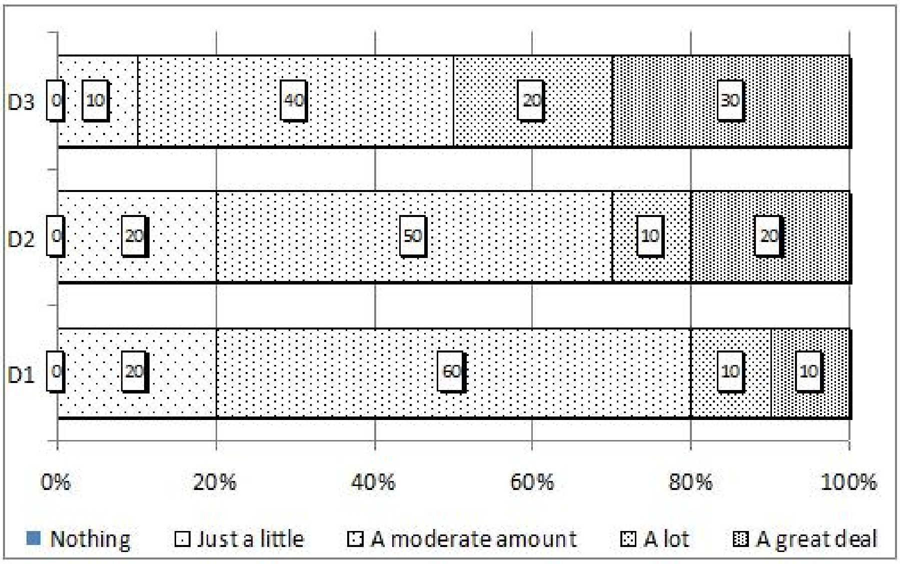


Figure 9.7: Results of the Part D question on 'How much of what you have learned in this class do you think you will REMEMBER and CARRY WITH YOU into other classes or other aspects of your life (i.e. daily, career etc.)?'

9.6 Concluding remarks

Incorporating sustainability into education is now a global commitment. Many agencies or educational boards and even countries are actively contributing to introducing sustainability in the education curriculum. Despite that, since sustainability involves multi criteria, decision making also plays an important role. Decision making is part of daily life. Life as engineers, researchers or even managers in chemical and process industries has demanded them to frequently make important decisions. Therefore, it is of great importance for the graduates, before entering the work market, to learn an effective decision making methodology. Motivated by this we conducted a 1-day lecture on sustainability assessment and decision making to chemical and process engineering students at TU Berlin. The course aims at introducing sustainability assessment to process design and to select a sustainable option using AHP. An oral presentation on sustainability assessment and AHP were given to the students and practical exercises were also given. They also have the opportunity to perform the assessment to two n-butane isomerization process designs and select which design is the most sustainable. At the end of the course, evaluation forms were distributed to see the response from the students. Overall the course was able to trigger the interest of the students to this new approach. We believed through this method it would add an extra edge to the students especially in systematically solving multi optional problems that they may encounter during their career.

Chapter 10

Summary and Concluding Remarks

10.1 Summary of contributions

Sustainability in industries offer a big challenge to engineers and managers. Particularly in PSE, it is important to address the challenges of design for sustainability especially in the early stages of development. Considering sustainability in process design is about finding the best solution that meet the three pillars of sustainability. Thus, assessing sustainable design needs to consider not only its techno-economic performance but also its environmental and social impacts. Many methodologies exist for that purpose, to name a few, process optimization, process synthesis and process intensification. It is important to note that whatever the method may be, decision making that involve multi criteria is often not straightforward. There may exist scenarios in which one or two criteria are not aligned with each other. This contradictory scenario sometimes creates problems in decision making. Therefore, deciding an option in such situations is difficult. There is a need to adopt a systematic and justified decision making methodology since what we decide today affects future generations. Therefore, decision makers need to be careful and to be more responsible when making decisions.

In this work, we proposed a new term called sustainability assessment and selection (SAS) for process decision making (PDM). It combines sustainability assessment and decision making methodologies which aim to perform sustainability assessment to several design alternatives and adopt a MCDM methodology called AHP/ANP which systematically selects a sustainable design. In doing so, we try to touch various aspects in the domain of PSE where PDM could be potentially useful. This includes computer aided process engineering and chemical engineering education. Below are the summaries of the thesis contributions:

- **Selection of sustainability indicators for assessing sustainable process design**
  This part presents some of the state of the art methodology to assess economic, environmental and social criteria to an industrial system. We then proposed indicators to assess sustainability at early stages of chemical process design which have a simple and easy to use algorithm, and need less

excessive data search but still remain its relevance and provide reasonable accuracy. The indicators are divided into two categories, hard (quantitative) and soft (qualitative) indicators. The economy and environmental criteria are categorized in the former category while soft indicators belong to the latter. Economy indicators were represented by NPV and DCFRR. WAR algorithms were used to represent the environmental performance of a system and social indicators used qualitative criteria suggested by experts. In all, by combining both analytic and heuristics evaluation, they can provide a more realistic and comprehensive assessment. However, we like to emphasize that the proposed indicators are non-definitive. It can be extended based on the problem, process and assessment objective.

- **m-SAS tool for assessing and selecting sustainable process design**
  With the advancement in computational tools, we developed a modular based sustainability assessment and decision making tool called m-SAS (modular-Sustainability Assessment and Selection). The tools were divided into four modules, namely Process Simulator (PS) module, Equipment and Inventory Assessment (EIA) module, Sustainability Assessment (SA) module and Decision Support (DS) module. The tool development fully utilizes the capability of a process simulator, Aspen Plus and Aspen Simulation Workbook (ASW), and EXCEL spreadsheets that systematically integrate case model development, data acquisition and analysis, team contribution assessment and decision support process. The aim of m-SAS is to assist engineers and managers to systematically assess the sustainability performance of a design and also aide them in performing process decision making for selection of sustainable design options. With its structured form, the assessors are able to focus on the real issues involving process design development. Furthermore, it allows the involvement of a multi-disciplinary team in process design evaluation.

- **Assessment and selection of sustainable biodiesel process design**
  To test the functionality of the m-SAS tool, two potential biodiesel process designs were used as case study. The first case is by using a conventional base-catalyzed system and the second case involves supercritical condition. The objective is to perform sustainability assessments on both cases and to select one that meets the sustainability criteria. Our findings show that, although with a slightly lower economic performance, the first case is selected to be the most sustainable design. It is important to note that the degree of preferability is affected by a few factors. Among them is the process models development, and selection of weights in the AHP comparison step. Overall, the methodology is able to show its effectiveness in assessing sustainable conscious process design and supporting persuasive decision making, thus showing its pre-eminence over commonly practiced techno-economy evaluation approaches.

- **Effect of indicators definition**
  In this part we study the effect of using different sustainability measurement methodologies to decision preferability. For that purpose, we perform a comparison between our proposed indicators and IChemE for the selection of four

biodiesel process designs. The aim is basically to observe the effect of different sustainability assessments in relation to the overall decision making result. Our findings show that the elucidation of result preference is much affected by definition of indicators, assessment boundaries, assessor's competency and weights setting. We conclude that for a more meaningful assessment and selection of sustainable process design, these factors should be carefully considered.

- **Incorporating negative values in AHP**
  Typical AHP problems are limited to handling only positive preferences while in reality negative preferences also exist. However, introduction of negative preferences into AHP often creates various contradicting scenarios that result in spurious and inconsistent decisions. Thus, to overcome this we proposed a rule-based scoring methodology. The methodology works by initially defining each indicator according to its value-desirability behavior. Next, using specific conversion factors that act accordingly to that behavior, the indicators value is converted into a credit-penalize scoring concept. Positive preference is credited with positive value while negative preference is penalized with negative values which show its undesirability. Using a rule-based approach, the scores spanning over positive and negative values are treated to elicit the final selection and ranking solution. The functionality of the proposed methodology were successfully implemented for selection and ranking of several biodiesel case scenarios in presence of positive and negative preferences.

- **Decision making using ANP**
  In this part we try to include dependencies among the decision elements using ANP. In addition, we also include the influence of engineers and managers in decision making. With increasing problem complexity, they make the decision making more complex and ANP is capable of handling such scenarios. Using ANP, a hierarchical decision network model using quantitative and qualitative-based indicators that are determinant to engineers and managers is developed. In addition, it also takes into account the dependencies that exist within the framework. An example of several biodiesel process designs from literature is used to show the applicability of the approach. Overall, the approach offers a practical and systematic tool for aiding decision making for selection of sustainable chemical process design alternatives in a complex and interacting decision environment.

- **Introduction of SAS in chemical engineering education**
  In this work we try to introduce the SAS concept to process/chemical engineering students. The aim is to find out their response to the methodology. A 1-day lecture has been carried out with oral presentations and exercises. In the last exercise they were given a task to assess and select which of the two n-butane isomerization process designs was the most sustainable. At the end of the course, evaluation forms were distributed to elicit response from the students. Overall, we were satisfied with the response from the students, and hopefully the course will bring an extra edge to the students, especially in performing sustainability assessment and systematically solving multi optional problems that they may encounter during their career.

10.2 Recommendation for future works

This work has been dedicated to the introduction of the SAS concept for process decision making (PDM) in PSE. This concept centers on performing sustainability assessment and decision making for the selection of sustainable alternatives. Several aspects as listed above have been highlighted which try to raise problems or answer questions surrounding it. Nevertheless, there still remain other opportunities for further improvements and development in this area. The m-SAS tool, for example, can be further improved. Development of a friendly graphical user interface (GUI) for instance can help decision makers to easily use and manage the tool. Apart from the, the effect of using different sustainability assessment methodologies could be expanded to more than two methodologies including the latest assessment for a more comprehensive investigation. In addition, a systematic and hierarchical approach can be suggested to aid selection of indicators that are relevant for assessment at different stages of project development. Another opportunity for improvement in this study is to clarify the definition of the social criteria. In this work, a qualitative based approach is suggested. It will also be interesting to include socially related criteria which can be quantified. One possible option is to include an operability study. The work by Vinson and Georgakis [44] could provide some insight for quantifying operability of process design. Besides that, other interesting the case studies could also be assessed, such as carbon capture and storage (CCS) technologies. Since CCS is a hot topic today, performing sustainability assessment and decision making to a few potential designs would be interesting. Lastly, besides process design, the concept could also be applied to other parts of process production. One interesting area to be explored in the future could be supply chain management.

Appendix A

Research contributions

Below are lists of contributions in form of publications and presentations:

Book series

- M.R. Othman, J.U. Repke & G. Wozny. 2010. "Incorporating Negative Values in AHP Using Rule-Based Scoring Methodology for Ranking of Sustainable Chemical Process Design Options". Computer Aided Chemical Engineering. Vol. 28, pp. 1045-1050A.

Journal publication

- M.R. Othman, J.U. Repke, G. Wozny & Y. Huang. 2011. "Sustainability Assessment & Decision Making for Sustainable Chemical Process Option". To be appear in Chinese Journal of Chemical Engineering.

- M.R. Othman, J.U. Repke, G. Wozny & Y. Huang. 2010. "A Modular Approach to Sustainability Assessment and Decision Support for Chemical Process Design". Industrial & Engineering Chemistry Research. 49 (17), pp. 7870-7881.

Conference presentation

- M.R. Othman, L. Hady, J.U. Repke & G. Wozny. 2011. "Introducing Decision Making Methodology into Chemical Engineering Education". 8th European Congress of Chemical Engineering. 25-29 September 2011. Berlin, Germany. POSTER

- M.R. Othman, J.U. Repke & G. Wozny. 2011. "Selection of Sustainable Chemical Process Design using ANP: A Biodiesel Case Study". International Symposium on the Analytic Hierarchy Process (ISAHP). 15-18 June 2011. Sorrento, Naples, Italy. ORAL

- M.R. Othman, J.U. Repke & G. Wozny. 2010. "Incorporating Negative Values in AHP Using Rule-Based Scoring Methodology for Ranking of Sustainable Chemical Process Design Options". 20th European Symposium on Computer Aided Process Engineering (ESCAPE 20). 6-9 June 2010. Ischia, Naples, Italy. ORAL

- M.R. Othman, J.U. Repke, G. Wozny & Y. Huang. 2010. "Sustainability Assessment and Decision Making for Sustainable Chemical Process Option". 2nd International Symposium on Sustainable Chemical Product & Process Engineering (ISSCPPE2). 9-12 May 2010. Hangzhou, China. ORAL & POSTER

- M.R. Othman, J.U. Repke, G. Wozny & Y. Huang. 2009. "A Modular Approach to Sustainability Assessment & Decision Support in Chemical Process Design". AIChE: 1st International Congress on Sustainability Science & Engineering (ICOSSE). 10-13 August 2009. Cincinnati, Ohio, USA. ORAL

Appendix B

Biodiesel process models

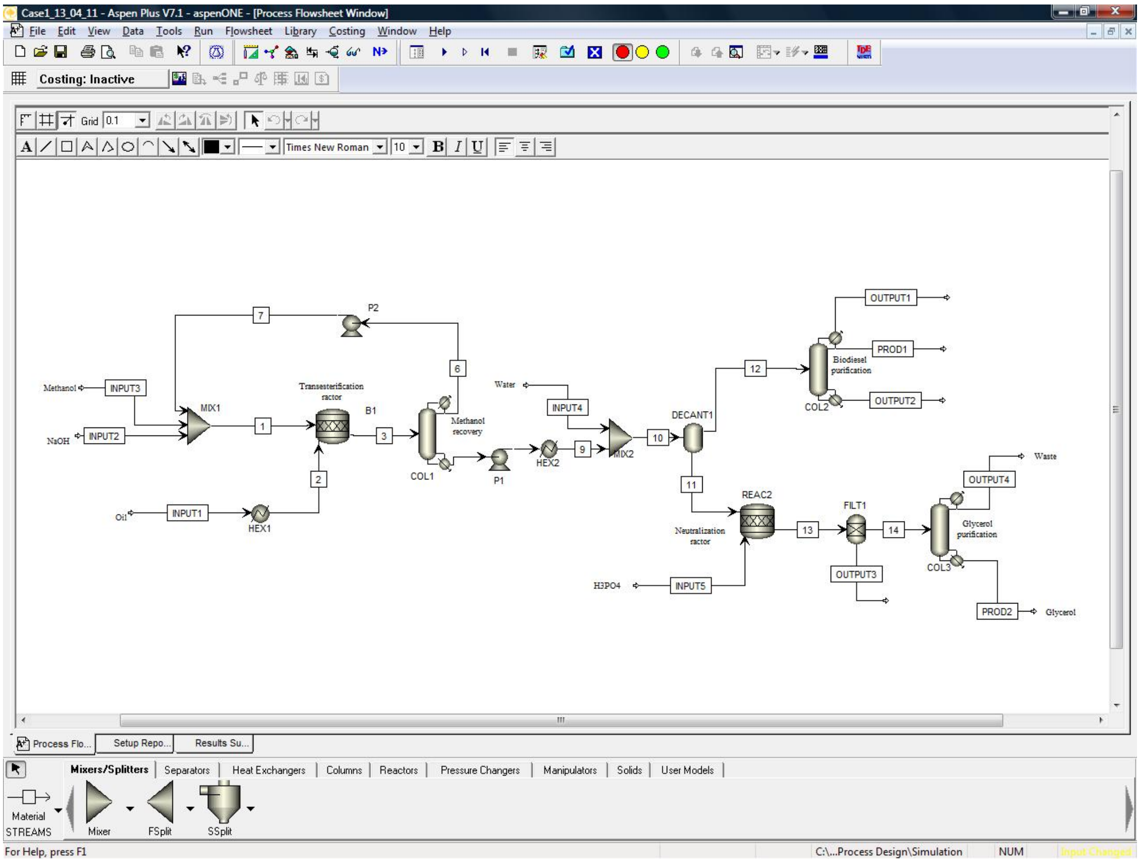


Figure B.1: Case 1: Process flowsheet for the alkali-catalyzed process (Case 1).

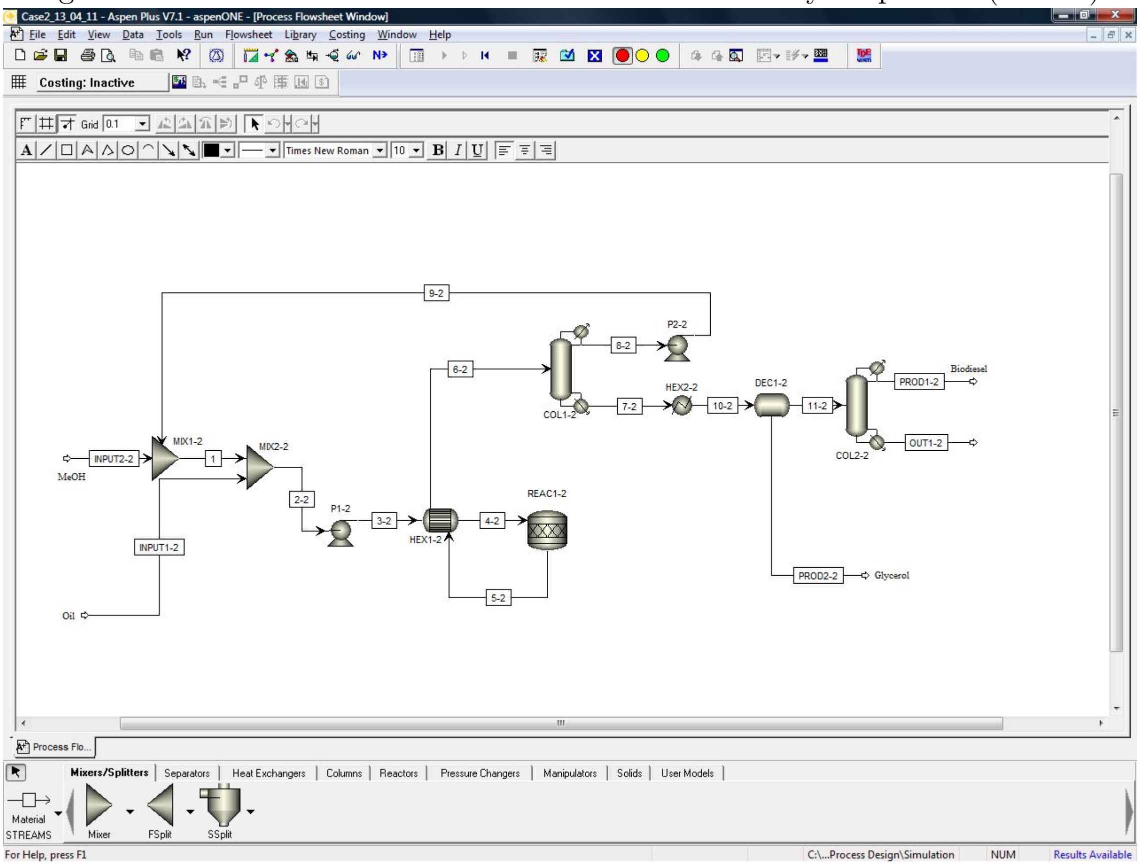


Figure B.2: Case 1: Process flowsheet for the supercritical methanol process (Case 2).

Stream	1	2	3	5	6	7	8	9	10	11	12	13
Temperature C	31,7	60	60	176	32,8	32,9	176,1	30	29,8	30	30	30
Pressure bar	1	1	1	0,3	0,25	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0	0	0	0	0	0	0
Mole Flow kmol/hr	8,329	1,186	9,515	4,869	4,646	4,646	4,869	4,869	5,424	1,918	3,506	2,003
Mass Flow kg/hr	268,863	1050	1318,863	1170	148,863	148,863	1170	1170	1180	122,883	1057,117	131,213
Volume Flow cum/hr	0,323	1,171	1,561	1,504	0,19	0,19	1,504	1,336	1,353	0,097	1,239	0,097
Enthalpy MMkcal/hr	-0,476	-0,516	-1,055	-0,724	-0,264	-0,264	-0,724	-0,81	-0,848	-0,233	-0,618	-0,258
Mass Flow kg/hr												
TG	0,005	1050	52,5	52,496	0,005	0,005	52,496	52,496	52,496	0,004	52,492	0,004
MEOH	258,858	0	150,567	1,709	148,858	148,858	1,709	1,709	1,709	0,778	0,93	0,778
NAOH	10	0	10	10	0	0	10	10	10	10	0	0
GLY	0	0	103,749	103,749	0	0	103,749	103,749	103,749	102,546	1,203	102,546
FAME	0	0	1002,046	1002,046	0	0	1002,046	1002,046	1002,046	0	1002,047	0
H2O	0	0	0	0	0	0	0	0	10	9,555	0,445	14,059
H3PO4	0	0	0	0	0	0	0	0	0	0	0	0,163
NA3PO4	0	0	0	0	0	0	0	0	0	0	0	13,662
Mass Frac												
TG	0	1	0,04	0,045	0	0	0,045	0,045	0,044	0	0,05	0
MEOH	0,963	0	0,114	0,001	1	1	0,001	0,001	0,001	0,006	0,001	0,006
NAOH	0,037	0	0,008	0,009	0	0	0,009	0,009	0,008	0,081	0	0
GLY	0	0	0,079	0,089	0	0	0,089	0,089	0,088	0,835	0,001	0,782
FAME	0	0	0,76	0,856	0	0	0,856	0,856	0,849	0	0,948	0
H2O	0	0	0	0	0	0	0	0	0,008	0,078	0	0,107
H3PO4	0	0	0	0	0	0	0	0	0	0	0	0,001
NA3PO4	0	0	0	0	0	0	0	0	0	0	0	0,104
Mole Flow kmol/hr												
TG	0	1,186	0,059	0,059	0	0	0,059	0,059	0,059	0	0,059	0
MEOH	8,079	0	4,699	0,053	4,646	4,646	0,053	0,053	0,053	0,024	0,029	0,024
NAOH	0,25	0	0,25	0,25	0	0	0,25	0,25	0,25	0,25	0	0
GLY	0	0	1,127	1,127	0	0	1,127	1,127	1,127	1,113	0,013	1,113
FAME	0	0	3,38	3,38	0	0	3,38	3,38	3,38	0	3,38	0
H2O	0	0	0	0	0	0	0	0	0,555	0,53	0,025	0,78
H3PO4	0	0	0	0	0	0	0	0	0	0	0	0,002
NA3PO4	0	0	0	0	0	0	0	0	0	0	0	0,083

Table B.1: Simulation results: Case 1.

Stream	14	INPUT1	INPUT2	INPUT3	INPUT4	INPUT5	OUTPUT1	OUTPUT2	OUTPUT3	OUTPUT4	PROD1	PROD2
Temperature C	60,5	30	30	30	30	30	194	329,7	60,5	71,1	194	221,9
Pressure bar	1	1	1	1	1	1	0,15	0,2	1	0,4	0,15	0,5
Vapor Frac	0	0	0	0	0	0	1	0	0	0	0	0
Mole Flow kmol/hr	1,92	1,186	0,25	3,433	0,555	0,085	0,034	0,072	0,083	0,751	3,399	1,169
Mass Flow kg/hr	117,55	1050	10	110	10	8,33	1,467	55,07	13,662	13,995	1000,58	103,556
Volume Flow cum/hr	0,096	1,159	0,005	0,14	0,01	0,002	8,92	0,076	0	0,015	1,339	0,094
Enthalpy MMkcal/hr	-0,23	-0,528	-0,017	-0,195	-0,038	-0,006	-0,002	-0,02	-0,028	-0,05	-0,501	-0,169
Mass Flow kg/hr												
TG	0,004	1050	0	0	0	0	0,002	50,501	0	0	1,989	0,004
MEOH	0,778	0	0	110	0	0	0,66	0	0	0,778	0,271	0
NAOH	0	0	10	0	0	0	0	0	0	0	0	0
GLY	102,546	0	0	0	0	0	0,004	0	0	0,006	1,2	102,54
FAME	0	0	0	0	0	0	0,589	4,569	0	0	996,889	0
H2O	14,059	0	0	0	10	0	0,213	0	0	13,059	0,232	1
H3PO4	0,163	0	0	0	0	8,33	0	0	0	0,151	0	0,012
NA3PO4	0	0	0	0	0	0	0	0	13,662	0	0	0
Mass Frac												
TG	0	1	0	0	0	0	0,001	0,917	0	0	0,002	0
MEOH	0,007	0	0	1	0	0	0,45	0	0	0,056	0	0
NAOH	0	0	1	0	0	0	0	0	0	0	0	0
GLY	0,872	0	0	0	0	0	0,003	0	0	0	0,001	0,99
FAME	0	0	0	0	0	0	0,401	0,083	0	0	0,996	0
H2O	0,12	0	0	0	1	0	0,145	0	0	0,933	0	0,01
H3PO4	0,001	0	0	0	0	1	0	0	0	0,011	0	0
NA3PO4	0	0	0	0	0	0	0	0	1	0	0	0
Mole Flow kmol/hr												
TG	0	1,186	0	0	0	0	0	0,057	0	0	0,002	0
MEOH	0,024	0	0	3,433	0	0	0,021	0	0	0,024	0,008	0
NAOH	0	0	0,25	0	0	0	0	0	0	0	0	0
GLY	1,113	0	0	0	0	0	0	0	0	0	0,013	1,113
FAME	0	0	0	0	0	0	0,002	0,015	0	0	3,362	0
H2O	0,78	0	0	0	0,555	0	0,012	0	0	0,725	0,013	0,056
H3PO4	0,002	0	0	0	0	0,085	0	0	0	0,002	0	0
NA3PO4	0	0	0	0	0	0	0	0	0,083	0	0	0

Table B.2: Simulation results: Case 1 (cont.).

Utility ID:	COL1-EC	COL1-ER	COL2-EC	COL2-ER	COL3-EC	COL3-ER	HEX1-E	HEX2-E	P1-E	P2-E
Utility type:	WATER	STEAM	WATER	STEAM	WATER	STEAM	STEAM	WATER	ELECTRICITY	ELECTRICITY
$/hr	0,971564	1,459847	1,233631	116,0738	0,057165	6,883366	0,136188	0,320941	0,00083	0,006132
kg/hr	14500,95	214,6834	18412,4	6975,587	853,2066	413,6638	22,39927	4790,164		
Gcal/hr	0,043359	0,110439	0,330291	0,42548	0,015305	0,025232	0,011987	0,085928	1,15E-05	8,50E-05
kcal/kg	-2,99005	514,425	-17,9385	60,99552	-17,9385	60,99552	535,1658	-17,9385		
$/kg	6,70E-05	0,0068	6,70E-05	0,01664	6,70E-05	0,01664	0,00608	6,70E-05		
$/kWhr									0,062	0,062
C	27	184	27	400	27	400	160	27		
C	30	150	45	300	45	300	125	45		
bar	1	10	1	41	1	41	5	1		
bar	1	9,9	1	40,9	1	40,9	4,9	1		
Inlet vapor fraction:	0	1	0	1	0	1	1	0		
Outlet vapor fraction:	0	0	0	1	0	1	0	0		
kcal/kg	-3787,43	-3149,17	-3787,43	-3047,07	-3787,43	-3047,07	-3154,03	-3787,43		
kcal/kg	-3784,44	-3663,6	-3769,5	-3108,07	-3769,5	-3108,07	-3689,2	-3769,5		

Table B.3: Simulation results: Case 1 (cont.).

Stream	1	2-2	3-2	4-2	5-2	6-2	7-2	8-2
Temperature C	48,5	44	96,5	250	350	232,5	158,3	64,5
Pressure bar	1	1	430	430	430	430	1,053	1,013
Vapor Frac	0	0	0	0	1	0	0	0
Mole Flow kmol/hr	49,988	51,173	51,173	51,173	51,173	51,173	4,744	46,43
Mass Flow kg/hr	1601,709	2651,709	2651,709	2651,709	2651,709	2651,709	1164	1487,709
Volume Flow cum/hr	2,095	4,177	6,322	7,648	7,158	5,531	1,959	2,628
Enthalpy MMkcal/hr	-2,819	-3,42	-3,238	-2,967	-2,783	-3,054	-0,724	-2,616
Mass Flow kg/hr								
TG	0	1050	1050	1050	52,5	52,5	52,5	0
MEOH	1601,709	1601,709	1601,709	1601,709	1493,418	1493,418	5,709	1487,709
GLY	0	0	0	0	103,749	103,749	103,749	0
FAME	0	0	0	0	1002,042	1002,042	1002,042	0
WATER	0	0	0	0	0	0	0	0
Mass Frac								
TG	0	0,396	0,396	0,396	0,02	0,02	0,045	0
MEOH	1	0,604	0,604	0,604	0,563	0,563	0,005	1
GLY	0	0	0	0	0,039	0,039	0,089	0
FAME	0	0	0	0	0,378	0,378	0,861	0
WATER	0	0	0	0	0	0	0	0
Mole Flow kmol/hr								
TG	0	1,186	1,186	1,186	0,059	0,059	0,059	0
MEOH	49,988	49,988	49,988	49,988	46,608	46,608	0,178	46,43
GLY	0	0	0	0	1,127	1,127	1,127	0
FAME	0	0	0	0	3,38	3,38	3,38	0
WATER	0	0	0	0	0	0	0	0
Mole Frac								
TG	0	0,023	0,023	0,023	0,001	0,001	0,012	0
MEOH	1	0,977	0,977	0,977	0,911	0,911	0,038	1
GLY	0	0	0	0	0,022	0,022	0,237	0
FAME	0	0	0	0	0,066	0,066	0,712	0
WATER	0	0	0	0	0	0	0	0

Table B.4: Simulation results: Case 2.

Stream	9-2	10-2	11-2	INPUT1-2	INPUT2-2	OUT1-2	PROD1-2	PROD2-2
Temperature C	64,5	40	30	30	30	356,4	49,8	30
Pressure bar	1	1,013	1	1	1	0,15	0,1	1
Vapor Frac	0	0	0	0	0	0	0	0
Mole Flow kmol/hr	46,43	4,744	3,54	1,186	3,558	0,073	3,467	1,204
Mass Flow kg/hr	1487,709	1164	1058,58	1050	114	56,58	1002	105,42
Volume Flow cum/hr	2,628	1,823	1,242	1,159	0,145	0,195	1,549	0,085
Enthalpy MMkcal/hr	-2,616	-0,81	-0,619	-0,601	-0,202	-0,02	-0,593	-0,18
Mass Flow kg/hr								
TG	0	52,5	52,458	1050	0	52,449	0,01	0,042
MEOH	1487,709	5,709	2,784	0	114	0	2,784	2,925
GLY	0	103,749	1,296	0	0	0	1,296	102,453
FAME	0	1002,042	1002,042	0	0	4,132	997,91	0
WATER	0	0	0	0	0	0	0	0
Mass Frac								
TG	0	0,045	0,05	1	0	0,927	0	0
MEOH	1	0,005	0,003	0	1	0	0,003	0,028
GLY	0	0,089	0,001	0	0	0	0,001	0,972
FAME	0	0,861	0,947	0	0	0,073	0,996	0
WATER	0	0	0	0	0	0	0	0
Mole Flow kmol/hr								
TG	0	0,059	0,059	1,186	0	0,059	0	0
MEOH	46,43	0,178	0,087	0	3,558	0	0,087	0,091
GLY	0	1,127	0,014	0	0	0	0,014	1,112
FAME	0	3,38	3,38	0	0	0,014	3,366	0
WATER	0	0	0	0	0	0	0	0
Mole Frac								
TG	0	0,012	0,017	1	0	0,81	0	0
MEOH	1	0,038	0,025	0	1	0	0,025	0,076
GLY	0	0,237	0,004	0	0	0	0,004	0,924
FAME	0	0,712	0,955	0	0	0,19	0,971	0
WATER	0	0	0	0	0	0	0	0

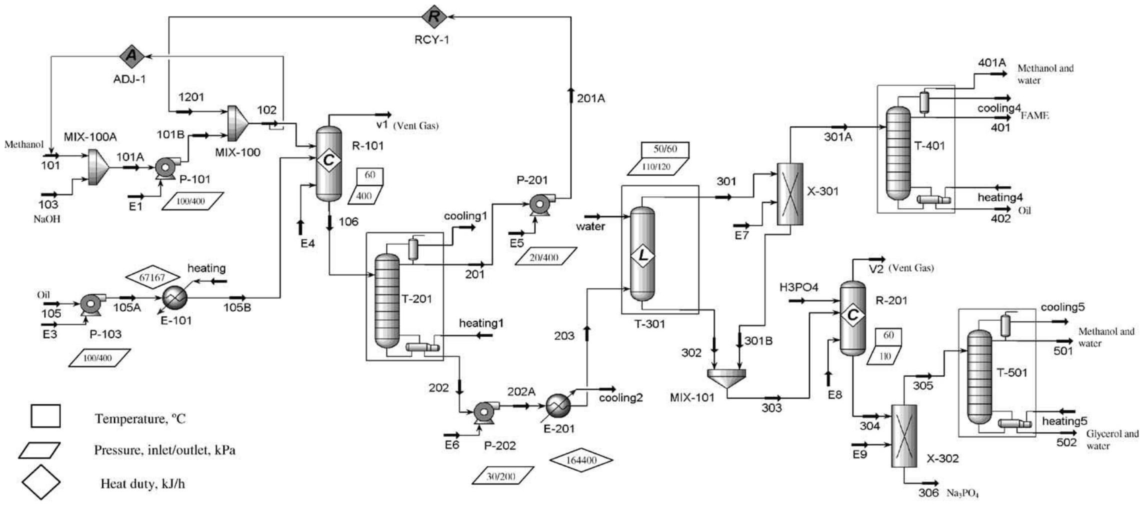
Table B.5: Simulation results: Case 2 (cont.).

Utility ID:	COL1-EC2	COL1-ER2	COL2-EC2	COL2-ER2	HEX2-E2	P1-E2	P2-E2	REAC1-E2
Utility type:	WATER	STEAM	WATER	STEAM	WATER	ELECTRICITY	ELECTRICITY	ELECTRICITY
$/hr	2,044851	3,672408	0,677693	56,92711	0,289153	13,09753	1,74E-05	13,30642
kg/hr	30520,16	604,0145	10114,83	3421,1	4315,72			
Gcal/hr	0,609707	0,323442	0,202066	0,208418	0,086216	0,181643	2,41E-07	0,18454
kcal/kg	-19,9772	535,4871	-19,9772	60,92134	-19,9772			
$/kg	6,70E-05	0,00608	6,70E-05	0,01664	6,70E-05			
$/kWhr						0,062	0,062	0,062
C	27	160	27	400	27			
C	47	125	47	300	47			
bar	1	5	1	41	1			
bar	0,9	4,9	0,9	40,9	0,9			
Inlet vapor fraction:	0	1	0	1	0			
Outlet vapor fraction:	0	0	0	1	0			
kcal/kg	-3789,79	-3155,89	-3789,79	-3049,75	-3789,79			
kcal/kg	-3769,81	-3691,38	-3769,81	-3110,67	-3769,81			

Table B.6: Simulation results: Case 2 (cont.).

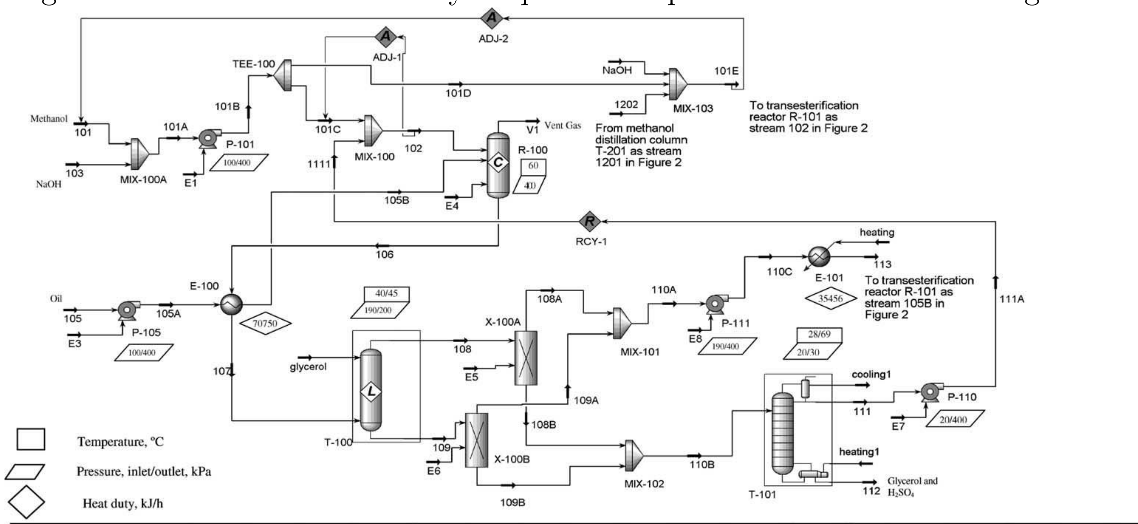
Appendix C

Biodiesel process models (Zhang et al., 2003a)



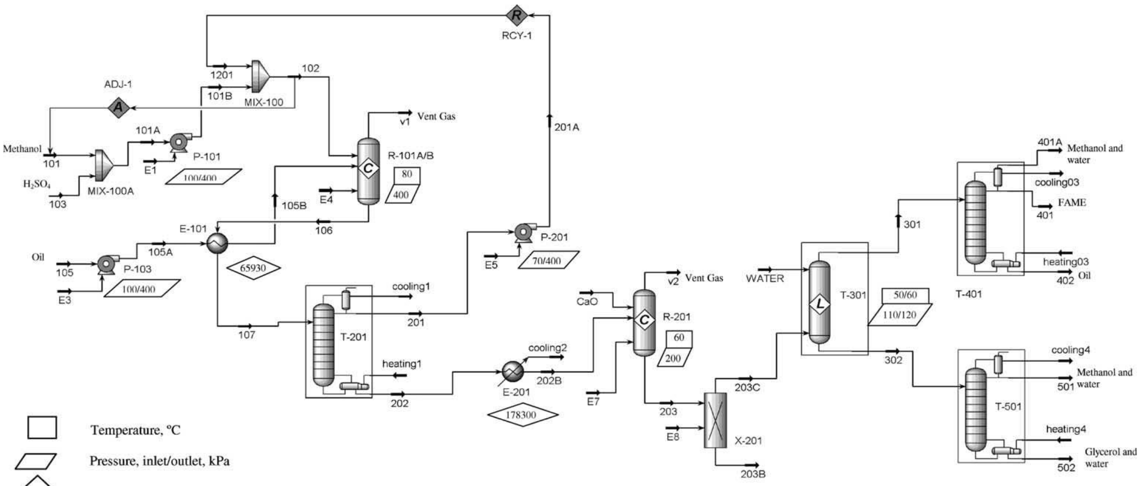
Stream name	101	102	103	105B	106	201	202	301A	305	306	401A	401	402	501	502
Temperature (ºC)	25.0	26.7	25.0	60.0	60.0	28.2	122.34	60.0	60.0	60.0	193.7	193.7	414.7	56.2	112
Pressure (kPa)	100	400	100	400	400	20	30	110	110	110	10	10	20	40	50
Molar flow (kg-mol/h)	3.66	7.13	0.25	1.19	8.51	3.47	5.04	3.60	2.04	0.084	0.155	3.384	0.06	0.42	1.52
Mass flow (kg/h)	117.20	238.39	10.00	1050.00	1288.40	111.19	1177.20	1060.21	122.31	13.73	7.82	999.88	52.50	9.02	113.29
Liquid volume flow (m^3/h)	0.147	0.287	0.006	1.167	1.440	0.140	1.300	1.208	0.102	0.005	0.009	1.140	0.058	0.010	0.092
Component mass fraction															
Methanol	1.000	0.956	0.000	0.000	0.092	1.000	0.006	0.003	0.032	0.000	0.388	0.000	0.000	0.363	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.041	0.000	0.045	0.050	0.000	0.000	0.000	0.000	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.779	0.000	0.853	0.946	0.002	0.000	0.504	0.997	0.000	0.000	0.000
Glycerol	0.000	0.000	0.000	0.000	0.081	0.000	0.088	0.000	0.850	0.000	0.000	0.000	0.000	0.000	0.850
NaOH	0.000	0.044	1.000	0.000	0.008	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.117	0.000	0.107	0.003	0.002	0.637	0.150
H_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000
Na_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.995	0.000	0.000	0.000	0.000	0.000

Figure C.1: Case 1: Alkali-catalyzed process to produce biodiesel from virgin oils.



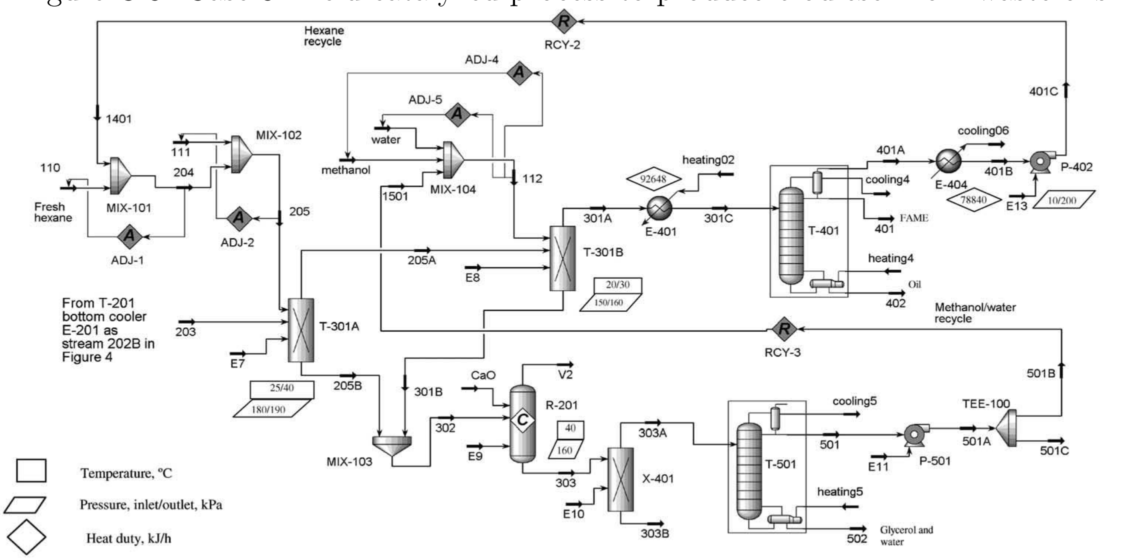
Stream name	101	102	103	105B	106	112	113	201	202	203	301A	305	306	401A	401	402	501	502
Temperature (ºC)	25.0	28.1	25.0	60.0	70.0	69.5	60.0	60.0	28.2	125.7	59.0	60.0	60.0	217.75	217.75	434.2	64.7	107.6
Pressure (kPa)	100	400	100	400	400	30	400	400	20	30	120	120	120	20	20	30	40	50
Molar flow (kg-mol/h)	4.00	6.60	0.10	1.34	7.94	1.91	1.32	8.05	3.10	4.95	3.48	3.97	0.092	0.04	3.38	0.05	2.02	1.95
Mass flow (kg/h)	128.10	218.01	10	1050.00	1268.01	147.16	1042.05	1261.32	99.52	1161.80	1048.19	152.61	15.03	2.27	997.29	48.62	38.87	113.74
Liquid volume flow (m^3/h)	0.161	0.266	0.005	1.167	1.434	0.124	1.160	1.409	0.125	1.284	1.194	0.134	0.006	0.003	1.137	0.054	0.040	0.094
Component mass fraction																		
Methanol	1.000	0.954	0.000	0.000	0.158	0.082	0.000	0.084	1.000	0.005	0.001	0.037	0.000	0.228	0.000	0.000	0.146	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	0.940	0.778	0.071	0.937	0.008	0.000	0.042	0.047	0.000	0.000	0.000	0.001	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.052	0.005	0.063	0.830	0.000	0.860	0.952	0.006	0.000	0.621	0.997	0.000	0.000	0.008
Glycerol	0.000	0.000	0.000	0.000	0.000	0.747	0.000	0.077	0.000	0.083	0.000	0.633	0.000	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.045	1.000	0.000	0.008	0.068	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
NaOH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.001	0.000	0.000	0.003	0.027	0.000	0.000	0.000	0.000	0.001	0.324	0.000	0.151	0.002	0.000	0.854	0.142
Oleic acid (Fatty acid)	0.000	0.000	0.000	0.060	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000

Figure C.2: Case 2: Acid-catalyzed process for pretreatment of waste oils prior to alkali-catalyzed production of biodiesel.



Stream Name	101	102	103	105B	106	201	202	203B	301	302	401A	401	402	501	502
Temperature (°C)	25.0	73.5	25.0	60.0	80.0	81.4	108.8	60.0	56.4	60.0	264.3	264.3	462.6	52.6	107.3
Pressure (kPa)	100	400	100	400	400	190	200	130	110	120	40	40	50	40	50
Molar flow (kg-mol/h)	6.75	59.03	1.53	1.16	59.06	49.75	9.31	1.53	3.46	10.86	0.04	3.386	0.035	8.63	2.22
Mass flow (kg/h)	216.28	1992.41	150.00	1030.00	2990.37	1593.99	1396.38	208.03	1035.24	328.86	4.31	1000.12	30.81	199.91	128.95
Liquid volume flow (m^3/h)	0.272	2.396	0.081	1.144	3.478	2.003	1.475	0.070	1.180	0.332	0.005	1.140	0.034	0.226	0.106
Component mass fraction															
Methanol	1.000	0.925	0.000	0.000	0.567	1.000	0.073	0.000	0.000	0.308	0.074	0.000	0.000	0.506	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.010	0.000	0.022	0.000	0.030	0.000	0.000	0.000	0.999	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.336	0.000	0.719	0.000	0.969	0.002	0.852	0.997	0.001	0.000	0.006
Glycerol	0.000	0.000	0.000	0.000	0.037	0.000	0.078	0.000	0.000	0.333	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.075	1.000	0.000	0.050	0.000	0.107	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.356	0.074	0.003	0.000	0.493	0.143
CaO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$CaSO_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Figure C.3: Case 3: Acid-catalyzed process to produce biodiesel from waste oils.



Stream name	101	102	103	105B	106	201	203	205A	301C	303A	303B	401A	401	402	501	502
Temperature (°C)	25.0	58.9	25.0	60.0	80.0	64.1	60.0	25.0	60.0	40.0	40.0	149.7	149.7	414.7	46.6	114.49
Pressure (kPa)	100	400	100	400	400	100	200	180	150	160	160	10	10	20	40	50
Molar flow (kg-mol/h)	6.72	59.03	1.53	1.165	60.89	51.52	9.37	4.98	4.85	10.73	1.53	1.400	3.42	0.035	8.84	1.89
Mass flow (kg/h)	215.50	1992.41	150.00	1030.00	3046.44	1650.82	1395.61	1160.75	1153.50	369.37	208.13	118.62	1004.00	30.88	246.92	128.45
Liquid volume flow (m^3/h)	0.271	2.396	0.081	1.144	3.551	2.074	1.477	1.364	1.358	0.400	0.070	0.177	1.146	0.034	0.298	0.102
Component mass fraction																
Methanol	1.000	0.925	0.000	0.000	0.576	1.000	0.075	0.004	0.000	0.542	0.000	0.004	0.000	0.000	0.811	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.010	0.000	0.022	0.027	0.027	0.000	0.000	0.000	0.000	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.330	0.000	0.720	0.865	0.890	0.014	0.000	0.031	0.996	0.000	0.000	0.041
Glycerol	0.000	0.000	0.000	0.000	0.034	0.000	0.075	0.001	0.000	0.282	0.000	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.075	1.000	0.000	0.049	0.000	0.107	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.162	0.000	0.008	0.000	0.000	0.189	0.109
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.101	0.101	0.000	0.000	0.957	0.004	0.000	0.000	0.000
CaO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$CaSO_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000

Figure C.4: Case 4: Alternative acid-catalyzed process to produce biodiesel from waste oils using hexane extraction.

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