MODELLING AND ENVIRONMENTAL ASSESSMENT OF HETEROGENEOUS CATALYSIS BIODIESEL PROCESS USING WAR ALGORITHM

AS ELEYANA BINTI ALI

UNIVERSITI MALAYSIA PAHANG

AS ELEYANA ALI   BACHELOR OF CHEMICAL ENGINEERING   2013   UMP

MODELLING AND ENVIRONMENTAL ASSESSMENT OF HETEROGENEOUS CATALYSIS BIODIESEL PROCESS USING WAR ALGORITHM

AS ELEYANA BINTI ALI

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of the degree of Bachelor of Chemical Engineering.

Signature :
Name : Dr. Ing. Mohamad Rizza bin Othman
Position : Senior Lecturer
Date :

STUDENT'S DECLARATION

I hereby declare that this thesis entitled "Modelling and Environmental Assessment of Heterogeneous Catalysis Biodiesel Process using WAR Algorithm" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any other degree.

Signature :
Name : As Eleyana binti Ali
ID Number : KA09177
Date :

Dedicated to my beloved parents

ACKNOWLEDGEMENT

Praise to God with His blessings, my Undergraduate Research Project (URP) is finally completed. I would like to take this opportunity to express my appreciation to those who helped me during completing this project. First and foremost, I would like to express my sincere gratitude to Dr. Ing. Mohamad Rizza bin Othman as my supervisor for the guidance, comments, supporting, commitment and advice in overseeing the progress of my URP from the initial phase until the completion of this project. I also would like to acknowledge my sincere indebtedness and gratitude to my parents for their love, dream and sacrifice throughout my life. My sincere appreciations also extend to every individual, family, colleagues, and lecturers who have assist me and help me in every occasion. From this project, I did learn a lot of new things and gain valuable knowledges that hopefully will be give benefits towards my career in future.

MODELLING AND ENVIRONMENTAL ASSESSMENT OF HETEROGENEOUS CATALYSIS BIODIESEL PROCESS USING WAR ALGORITHM

ABSTRACT

Environmental assessment in a preliminary designing stage of a process is important to evaluate the environmental friendliness of a process design, minimizing the environmental impact of the process. WAR algorithm, a methodology for determining the potential environmental impact (PEI) of a chemical process is developed to describe the flow and the generation of PEI through a chemical process. WAR algorithm which acts as a comparison tool in selecting the environmentally benign design option is developed using heterogeneous catalysis and alkali homogeneous catalysis of biodiesel process as case study. Heterogeneous catalysis of biodiesel process flowsheeting is first developed and simulated using Aspen Plus 7.0. Data and simulation results are then exported to the spreadsheet for environmental assessment of WAR algorithm. Four PEI indexes (TRO,TOP,TRG,TGP) are used to evaluate the environmental friendliness of a process design while eight PEI categories (four global and four toxilogical) are used to evaluate the PEI indexes. Comparison of the PEI indexes concluded that heterogeneous catalysis of biodiesel process showed more environmentally friendly process with minimum amount of PEI value compared to homogeneous catalysis process.

PENILAIAN ALAM SEKITAR TERHADAP PEMPROSESAN BIODIESEL MELALUI PEMANGKIN HETERO MENGGUNAKAN KAEDAH WAR ALGORITMA

ABSTRAK

Penilaian Alam Sekitar di peringkat awal rekabentuk proses adalah penting untuk menilai tahap mesra alam sesuatu reka bentuk proses, mengurangkan kesan alam sekitar disebabkan proses tersebut. WAR algoritma, kaedah untuk mengenalpasti potensi impak alam sekitar (PEI) sesuatu proses kimia, dirangka untuk menerangkan aliran dan penghasilan PEI di dalam proses. WAR algoritma yang bertindak sebagai alat perbandingan dalam memilih reka bentuk pilihan yang mesra alam dibangunkan dengan menggunakan proses penghasilan biodiesel menggunakan pemangkin heterogen dan pemangkin homogen alkali sebagai kajian kes. Rangka proses penghasilan biodiesel menggunakan pemangkin heterogen dirangka dan disimulasi menggunakan Aspen Plus 7.0. Data dan keputusan simulasi kemudiannya dieksport ke spreadsheet untuk penilaian alam sekitar menggunakan kaedah WAR algoritma. Empat PEI indeks (TRO, TOP, TRG, TGP) digunakan untuk menilai keramahan alam sekitar rekabentuk proses manakala lapan kategori PEI (empat global dan empat toxilogical) digunakan untuk menilai indeks PEI. Perbandingan indeks PEI menyimpulkan bahawa pemangkinan heterogen proses biodiesel menunjukkan proses yang lebih mesra alam dengan jumlah nilai PEI yang minimum berbanding dengan proses penghasilan biodiesel menggunakan pemangkin homogen.

TABLE OF CONTENTS

3 PROCESS SIMULATION

4 ENVIRONMENTAL ANALYSIS AND COMPARISON

5 CONCLUSION AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AP	Acidification Potential
ASTM	The American Society For Testing and Material
ATP	Aquatic Toxicity Potential
$C_{19}H_{36}O_2$	Methyl Oleate
$C_3H_8O_3$	Glycerol
$C_{57}H_{104}O_6$	Triolein
CH_4O	Methanol
FAME	Fatty Acid Methyl Ester
GWP	Global Warning Potential
H_2O	Water
HTPE	Human Toxicity Potential by Inhalation/ Dermal Exposure
HTPI	Human Toxicity Potential by Ingestion
ODP	Ozone Depletion Potential
PCOP	Photochemical Oxidation Potential
PEI	Potential Environmental Impact
PFD	Process Flow Diagram
TGP	Total Rate Generation/Product
TGR	Total Rate Generation
TOP	Total Rate Output/Product
TRO	Total Rate Output
TTP	Terrestrial Toxicity Potential
WAR	Waste reduction algorithm

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biodiesel is the name given to a clean burning mono-alkyl ester based oxygenated fuel made derived from renewable lipid feedstock such as vegetable oil or animal fat. Biodiesel is normally derived using catalyzed transesterification reaction in which the renewable lipid feedstock reacts with alcohol (Zhang *et al.*, 2002). Homogeneous acid and alkali process design are conventional methods that are widely used in industry. However, heterogeneous catalysis and supercritical methanol process have been reviewed to show advantageous over the conventional process.

West *et al.*, (2008), reviewed on methods to reduce the production cost of biodiesel which is first by replacing the virgin oil feedstock with a waste cooking oil feedstock. The second method is by the uses of solid catalyst replacing the rely on homogeneous catalyst which consume energy, time and cost due to the purification step of catalyst. Both methods can be achieved using heterogenous catalysis biodiesel process. The third method is by the uses of alcohol in its supercritical state and eliminates the need for catalyst. Based on his study which compared the feasibility of homogenous, heterogenous, and supercritical methanol process, heterogeneous catalysis process had showed advantageous over the other process. Thus, the production of biodiesel from waste cooking oil based on continuous heterogeneous catalysis process is used as a case study and model for the simulation and environmental assessment in this study.

In this study, pollution prevention technique is incorporated into the biodiesel process design by determining the flow and generation of potential environmental impact (PEI) through the process using WAR algorithm method. In process design stage, environmental assessment or pollution prevention is normally not taking into consideration as economics, operating and capital issue predominant the entire design. Method of WAR algorithm is used in evaluating the relative environmental impact of chemical process. It is a methodology that are considered only during the manufacturing level of chemical process which is therefore suitable to be used during the design stage of new process or for the modification of the existent process. Besides, it adopts simple algorithms and parameters which are therefore suitably used in accessing the environmental performance of biodiesel design in this study.

1.2 Problem Statement

Economics assessment, operating and capital design were the predominant issue in process design stage while environmental assessment was rarely introduced in a process design. Environmental concern received more attention in recent years thus implementing environmental assessment is an advantage in process design.

In environmental assessment of process design, common environmental performance used was LCA which was time consuming and costly. Alternatively, WAR algorithm was used as it is best performed during designing stage due to the simpler approaches it have. (Othman, 2011). Environmental assessment using WAR algorithm method determined the potential environmental impact (PEI) through a process thus help to evaluate the effect that the mass and energy of the process would have on the environment if they were to be emitted to the environment.

1.3 Objectives

The objectives of this thesis are to simulate the process flowsheet of heterogeneous biodiesel production using Aspen Plus Simulator and carry out the environmental analysis of the process using WAR Algorithm.

1.4 Scope of Study

In this study, continuous process of biodiesel production at a rate of 8000 tonnes/year using heterogeneous catalyst is modeled and simulated based on the design and parameters referred from West (2007). Results from simulation are then used to perform economic and environmental analysis. The scopes of this study include:

i. Simulate the continuous process flowsheets of heterogenous catalysis biodiesel process using Aspen Plus 7.0 process simulator.

ii. Determine the potential environment impact (PEI) of biodiesel process using WAR algorithm method performed in spreadsheet of Microsoft Excel and comparing the results with homogeneous catalysis biodiesel process.

1.5 Significance of Proposed Study

The significance of this study is to provide another perspective of analyzing process design which is by taking account the environmental criteria. Analyzing of potential environmental impact (PEI) in process design improved the economic and environmental aspect of the process itself.

1.6 Thesis Structure

This thesis consist of five chapters which are, Introduction in the first chapter, Literature Review in chapter 2, Process Simulation in chapter 3, Environmental Analysis and Comparison in chapter 4, and Conclusion and Recommendation in chapter 5.

In this introduction chapter, background of proposed study, the problem statement, objectives, scopes and significance of proposed study are presented. As for the next chapter on Literature Review, previous study from researchers related with biodiesel productions and technologies, process synthesis of heterogeneous process, and environmental assessment of WAR algorithm are reviewed. In Chapter 3 on Process Simulation, parameters used for simulation process and the process design modeled are presented in details in this chapter. Simulation result is attached at the end of the chapter which is further used in Chapter 4 for environmental assessment.

Chapter 4 on Environmental Analysis and comparison discussed and compared the results of four PEI indexes and eight PEI categories within homogeneous and heterogenous process. Chapter 5 concluded the findings of this study and discussed points on improvement of the study. In overall, this study can be summarized as below:

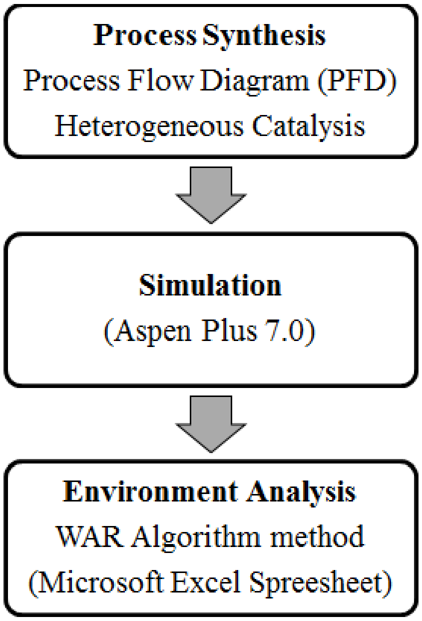


Figure 1.1 Schematic of the process design approach

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, background on the biodiesel and technical description on the heterogeneous catalysis biodiesel process are reviewed. Discussion on the environmental analysis using WAR algorithm method is reviewed.

2.2 Biodiesel

Biodiesel is a renewable energy produced by a catalyzed transesterification reaction of alcohol and natural triglycerides from vegetables oil or animal fats. The decreasing of fossil fuel supplies, the increasing of petroleum price, and the community concern on the environmental and human health impact from the uses of petroleum fuel do encourage the research and development on biodiesel.

Biodiesel is derived from vegetable oil or animal fat, a renewable, domestic resource which reduce the reliance on petroleum. The properties of biodiesel make it safe and useful for transportation. (West *et al*., 2008; Zhang *et al*., 2002). As biodiesel is biodegradable and non-toxic, it is suitably applied for transportation in highly sensitive environments while the high flash point of biodiesel (approximately 150 °C) compared to petroleum diesel which is around 50°C making it safe for transportation or when handling it because it is less volatile (Zhang *et al*., 2002). Biodiesel also improve the performance of engine exhaust emission by reducing the lifecycle of carbon dioxide emissions by 78% compared to diesel fuel engine. Reduction in carbon monoxide emission by 66.7%, particulate matter by 66.7%, unburned hydrocarbon by 45.2% and almost no sulfur or aromatic compound compared to petroleum diesel (West *et al*., 2008).

2.2.1 Biodiesel Production

Zhang *et al*., (2002) briefly described on four potential ways to reduce the viscosity of vegetable oil for the production of biodiesel which are: dilution, pyrolysis, microemulsion and transesterification. Transesterification reduced the molecular weight of oil, thus reducing the viscosity making it the best method for biodiesel production process which is therefore use in this study.

Several commercial processes to produce biodiesel have been developed and they are commercially produced in Europe and United States. In Europe, Austria, Italy, Germany and France commercially used biodiesel since 1988 with Germany as the largest biodiesel producer in Europe with total production capacity of 1.060.000 tons, followed by France with 520.000 tons in 2004 (Othman, 2011).

One limitation of large-scale commercialization is because of the high production cost (Zhang *et al.*, 2002; West *et al.*, 2008; Othman, 2011). West *et al*, (2008) suggested three methods in reducing the production cost which is first by replacing a virgin oil feedstock with a waste cooking oil feedstock. The second method is by the uses of alcohol in its supercritical state avoiding the uses of catalyst. The last method is by the uses of solid heterogeneous catalyst replacing the conventional liquid catalyst. In his study, production of biodiesel via continuous transesterification process using waste cooking oil as the feedstock and heterogeneous acid catalyst is concluded to have advantageous over the other processes with simple process design and much economically. Thus, the same technology in producing biodiesel will be focus in this study.

2.3 Process Description

2.3.1 Transesterification Technology

Transesterification reaction is the reaction within triglycerides from vegetables oil or animal fats with alkyl alcohol in the presence of catalyst to produce alkyl esters and glycerol. Recommended alcohols are those with low carbon chain such as methanol, ethanol and butanol. Methanol is commonly used, having fatty acid methyl esters (FAME or biodiesel) as the product and glycerol as the byproduct.

While for the feedstock, vegetable and animal fat such as soybean oil, canola oil, rapeseed oil, sunflower oil and beef tallow are commonly used (Zhang, 2002). Besides, the uses of low cost feedstock such as waste cooking oil may be adopted to reduce the production cost.

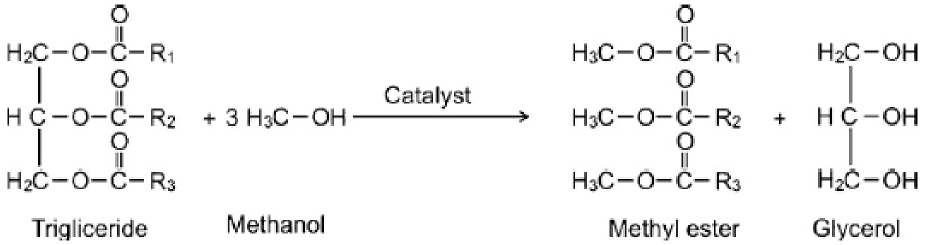


Figure 2.1 Biodiesel reaction
(Source: Chouhan & Sarma, 2011)

Since the reaction is not fast enough at low temperature, catalyst is use to fasten up the reaction. The catalyst can be an alkali, acid or enzyme either in liquid (homogeneous) or solid (heterogeneous) form. Common homogeneous catalyst used are sodium hydroxide, potassium hydroxide and sulfuric acid while for heterogeneous catalyst, metal oxide such as zinc oxide are frequently used. Due to the expensive processing stages of homogenous catalysis, heterogeneous catalysis is preferable.

From figure 2.1, the reaction required 3:1 molar alcohol to oil ratio, minimum ratio for the transesterification reaction to take place. However, excess alcohol is usually added to achieve higher ester yield (Dimian & Bildea, 2008; West *et al*., 2008; Othman, 2011). As for the condition of the reaction, it is normally run at temperature closed to the boiling point of alcohol and pressure slightly above the atmosphere pressure.

2.3.2 Heterogeneous Catalysis System

Heterogeneous catalytic transesterification is classified as green technology because the catalyst can be recycle, less amount of waste water is produce during the process, and ease separation of biodiesel from glycerol (Chouhan & Sarma, 2011). Heterogeneous catalysis process eliminated the purification step of catalyst and avoided the side reaction within free fatty acid and base alcohol therefore reducing the production cost of biodiesel (Othman, 2011).

Othman, (2011) had reviewed on the study by Furuta et al. in 2004 whereby in their study, they used solid superacid catalysis, tungstated zirconia, sulfated tin oxide and sulfated zirconia catalyst in the reaction. Various types of heterogeneous catalysts have been used for lab scale biodiesel production. Detailed reviewed and discussion on this is presented by Chouhan and Sarma, (2011).

In this study, biodiesel process is based on the study done by West *et al*., (2007). Basic heterogeneous catalysis biodiesel process includes transesterification reaction in the stoichiometric reactor, methanol recovery by the distillation column, glycerol separation through decanter and biodiesel purification in the distillation column.

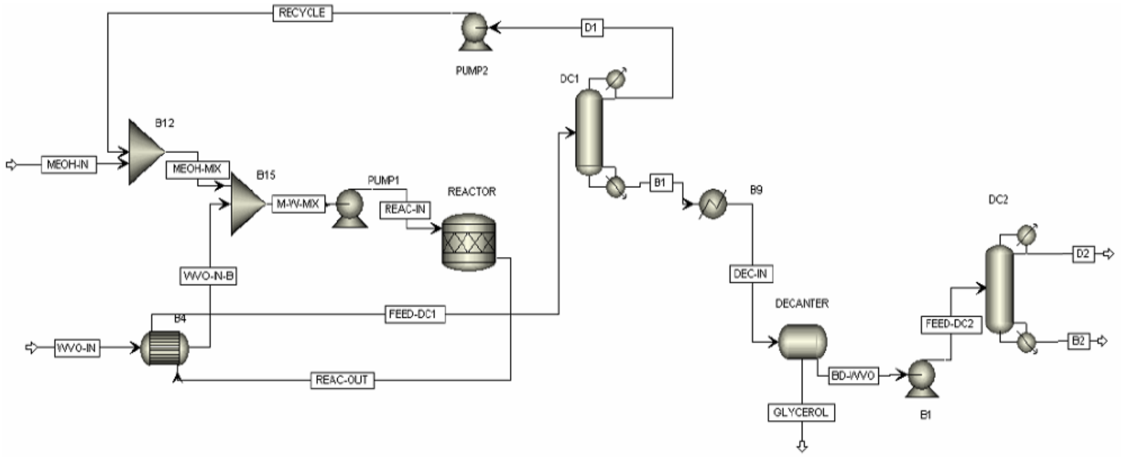


Figure 2.2 Heterogeneous acid-catalyzed process flowsheet
(Source: West *et al*., 2007)

2.4 Environmental Analysis using WAR Algorithm

Environmental assessment is important in a process plant in order to minimize the potential impact of hazardous chemical from process towards the environment. In designing a chemical process, pollution prevention technique is implemented into the process due to the environmental concerns. Young *et al.*, (2000) reviewed on the first implementation of pollution prevention which are via heat exchange networks (HENs) and mass exchange networks (MENs) in 1970s. While HENs focusing on reduction of energy consumption during manufacturing process, MENs concerning on reduction of waste generated from a process that require treatments. Waste reduction (WAR) algorithm is introduced by Hilaly and Sikdar (1994) to evaluate the environmental impact of the waste from chemical process. WAR algorithm originally introduced the concept of pollution balance, a methodology that allowed pollutants to be tracked throughout the process (Young *et al.*, 1999).

Generalized WAR algorithm with a potential environmental impact (PEI) is then introduced by Cabezas *et al.*, (1997) in order to consider the impact of the pollution generated within a process. While pollution balance tracked the pollutants, PEI balance quantifies the impact that indicates either the process is environmental friendliness or not (Young *et al.*, 1999).

Different methodologies may be applied as reviewed by Young *et al.,* (2000). However, WAR algorithm will be used to assess environmental performance of process design in this paper. This is because of the simple approaches it takes in describing and analyzing the environmental impact of the input-output material and energy stream in a process. The uses of simple algorithms as well as easy to find parameters making this method is preferable in analyzing the environmentally friendliness of chemicals in process towards the environment.

WAR algorithm is a tool used in evaluating the relative environmental impact of a chemical process. It is a methodology that only considers during the manufacturing process by not taking accounts the overall life cycle analysis (LCA). Thus, WAR algorithm is suitably used during the design stage of a new process or for modification of existent process design. Brief reviewed and comparison within LCA and WAR algorithm is presented by Othman, (2011).

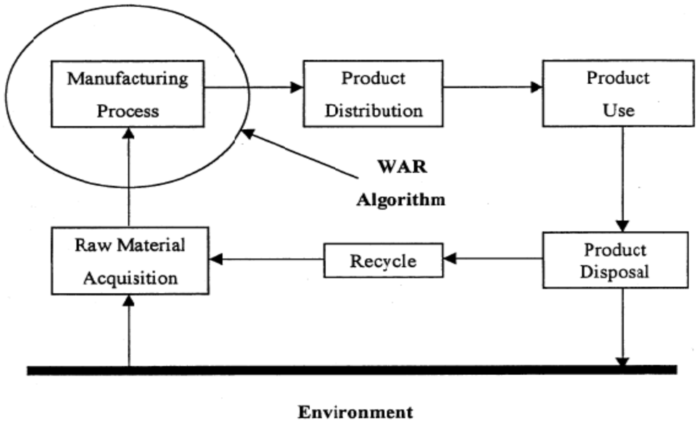


Figure 2.3 Product Life Cycle
WAR algorithm is performed during manufacturing process.
(Source: Young & Cabezas, 1999)

To be used in designing stage of process, WAR algorithm must be used in conjunction with chemical process simulators (Othman, 2011, Young *et al.*, 1999). WAR algorithm has been integrated into several process simulators such as ChemCAD, Integrated Computer Aided System (ICAS) and AspenTech (under negotiation) and a download version of WAR software can be found at US EPA website (Othman, 2011). In this study, WAR calculation is done in the spreadsheet of Microsoft Excel.

Detailed discussion of the WAR theories such as potential environment impact and indexes, weighing factors and economic evaluation are presented by Young and Cabezas (1999). Brief summary of the theory will be presented here.

2.4.1 Potential Environmental Impact Theory

Potential environmental impact (PEI) in WAR algorithm is defined as the effect that the specified quantity of material and energy would have on the environment when they are exposed to the environment (Young & Cabezas, 1999).

At steady state, PEI balance may be expressed as:

$$0 = I_{in}^{(cp)} + I_{in}^{(ep)} - I_{out}^{(cp)} - I_{out}^{(ep)} - I_{we}^{(cp)} - I_{we}^{(ep)} + I^{t}_{gen} \qquad (2.1)$$

Where $I_{in}^{(cp)}$ and $I_{out}^{(cp)}$ are the mass input and output rates of PEI to the chemical process, $I_{in}^{(ep)}$ and $I_{out}^{(ep)}$ are the input and output rate of PEI to the energy generation process, $I_{we}^{(cp)}$ and $I_{we}^{(ep)}$ are the outputs of PEI associated with waste energy lost from the chemical process and the energy generation process which will be neglected due to the minor impact they give. I^{t}_{gen} is the rate of generation of PEI inside the system.

The equation is then reduced to:

$$0 = I_{in}^{(cp)} + I_{in}^{(ep)} - I_{out}^{(cp)} - I_{out}^{(ep)} + I^{t}_{gen} \tag{2.2}$$

PEI generation index, I^{t}_{gen} can be calculated by the equation below:

$$I^{t}_{gen} = I_{out}^{(t)} - I_{in}^{(t)} \tag{2.3}$$

$$I_{in^{(t)}} = \sum_{i}^{EnvCat} \alpha_i I^{(t)}{}_{i,in} = \sum_{i}^{EnvCat} a_i \sum_{j}^{Streams} M_{j,in} \sum_{k}^{Comps} x_{kj} \varphi^{s} ki \tag{2.4}$$

Where α_i is the weighting factor associated with PEI category I, $I^{(t)}{}_{i,in}$ is the PEI input index for category i, $M_{j,in}$ is the mass flow rate of input stream j, x_{kj} is the mass fraction of component kin stream j, and $\varphi^{s} ki$ is the specific PEI of component k associated with environmental impact category i.

$$I_{out^{(t)}} = \sum_{i}^{EnvCat} \alpha_i I^{(t)}{}_{i,out} = \sum_{i}^{EnvCat} a_i \sum_{j}^{Streams} M_{j,out} \sum_{k}^{Comps} x_{kj} \varphi^{s} ki \tag{2.5}$$

Where $I^{(t)}{}_{i,out}$ is the PEI output index for category I and $M_{j,out}$ is the mass flow rate of the product output stream j.

2.4.2 Potential Environmental Impact Indexes

Four types of environmental impact indexes are used in analyzing the environmental friendliness of chemical process which are: PEI output indexes and PEI generation indexes. (Young *et al.*, 2000).

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

$$\text{(TRG)} \qquad I^t{}_{gen} = I^{cp}_{out} - I^{cp}_{in} + I^{ep}_{out} \qquad (2.6)$$

$$\text{(TRO)} \qquad I^t_{out} = I^{cp}_{out} - + I^{ep}_{out} \qquad (2.7)$$

The output indexes can be in the terms of rate PEI/h or on production basis, PEI/kg. The algorithms used earlier are on a rate basis (PEI/h). In the production basis form (PEI/kg), the equations below are used:

$$\text{(TOP)} \qquad \hat{I}^t_{out} = \frac{I^t out}{\sum_P^{ProdStreams} P_p} \qquad (2.8)$$

$$\text{(TGP)} \qquad \hat{I}^t_{gen} = \frac{I^t gen}{\sum_P^{ProdStreams} P_p} \qquad (2.9)$$

Where $\hat{I}^t_{out}$ is the PEI output index, $\hat{I}^t_{gen}$ is the PEI generation index, and P_p is the mass flow rate of the product streams.

$I^t out$, $\hat{I}^t_{out}$, $I^t gen$, $\hat{I}^t_{gen}$, are used to compare the environmental friendliness of the process design. $I^t out$ is useful in identifying the appropriate site for a plant where a plant with low $I^t out$ must be located in ecologically sensitive area. $\hat{I}^t_{out}$, measures the efficiency of material utilization by a specific process per unit mass of products where it is decreases with the reduction of $I^{t}out$ or when the production rate is increased. Thus, improved the material utilization efficiency through process modification decreased the output PEI/kg of product. $\hat{I}^{t}_{\text{gen}}$, is used for comparing processes and products based on the amount of new PEI generated in product manufacturing. (Othman, 2011). The environmentally desirable design is those with the lowest PEI index values.

2.4.3 Specific PEI of Chemical Components

In implementing the WAR algorithm, the specific PEI of each chemical over certain impact category, $\varphi^{s}ki$, must be determined. Eight environmental impacts are used in this study which can be categorized into two categories:

Global atmospheric:

i. Global warming potential (GWP)
ii. Ozone depletion potential (ODP)
iii. Acidification potential (AP)
iv. Photochemical oxidation potential (PCOP)

Local toxilogical:

i. Human toxicity potential by ingestion (HTPI)
ii. Human toxicity potential by inhalation/dermal exposure (HTPE)
iii. Aquatic toxicity potential (ATP)
iv. Terrestrial toxicity potential (TTP)

The value of specific PEI of each chemical components involved are then exported the Microsoft Excel together with the data get from simulation process such as the stream flowrates and compositions, utilities, and operating conditions of pressure and temperature. Mass and energy balances are then performed using the equations above. Results obtained are then analyzed. Those with lower PEI value are preferable. (Othman, 2011).

CHAPTER 3

PROCESS SIMULATION

3.1 Introduction

Process simulation was carried out to assess the feasibilities of commercial process from the proposed process. From the simulation process, mass, component and energy balances of each unit operation as well as the operating conditions were obtained which will further used in environmental assessment.

3.2 Computational Tools

In this study, the process was modeled using Aspen Plus 7.0. Aspen Plus is a software package designed to allow a user to build a process model and then simulate the model without tedious calculations. It enables the optimization of plant performance and profitability.

3.3 Process Simulation

Basic steps in simulation process as stated by Othman (2011) and Zhang *et al.*, (2002) are; defining chemical components, selecting thermodynamic model and method, designing process flowsheet, determining plant capacity and setting up input parameters. All the parameters used were based on the design and parameters referred from West *et. al*, (2007).

3.3.1 Chemical Components

In this study, Waste Canola oil (Waste cooking oil) used was represented by triolein. Methyl-oleate was taken as the product of the transesterification reaction. Sulphated zirconia was chosen as the catalyst. The remaining components were methanol and glycerol.

Table 3.1 Compounds defined in Aspen Plus

Component name	Component ID	Formula
Triolein	TRIOL-01	C57H104O6
Methyl-oleate	METHY-01	C19H36O2
Methanol	METHA-01	CH4O
Glycerol	GLYCE-01	C3H3O3
Water	WATER	H2O

3.3.2 Thermodynamic Model and Method

Due to the presence of polar compounds in the process which were methanol and glycerol, NRTL thermodynamic models were selected to predict the activity coefficients of components in liquid (West *et. al*, 2008; Othman, 2011).

3.3.3 Process Flowsheet Design

In this study, continuous heterogeneous catalysis process from West *et al.*, (2007) was used as the model while considering all the parameter available.

Plant capacity was specified at 8000 metric tonnes/year, with oil (triolein) feed input of 1050 kg/hr. The major process units were transesterification reactor, distillation column for methanol recovery, gravity separator (decanter) for glycerol separation and distillation column for biodiesel purification. Detail process descriptions were as followed.

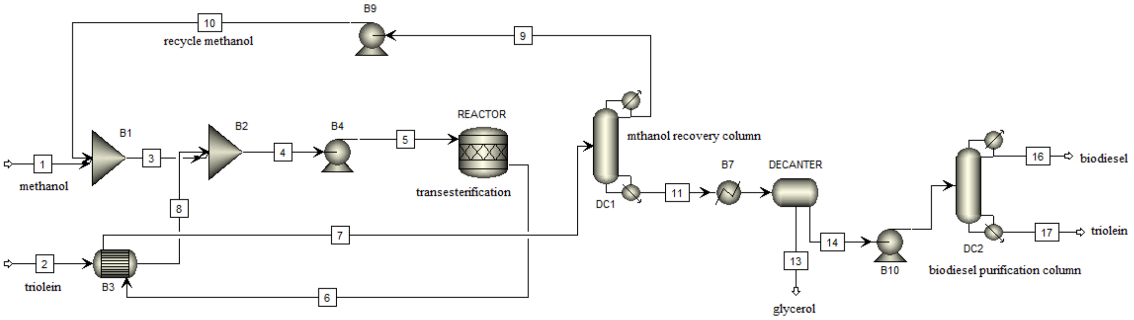


Figure 3.1 Heterogeneous acid-catalyzed process flowsheet

3.3.3.1 Transesterification (Reactor)

The reaction was carried out in stoichiometric reactor (RStoic) that represented a packed bed reactor with sulphated zirconia (SO_4/ZrO_2) catalyst inside. The rate of reaction was set up based on the stoichiometric as below:

$$\text{Triolein} + 3\ \text{Methanol} \rightarrow 3\ \text{FAME} + \text{Glycerol}$$

$$C_{57}H_{104}O_6 + 3CH_3OH \rightarrow 3C_{19}H_{36}O_2 + C_3H_8O_3$$

The conversion was set at 90.4% of triolein with assumption that no side reactions involving glycerol and no leaching of sulphate groups occurred (West *et al.*, 2007). Reactor was set at temperature of 200°C and pressure of 4050 kPa. Using the molar ratio of 6:1 methanol to oil, 1050 kg/h of triolein from the heat exchanger was mixed with methanol at B2 mixer with total methanol input flowrate of 228kg/h. In reactor, 90.4% of triolein was assumed to be converted to FAME, producing approximately 950 kg/h FAME and 98 kg/h glycerol in stream 6. There was some methanol and triolein remained in stream 6 since methanol was in excess. In brief, a total of 1278 kg/h in stream 6, contained 74.4% FAME, 7.7% glycerol, 9.8% methanol and 8.1% triolein.

3.3.3.2 Methanol Recovery (Distillation Column 1, DC1)

Radfract distillation column, DC1 used for methanol recovery was setup with 8 numbers of stages with feed stream at stage 5. Equilibrium type calculation was applied. Reflux ratio of 1.06 was used with total condenser and kettle reboiler. Distillate rate value was set at 125.295 kg/h according to the methanol flowrate input to DC1 to obtain 100% methanol recovery at the top stream recycled back to the reactor. Condensor pressure and column pressure drop were set at 20 kPa and 10kPa. In column 1, since the recovery is assumed of 100%, top stream 9 of distillate recycle about 125 kg/h methanol back to the mixer B1 mixed up with fresh methanol and charged back to the reactor. Bottom stream 11 of the column with total mass flowrate of 1152 kg/h contained about 82.4% FAME, 8.5% glycerol, and 9.0% triolein.

3.3.3.3 Glycerol Separation (Decanter)

Glycerol was separated from biodiesel using decanter which separate based on the density of the component. Methanol was able to dissolve almost entirely in the glycerol phase of methanol-glycerol-biodiesel mixture indicating that theoretically, decanter was able to achieve high purity separation (*West et al*., 2007). Operating temperature and pressure for decanter were set at 50°C and 101.3 kPa. The glycerol was removed from the system through output stream 13 of the decanter. A total flowrate of 98.248 kg/h in stream 13 of glycerol removal contained about 98.247 kg/h glycerol and 0.002 kg/h FAME. Satisfactory glycerol separation which is almost 100% with little present of FAME is achieved. A total flowrate of 1054.457 kg/h in output stream 14 of decanter is sent to the final FAME purification column. About 90.1 % FAME, 9.9% triolein and a small fraction of glycerol impurities were presented in the stream.

3.3.3.4 FAME Purification (Distillation Column 2, DC2)

Radfract distillation column, DC2 used for methyl-oleate (biodiesel) purification was setup with 5 numbers of stages with feed stream at stage 2. Equilibrium type calculation was applied. Reflux ratio of 1.2 was used with total condenser and kettle reboiler. Distillate rate value was set at 950.356 kg/h according to the methyl-oleate flowrate input to DC2 to obtain biodiesel purity of more than 99.6% according to ASTM specifications. Condensor pressure and column pressure drop were set at 101.3 kPa and 7.5 kPa. In DC2, a total flowrate of 950.356 kg/h at the top stream 16 contains about 99.98% FAME product with 950.205 kg/h with little impurities of glycerol. Biodiesel is able to achieve up to 99.9% purity exceeded the ASTM standard for biodiesel of >99.6 wt%. The bottom stream 17 of the purification column with flowrate of 104.101 kg/h contained about 99.9% triolein and 0.1% FAME.

3.3.3.4 Summary of Process Flowsheet Design

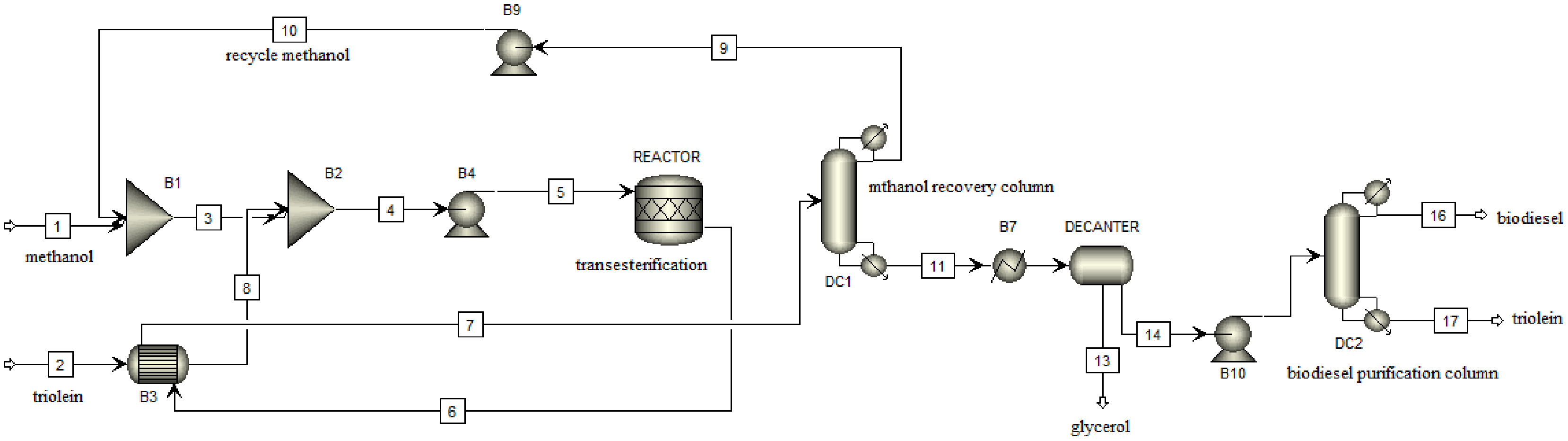
Summary of the unit operating conditions were listed in Table 3.2 below.

Table 3.2 Summary of unit operating conditions

Operating Specifications	Heterogeneous catalysis
Transesterification	
Catalyst	SO_4/ZrO_2
Reactor type	Packed bed (RStoic)
Temperature (°C)	200
Pressure (kPa)	4050
Alcohol-to-toil ratio	6:1
Conversion (%)	90.4
Methanol recovery	
Reflux ratio	1.06
Number of stages	8
Feed stage position	5
Condenser pressure (kPa)	20
Column pressure drop (kPa)	10
Distillate flowrate (kg/h)	125.295
Percentage recovery (%)	100
Distillate purity (%)	99.9
Glycerol Separation	
Temperature (°C)	50
Pressure (kPa)	101.3
Biodiesel Purification	
Reflux ratio	1.2
Number of stages	5
Feed stage position	2
Condenser pressure (kPa)	101.3
Column pressure drop (kPa)	7.5
Distillate flowrate (kg/h)	950.356
Percentage Recovery (%)	99.98
Final purity	99.9
Pumps Discharge Pressure	
Pump B4 (kPa)	101.3
Pump B9 (kPa)	20
Pump B10 (kPa)	109

Heat Exchanger B3	
Calculation	Shortcut
Temperature cold (°C)	150
U methods	Constant U values
Cooler B7	
Temperature (°C)	50
Pressure (kPa)	101.3

Results from simulation provided the mass and energy balances and operating conditions for the equipment where the information was exported to the spreadsheet for environmental assessment of the process using WAR Algorithm method. Detailed compositions of all the streams are shown in Figure 4.1.



HETEROGENEOUS CATALYSIS BIODIESEL PROCESS																		
Stream ID		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Temperature	C	25.0	25.0	26.8	25.8	26.7	200.0	199.8	175.0	28.3	28.3	274.9	50.0	50.0	50.0	50.2	344.2	791.8
Pressure	bar	1.013	1.013	0.200	0.200	1.013	40.500	40.500	1.013	0.200	0.200	0.300	1.013	1.013	1.013	1.090	1.013	1.088
Vapor Frac		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
Mole Flow	kmol/hr	3.205	1.186	7.116	8.301	8.301	8.301	8.301	1.186	3.910	3.910	4.391	4.391	1.067	3.324	3.324	3.206	0.118
Mass Flow	kg/hr	102.705	1050.000	228.000	1278.000	1278.000	1278.000	1278.000	1050.000	125.295	125.295	1152.705	1152.705	98.248	1054.457	1054.457	950.356	104.101
Enthalpy	kcal/hr	-1.8265E+5	-5.3046E+5	-4.0516E+5	-9.3581E+5	-9.3565E+5	-8.8242E+5	-8.8260E+5	-5.3065E+5	-2.2251E+5	-2.2251E+5	-6.3250E+5	-7.6732E+5	-1.6888E+5	-5.9834E+5	-5.9833E+5	-3.7777E+5	-52613.748
Mass Frac																		
CH4O		1.000		1.000	0.178	0.178	0.098	0.098		1.000	1.000	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1.000	1.000	0.822	0.822	0.081	0.081	1.000	1.000	1.000	0.090	0.090	trace	0.099	0.099	trace	0.999
C3H8O-01				2 PPB	trace	trace	0.077	0.077		4 PPB	4 PPB	0.085	0.085	1.000	143 PPM	143 PPM	159 PPM	4 PPB
C19H3-01				trace	trace	trace	0.744	0.744		trace	trace	0.824	0.824	16 PPM	0.901	0.901	1.000	0.001
H2O																		
Mole Frac																		
CH4O		1.000		1.000	0.857	0.857	0.471	0.471		1.000	1.000	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1.000	trace	0.143	0.143	0.014	0.014	1.000	trace	trace	0.027	0.027	trace	0.035	0.035	trace	0.996
C3H8O-01				trace	trace	trace	0.129	0.129		1 PPB	1 PPB	0.243	0.243	1.000	493 PPM	493 PPM	511 PPM	38 PPB
C19H3-01				trace	trace	trace	0.386	0.386		trace	trace	0.730	0.730	5 PPM	0.964	0.964	0.999	0.004
H2O																		

Figure 3.2 Flow Diagram and Stream Results of Heterogeneous Catalysis of Biodiesel- Process

3.4 Concluding Remarks

In this chapter, heterogeneous catalysis process using waste cooking oil as the raw material was designed and simulated with a biodiesel production rate of 8000 tonnes/year Process flowsheet as well as detailed operating conditions and major equipment designs for the process were presented. Throughout the simulation process, errors are frequently occurred at the columns which are mostly due to the dried up of the components upon stages. Reflux value and stages numbers were manipulated to solve the error. Used of decanter show satisfaction removal of glycerol. However, the separation was only achieved by using Unifaque-DMD-M thermodynamic model, which was differs from the overall NRTL properties used in the simulation. For a matter of simplicity, the simulation was run simply by using the data from Aspen Plus databank and auto estimating the properties. No kinetic data inserted or modified for SO_4/ZrO_2 catalyst and triolein.

Improvement on the simulation process can be made by considering the sensitivity analysis and optimization for the simulated design. Different value for the boiling point and critical temperature which were available in journal might be used to estimate the Antoine's vapour pressure coefficients without only relies on the Aspen Plus Databank only, as suggested by West *et. al.* (2007). Closing this chapter, simulated design of heterogeneous biodiesel process showed satisfactory results with FAME output of 99% purity exceeded the ASTM standard for biodiesel. Thus, results of the simulation were further used in environmental assessment of biodiesel process.

CHAPTER 4

ENVIRONMENTAL ANALYSIS AND COMPARISON

4.1 Introduction

WAR algorithm which acts as a comparison tool in selecting the environmentally benign design option is developed using heterogeneous catalysis and alkali homogeneous catalysis of biodiesel process as case study. Four PEI indexes (TRO, TOP, TRG, TGP) are used to evaluate the environmental friendliness of a process design while eight PEI categories (four global and four toxilogical) are used to evaluate the PEI indexes. Comparisons on the analysis within both processes are made.

4.2 Data Acquisition

In WAR algorithm method, the component-specific PEI parameters were key in to the spreadsheet together with the data from the process simulation in Aspen Plus 7.0.

4.2.1 Data from Process Simulation

The data were specified based on the aspen results of input and product streams, and non-product or waste steam. In this process, input streams were methanol (stream 1) and triolein (stream 2). Product streams were glycerol (stream 13) and biodiesel (stream 16). Non-product or waste stream went to triolein output (stream 17).

Parameters defined included the operating temperature and pressure of each streams involved, and the mole and mass flowrates and composition of each component present in the stream.

Table 4.1 Input, Product and Waste Streams results

	Input Streams		Product Streams		Waste Stream
	1	2	13	16	17
Temperature (°C)	25.0	25.0	50.0	344.2	791.8
Pressure (bar)	1.013	1.013	1.013	1.013	1.088
Mole flow (kmol/h)	3.205	1.186	1.067	3.206	0.118
Mass flow (kg/h)	102.705	1050.000	98.248	950.356	104.101
Mass Fraction					
Methanol	1.000	0.000	0.000	0.000	0.000
Triolein	0.000	1.000	0.000	0.000	0.999
FAME	0.000	0.000	0.000	1.000	0.001
Glycerol	0.000	0.000	1.000	0.000	0.000

4.2.2 Score Value of PEI component Data

Table 4.2 Score value of the PEI of each component (Othman, 2011)

Comp.	HTPI (mg/kg)	HTPE (ppm)	ATP (ppm)	TTP (mg/kg)	GWP	PCOP	AP	ODP	EF
TG	-	-	-	-	-	-	-	-	-
MeOH	5628	200	29400	5628	-	0.123	-	-	-
Glycerol	12600	10	58.5	12600	-	-	-	-	-
FAME	-	-	-	-	-	0.223	-	-	-

Table 4.3 Specific and normalized PEI of chemical component

Component	HTPI		HTPE		ATP		TTP		GWP		PCOP		AP		ODP	
	LD50	N. PEI	TWA-TLV	N. PEI	LC50	N. PEI	LD50	N. PEI	IF	N. PEI	IF	N. PEI	IF	N. PEI	IF	N. PEI
TG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MEOH	0.000178	1.3824885	200	1.904762	3.4E-05	0.00397169	0.00018	1.38248848	0	0	0.123	0.710983	0	0	0	0
GLY	7.94E-05	0.6175115	10	0.095238	0.01709	1.99602831	7.9E-05	0.61751152	0	0	0	0	0	0	0	0
FAME	0	0	0	0	0	0	0	0	0	0	0.223	1.289017	0	0	0	0
TOTAL	0.000129	2	105	2	0.00856	2	0.00013	2	0	0	0.173	2	0	0	0	0

4.3 PEI Indexes Results

The parameters that are considered within this table are four PEI indexes which are: TRO, TOP, TRG and TGP values for with product and without product stream which are summarized as in Table 4.4 below. Discussion on environmental impact is not only considered the waste (non-product) stream only, but also the product stream. This is particularly important when the products of a process are likely to eventually be emitted to the environment such as consumer products.

Table 4.4 Environmental indicator total results

Environmental Indicator	Heterogeneouss Catalyis (1)		Homogeneous Catalysis (2)	
	With product	Without product	With product	Without product
TRO	1552.33	0.19	1736.20	37.68
TOP	1.48	0.00	1.49	0.03
TRG	999.29	-552.84	241.09	-1457.42
TGP	0.95	-0.53	0.21	-1.25

The values obtained can be used as an index to compare several design options which is in this study within homogeneous and heterogeneous process. For much clear comparison within both processes, bar charts of all the PEI indexes are plotted based on with and without product streams. The overall PEI result is shown in Table 4.5 for heterogeneous process and Table 4.6 for homogeneous process.

4.3.1 PEI Indexes for With Product Streams

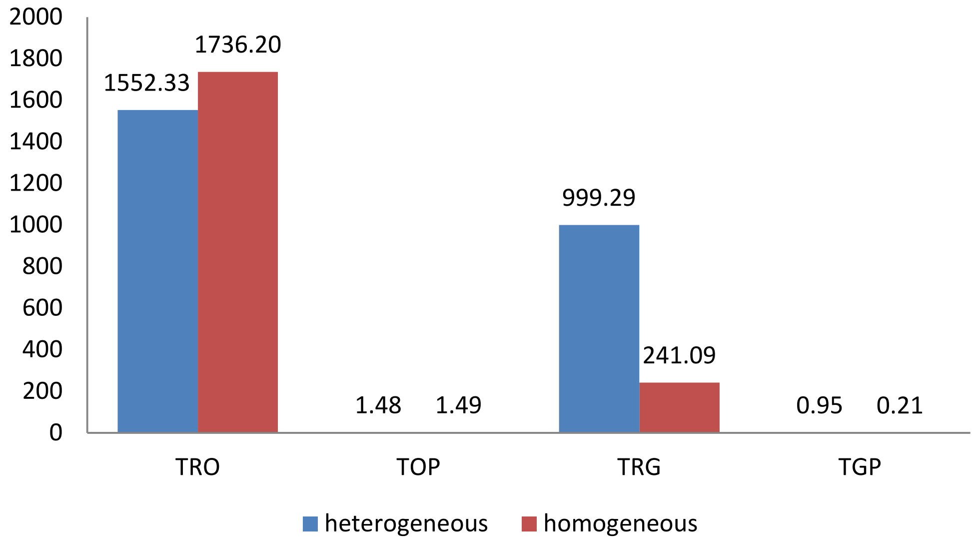


Figure 4.1 PEI indexes of heterogeneous and homogeneous processes for with product streams

TRO and TOP define the external environmental efficiency of the process which allowed the comparison of process designs in terms of their potential effect on the environment external to the process. TRO is most useful in assessing whether a particular site is or is not able to accommodate a given process plant. Heterogeneous process with lower TRO value might have the surrounding environment which is more likely to be able to dissipate the impact being emitted than the cases of homogeneous process. Thus, heterogeneous process with lower TRO value can be located in a more ecologically sensitive area. TOP show almost identical values for both processes. TOP measures the efficiency of material utilization by a specific process per unit mass of products. TOP value decreases when the mass rate of PEI and TRO is reduced and the production rate is increased. Thus, improving material utilization efficiency through process modification tends to lower the PEI output per unit mass of products. From the results, it can be concluded that heterogeneous process is environmentally preferable due to the lower impact output of TRO and TOP it gave.

TRG and TGP define the internal environmental efficiency of the process which allowed the comparison within different process in terms of their generation of new potential environmental impact within the process. TRG is a result that is affected by the selection of process operating conditions. TRG is used as an indicator in comparing process based on how fast they generate impact. Results show that heterogeneous process tends to generate the environmental impact faster than homogeneous process. Thus, modification on the operating condition for heterogeneous process needs to be made to reduce the output impact as low as possible. TGP is used for comparing processes and products based on the amount of new potential environmental impact generated in product manufacturing. Thus, in this PEI index, homogeneous process with lower TRG and TGP values shows advantageous over the heterogeneous process.

4.3.2 PEI Indexes for Without Product (Waste) Streams

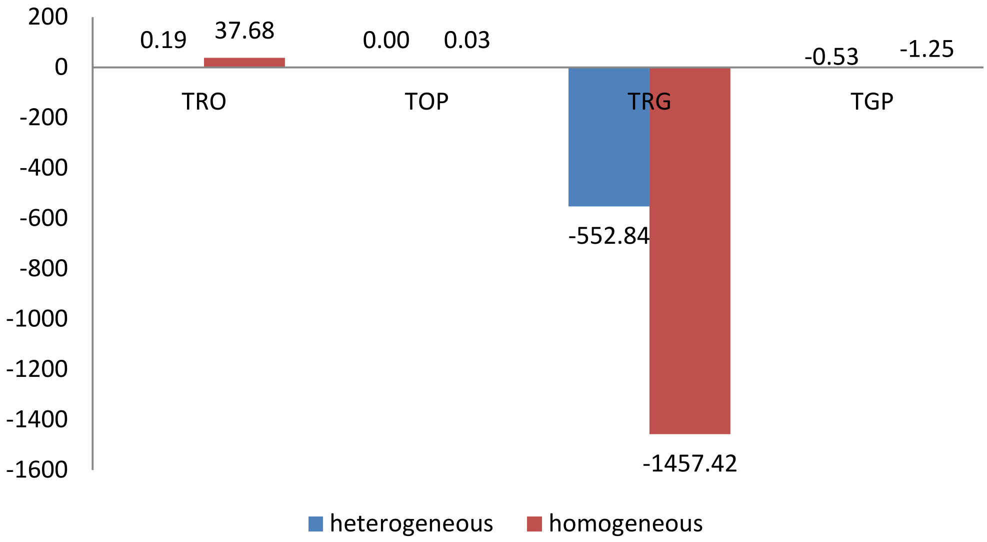


Figure 4.2 PEI indexes of heterogeneous and homogeneous processes for without product (waste) streams

Result of output impact shows negative values of TRG and TGP for both processes while heterogeneous process shows advantageous upon homogeneous process with lower TRO and TOP values. The results can be explained by the existence of only one output waste stream for heterogeneous process which mainly consists of unreacted triglyceride (triolein), a little amount of FAME, and almost neglected amount of methanol and glycerol. Thus, current simulation can be improved by improving the purification step of FAME which is by increasing the reflux ratio of the column so that almost all the main product FAME goes to the top stream and not exist in the waste stream.

Homogeneous process consist of two waste streams where in both streams, large amount of methanol, glycerol, sodium hydroxide and water are present. Impact generated in the waste stream can be reduced by optimizing the simulation so that the efficiency of separation either for glycerol removal or in the final FAME purification can be improved. The existence of too many components in the waste stream leads to higher impact output.

Table 4.5 Overall PEI results with and without product streams for heterogeneous process

Indicator	Input stream	Output stream		With product stream					Without product stream				
		Product stream	Non-prod. stream	Output/ prod.	TRO	TOP	TRG	TGP	Output/ prod.	TRO	TOP	TRG	TGP
HTPI	141.99	60.76	0.00	0.06	60.76	0.06	-81.23	-0.08	0.00	0.00	0.00	-141.99	-0.14
HTPE	195.63	9.37	0.00	0.01	9.37	0.01	-186.26	-0.18	0.00	0.00	0.00	-195.63	-0.19
ATP	0.41	196.40	0.00	0.19	196.40	0.19	196.00	0.19	0.00	0.00	0.00	-0.41	0.00
TTP	141.99	60.76	0.00	0.06	60.76	0.06	-81.23	-0.08	0.00	0.00	0.00	-141.99	-0.14
GWP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCOP	73.02	1224.83	0.19	1.17	1225.03	1.17	1152.01	1.10	0.00	0.19	0.00	-72.83	-0.07
AP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
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
Total	553.04	1552.13	0.19	1.48	1552.33	1.48	999.29	0.95	0.00	0.19	0.00	-552.84	-0.53

Table 4.6 Overall PEI results with and without product streams for homogeneous process

Indicator	Input stream	Output stream		With product stream					Without product stream				
		Product stream	Non-prod. stream	Output/ prod.	TRO	TOP	TRG	TGP	Output/ prod.	TRO	TOP	TRG	TGP
HTPI	165.67	29.99	3.14	0.03	33.13	0.03	-132.55	-0.11	0.00	3.14	0.00	-162.54	-0.14
HTPE	1000.59	23.86	4.77	0.02	28.63	0.02	-971.96	-0.84	0.00	4.77	0.00	-995.82	-0.86
ATP	1.07	257.41	23.89	0.24	281.30	0.24	280.23	0.24	0.02	23.89	0.02	22.82	0.02
TTP	165.67	29.99	3.14	0.03	33.13	0.03	-132.55	-0.11	0.00	3.14	0.00	-162.54	-0.14
GWP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCOP	162.09	1357.27	2.73	1.17	1360.00	1.17	1197.91	1.03	0.00	2.73	0.00	-159.36	-0.14
AP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
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
Total	1495.10	1698.52	37.68	1.49	1736.20	1.49	241.09	0.21	0.03	37.68	0.03	-1457.42	-1.25

4.4 PEI Categories Results

TOP value is used to discuss the PEI for all the environmental categories which are categorized into two: with product and without product. TOP allowed comparisons of different process alternatives on the basis of the potential environmental impact emitted by the process per unit mass of products. Thus, comparisons can be made regardless of manufacturing plant size. Therefore, TOP is considered to be used as comparisons within PEI categories of homogeneous and heterogeneous process. Table 4.8 below shows the TOP values of all impact categories for both homogeneous and heterogeneous process.

Table 4.7 TOP value of PEI categories

PEI Categoriesr	Heterogeneouss Catalyis (1)		Homogeneous Catalysis (2)	
	With product	Without product	With product	Without product
HTPI	0.06	0.00	0.03	0.00
HTPE	0.01	0.00	0.02	0.00
ATP	0.19	0.00	0.24	0.02
TTP	0.06	0.00	0.03	0.00
GWP	0.00	0.00	0.00	0.00
PCOP	1.17	0.00	1.17	0.00
AP	0.00	0.00	0.00	0.00
ODP	0.00	0.00	0.00	0.00

Each category is assessed based on eight different environmental impacts which are HTPI, HTPE, ATP, TTP, GWP, PCOP, AP, and ODP.

4.4.1 TOP for With Product Streams

Bar chart is plotted based on the total rate output over product, TOP of each impact categories.

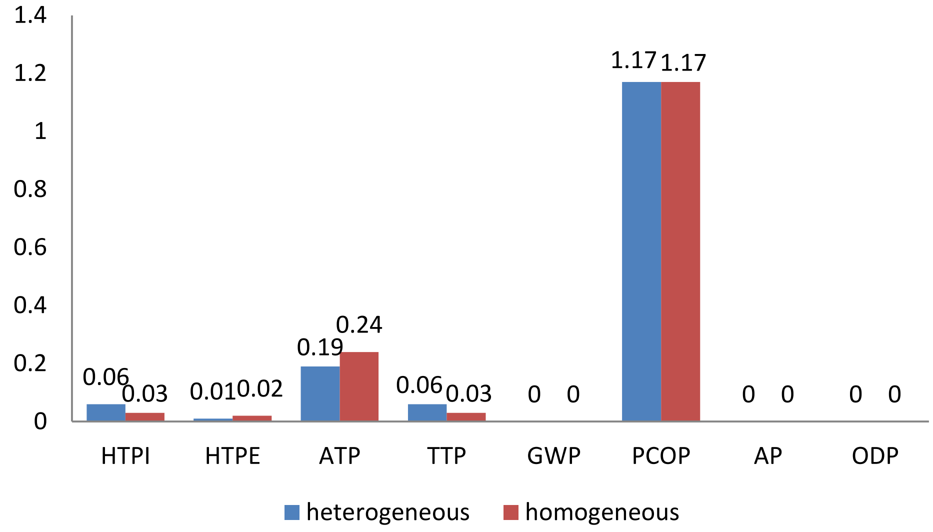


Figure 4.3 TOP of PEI categories for with product stream

Results show that PCOP give the highest TOP value for both process among the environmental categories since the product is mostly covered by FAME. Besides, the existence of little amount of methanol which is a high volatile organic compound in the product streams also lead to the high value of PCOP. It is followed by ATP while HTPI and TTP show the same values for both homogeneous and heterogeneous process. They show that toxicity potential exist in the product streams even in a very small amount of value. HTPE show the lowest TRO value while GWP, AP and ODP show zero value of TRO. Since both process involved no acidic chemicals and produce no greenhouse effect gases such as CO_2, CH_4, and CO, acidification, global warming and ozone depletion potentials seems impossible.

WAR algorithm is useful in emphasize or deemphasize the impact categories where from the bar chart above, we can identify some impact categories that may be highlighted and others that may not be significant. TOP of PCOP shows the highest value which allows the user to focus on reducing the effect of photochemical oxidation (smog formation). Toxicity control upon the process may be focus as well since the PEI results showed the existence of toxicity potential to aquatic and terrestrial, and toxicity potential to human either by ingestion or inhalation/dermal exposure.

From the results, it can be concluded that heterogeneous process offers a better results than homogeneous process since the lower value it give from three out of five categories above.

4.4.2 TOP for Without Product Stream

Bar chart is plotted based on the total rate output over product, TOP of each impact categories.

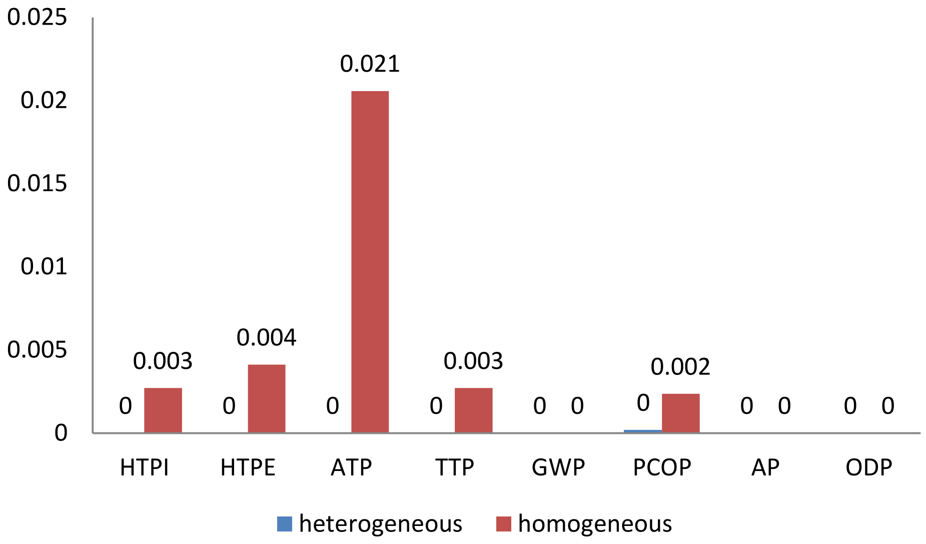


Figure 4.4 TOP of PEI categories for without product streams

For heterogeneous process, only TOP value of PCOP which is 0.00018554 is exists. Other categories show zero output. PCOP value dominates the effect to the environment compared to others due to the presence of little amount of FAME in the non-product output stream of heterogeneous process. FAME leads to the result due to the high value of its PCOP specific PEI.

Compared to heterogeneous process, homogeneous process shows the TOP value of most of the PEI categories which might due to the existence of numbers of components in the waste stream. ATP shows the highest at followed by HTPE, HTPI and TTP while PCOP shows the lowest. The results is due to the least amount of methanol exist in the waste stream compared to other components. Glycerol and water which is used in the washing step of sodium hydroxide dominates the components exist in the waste stream where both components may lead to toxicity potential to the human and aquatic. Precaution need to be taken to handle the waste in correct ways.

WAR algorithm results act as retrofitting tool which allows users to identify spots or points in the design for further improvement. In this case, improvement on FAME purification can be made to reduce the amount of FAME in the non-product stream thus reducing the smog potential due to the effect of waste. This can be done by increasing the reflux ratio of column which is however lead to increasing in energy used and increase the economic part of the process. So, any modification to be made must consider other factors as well not only the environment part of it. The highest value of ATP shown in homogeneous process is due to the presence of methanol and high amount of glycerol. Improvement can be made by setting methanol recovery to its highest value and improve the efficiency of glycerol separation.

Concluding the result, heterogeneous catalysis process with almost negligible TOP values for all the PEI categories show advantageous over the homogeneous process. Thus, either for with or without product streams, heterogeneous process is preferable and offer a better environmentally friendly of biodiesel process.

4.5 Concluding Remarks

In this chapter, PEI results were discussed and compared within homogeneous catalysis and heterogeneous alkali catalysis of biodiesel process. Since both processes were set with the same production rate of 8000 tonnes/year, comparisons were easily made and the outcome results showed advantageous on heterogeneous process upon homogeneous process. Improvement can be made by the inclusion of energy balance into the WAR algorithm calculation. Since, economic assessment is not conducted, WAR algorithm only considered the effect of mass balances in the process to the PEI results neglecting the effect of energy. Concluding the chapter, the case study on both biodiesel process evaluations showed the environmental analysis effectiveness in assessing and selecting sustainable and environmentally friendly process design. Thus, considering the environmental assessment in process design will be an advantageous upon the design.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From this study, comparison on PEI results within homogeneous catalysis and heterogeneous alkali catalysis of biodiesel process both with the production rate of 8000 tonnes/year have been made. Results show that heterogeneous catalysis of biodiesel process offers an advantageous over homogeneous process with less amount of PEI output. Eventhough TRG and TGP value for homogeneous processes are lower than the heterogeneous process for with products stream, heterogeneous process gives lower TRO and TOP value for with products stream and all the PEI indexes are lower than homogeneous process for without product stream. PEI categories at with products stream for heterogeneous process also show lower TOP values with almost negligible impact exist at without product stream. Thus, heterogeneous catalysis of biodiesel process offers a more environmentally friendly design which may be considered in the selection of process design of biodiesel process.

5.2 Recommendation

As a recommendation, improvement on the simulation process can be made by considering the sensitivity analysis and optimization for the simulated process. Besides comparing within the process selection, results of WAR algorithm can also be further used in the modification and optimization of the design, to see the effect of modification will have on PEI output. As for the environmental assessment, improvement can be made by the inclusion of energy balance into the WAR algorithm calculation. Since, economic assessment is not conducted, WAR algorithm only considered the effect of mass balances in the process to the PEI results neglecting the effect of energy. Improvement in both simulation process and environmental analysis will eventually improve the overall results of this study.

REFERENCES

Cabezas, H., Bare, J.C., and Mallick, S.K. (1997). Pollution Prevention with Chemical Process Simulators: The Generalized Waste Reduction (WAR) Algorithm. *Computers and Chemical Engineering, 21*, 305-310.

Chouhan, A.P.S. and Sarma, A.K. (2011). Modern Heterogeneous Catalyst for Biodiesel Production: A Comprehensive Review. *Renewable and Sustainable Energy Reviews, 15*, 4378-4399.

Dimian, A.C., and Bildea, C.S. (2008). *Chemical Process Design: Computer-Aided Case Studies.* Weinheim: WILEY-VCH Verlag GmbH & Co.

Furuta, S., Matsuhashi, H., and Arata, K. (2004). Biodiesel Fuel Production with Solid Superacid Catalysis in Fixed Bed Reactor under Atmospheric Pressure. *Catalysis Communication 5(12)*, 721-723.

Haas, M.J., McAloon, A.J., Yee, W.C., and Foglia, T.A. (2006). A Process Model to Estimate Biodiesel Production Costs. *Bioresource Technology 97*, 671-678.

Hilaly, A.K., and Sikdar, S.K. (1994). Pollution Balance: A New Methodology for Minimizing Waste Production in Manufacturing Process. *Journal of the Air & Waste Management Association, 44,* 1303-1308.

Hillion, G., Delfort, B., Pennec, D., Bournay, L., and Chodorge, J.A. (2003). Biodiesel Production by a Continuous Process using Heterogeneous Catalyst. *Div. Fuel Chem, 48(2),* 636-638.

Myint, L.L. and El-Halwagi, M.M. (2009). Process Analysis and Optimization of Biodiesel Production from Soybean Oil. *Clean Technology Environment Policy 11*, 263-276.

Nathanson, R.B., Adams II, T.A., and Seider, W.D. (2008). Aspen Icarus Process Evaluator (IPE). University of Pennyslvania.

Othman, M.R. (2011). *Sustainability Assessment and Decision Making in Chemical Process Design.* PhD Thesis. Technical University of Berlin, German.

Turton R., Bailie, R.C., Whiting, W.B. and Shaeiwitz, J.A. (2009). *Analysis, Synthesis, and Design of Chemical Processes*. Boston: Pearson Education Inc.

West, A.H., Posarac, D., and Ellis, N. (2007). Simulation, Case Studies and Optimization of a Biodiesel Process with a Solid Acid Catalyst. *International Journal of Chemical Reactor Engineering, 5*.

West, A. H., Posarac, D., and Ellis, N. (2008). Assessment of Four Biodiesel Production Processes using HYSIS.Plant. *Bioresource Technology, 99*, 6587-6601.

Young, D.M., and Cabezas, H. (1999). Designing Sustainable Processes with Simulation: The Waste Reduction (WAR) Algorithm. *Computers and Chemical Engineering, 23,* 1477-1491.

Young, D., Scharp, R., and Cabezas, H. (2000). The Waste Reduction (WAR) Algorithm: Environmental Impacts, Energy Consumption, and Engineering Economics. *Waste Management*, *20,* 605-615.

Zhang, Y. (2002). Design and Economic Assessment of Biodiesel Production from Waste Cooking Oil. Master Thesis. Department of Chemical Engineering University of Ottawa, Canada.

Zhang, Y., Dub, M. A., McLean, D.D., and Kates, M. (2007). Biodiesel Production from Waste Cooking Oil: Economic Assessment and Sensitivity Analysis. *Bioresource Technology 90*, 229-240.

APPENDIX A
BIODIESEL PROCESS MODEL

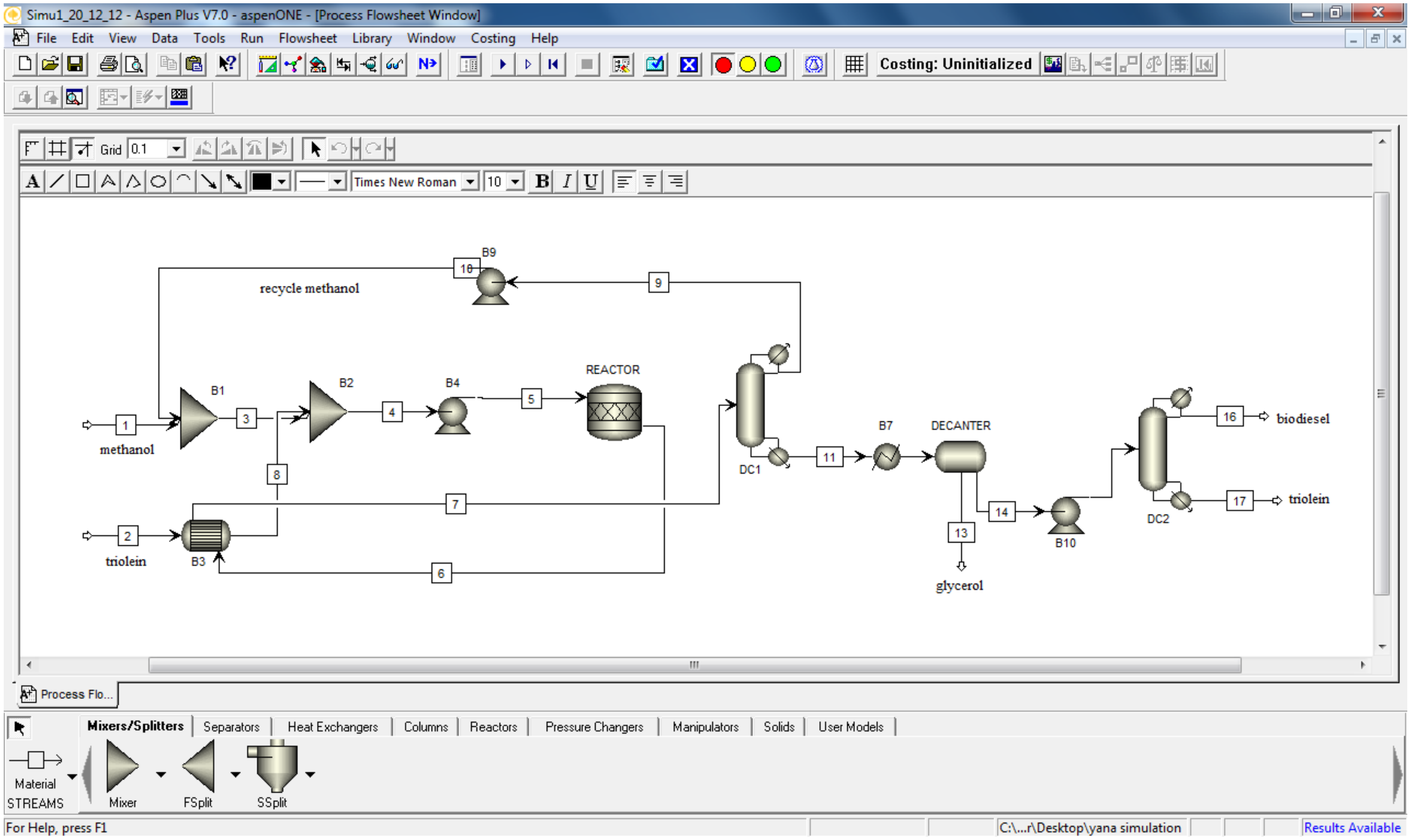
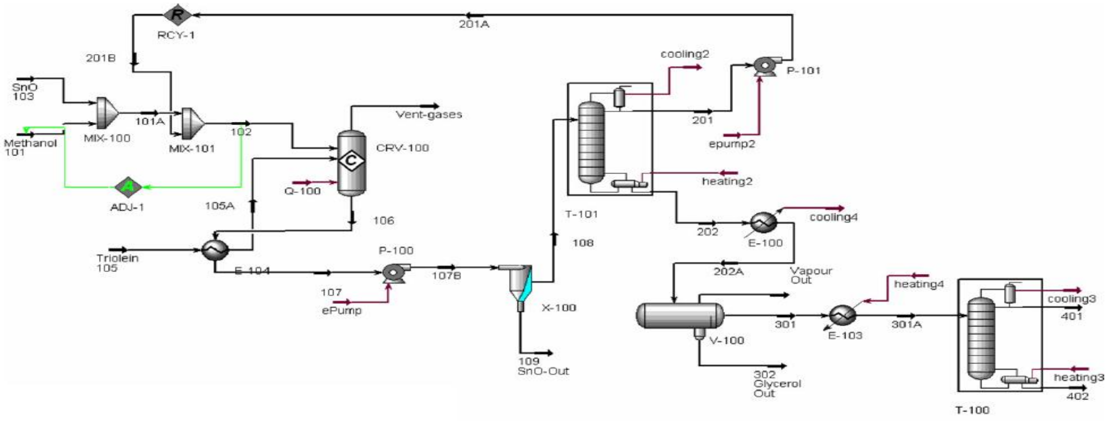


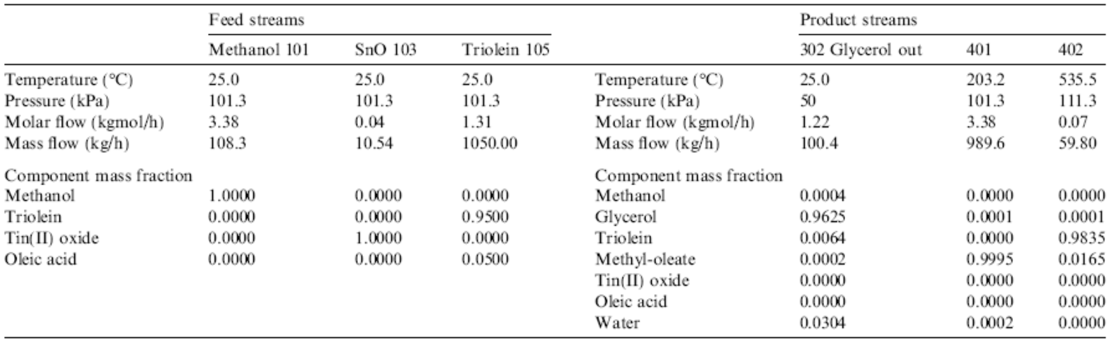
Figure A.1 Process flowsheet for heterogeneous catalysis of biodiesel process

Table A.1 Simulation results of heterogeneous catalysis biodiesel process

HETEROGENEOUS CATALYSIS BIODIESEL PROCESS																		
Stream ID		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Temperature	C	25.0	25.0	26.8	25.8	26.7	200.0	199.8	175.0	28.3	28.3	274.9	50.0	50.0	50.0	50.2	344.2	791.8
Pressure	bar	1.013	1.013	0.200	0.200	1.013	40.500	40.500	1.013	0.200	0.200	0.300	1.013	1.013	1.013	1.090	1.013	1.088
Vapor Frac		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
Mole Flow	kmol/hr	3.205	1.186	7.116	8.301	8.301	8.301	8.301	1.186	3.910	3.910	4.391	4.391	1.067	3.324	3.324	3.206	0.118
Mass Flow	kg/hr	102.705	1050.000	228.000	1278.000	1278.000	1278.000	1278.000	1050.000	125.295	125.295	1152.705	1152.705	98.248	1054.457	1054.457	950.356	104.101
Volume Flow	cum/hr	0.130	1.157	0.288	2.370	2.371	1.862	1.862	1.222	0.159	0.159	1.808	1.449	0.078	1.326	1.326	1.551	0.165
Enthalpy	MMkcal/hr	-0.183	-0.530	-0.405	-0.936	-0.936	-0.882	-0.883	-0.531	-0.223	-0.223	-0.633	-0.767	-0.169	-0.598	-0.598	-0.378	-0.053
Mass Flow	kg/hr																	
CH_4O		102.705		228.000	228.000	228.000	125.295	125.295		125.295	125.295	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1050.000	trace	1050.000	1050.000	103.950	103.950	1050.000	trace	trace	103.950	103.950	trace	103.950	103.950	trace	103.950
C3H8O-01				trace	trace	trace	98.398	98.398		trace	trace	98.398	98.398	98.247	0.151	0.151	0.151	trace
C19H3-01				trace	trace	trace	950.358	950.358		trace	trace	950.358	950.358	0.002	950.356	950.356	950.205	0.151
H_2O																		
Mass Frac																		
CH_4O		1.000		1.000	0.178	0.178	0.098	0.098		1.000	1.000	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1.000	1.000	0.822	0.822	0.081	0.081	1.000	1.000	1.000	0.090	0.090	trace	0.099	0.099	trace	0.999
C3H8O-01				2 PPB	trace	trace	0.077	0.077		4 PPB	4 PPB	0.085	0.085	1.000	143 PPM	143 PPM	159 PPM	4 PPB
C19H3-01				trace	trace	trace	0.744	0.744		trace	trace	0.824	0.824	16 PPM	0.901	0.901	1.000	0.001
H_2O																		
Mole Flow	kmol/hr																	
CH_4O		3.205		7.116	7.116	7.116	3.910	3.910		3.910	3.910	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1.186	7.116	1.186	1.186	0.117	0.117	1.186	3.910	3.910	0.117	0.117	trace	0.117	0.117	trace	0.117
C3H8O-01				trace	trace	trace	1.068	1.068		trace	trace	1.068	1.068	1.067	0.002	0.002	0.002	trace
C19H3-01				trace	trace	trace	3.205	3.205		trace	trace	3.205	3.205	trace	3.205	3.205	3.205	0.001
H_2O																		
Mole Frac																		
CH_4O		1.000		1.000	0.857	0.857	0.471	0.471		1.000	1.000	trace	trace	trace	trace	trace	trace	trace
C57H1-01			1.000	trace	0.143	0.143	0.014	0.014	1.000	trace	trace	0.027	0.027	trace	0.035	0.035	trace	0.996
C3H8O-01				trace	trace	trace	0.129	0.129		1 PPB	1 PPB	0.243	0.243	1.000	493 PPM	493 PPM	511 PPM	38 PPB
C19H3-01				trace	trace	trace	0.386	0.386		trace	trace	0.730	0.730	5 PPM	0.964	0.964	0.999	0.004
H_2O																		

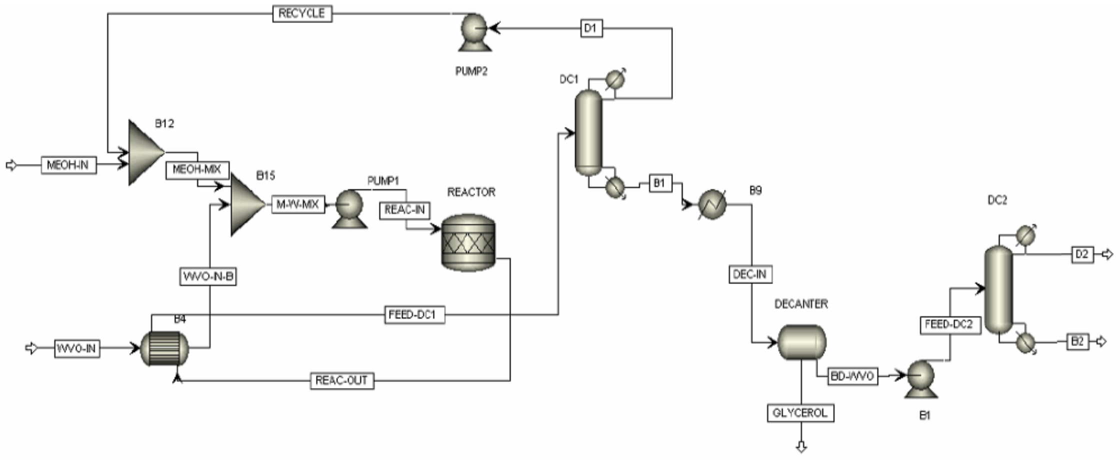
APPENDIX B
BIODIESEL PROCESS MODEL
(West *et al.*, 2007, 2008)





	Feed streams				Product streams		
	Methanol 101	SnO 103	Triolein 105		302 Glycerol out	401	402
Temperature (°C)	25.0	25.0	25.0	Temperature (°C)	25.0	203.2	535.5
Pressure (kPa)	101.3	101.3	101.3	Pressure (kPa)	50	101.3	111.3
Molar flow (kgmol/h)	3.38	0.04	1.31	Molar flow (kgmol/h)	1.22	3.38	0.07
Mass flow (kg/h)	108.3	10.54	1050.00	Mass flow (kg/h)	100.4	989.6	59.80
Component mass fraction				Component mass fraction			
Methanol	1.0000	0.0000	0.0000	Methanol	0.0004	0.0000	0.0000
Triolein	0.0000	0.0000	0.9500	Glycerol	0.9625	0.0001	0.0001
Tin(II) oxide	0.0000	1.0000	0.0000	Triolein	0.0064	0.0000	0.9835
Oleic acid	0.0000	0.0000	0.0500	Methyl-oleate	0.0002	0.9995	0.0165
				Tin(II) oxide	0.0000	0.0000	0.0000
				Oleic acid	0.0000	0.0000	0.0000
				Water	0.0304	0.0002	0.0000

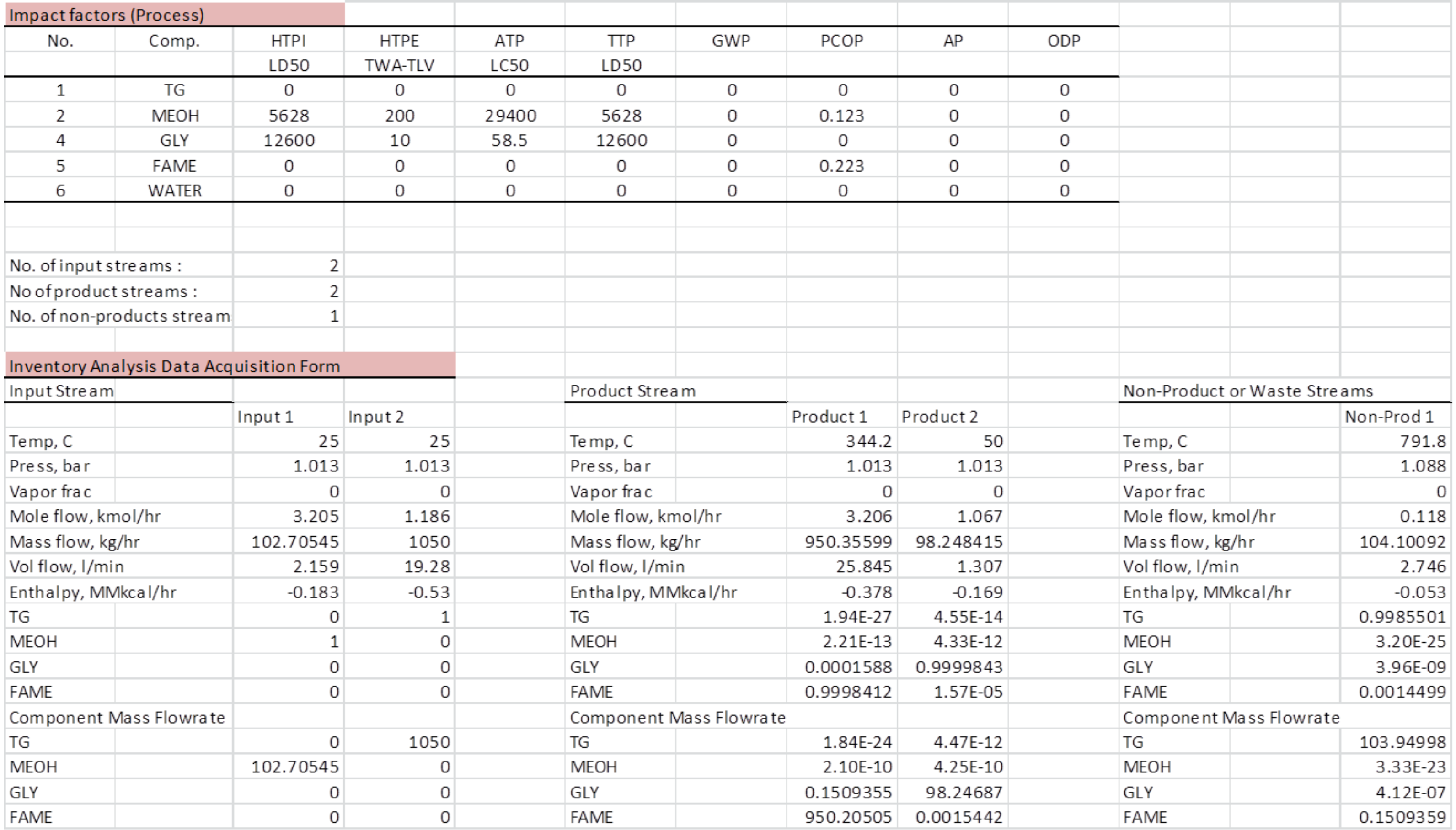
Figure B.1 Heterogeneous acid-catalyzed process flowsheet
(Source: West *et al.*, 2008)



Feed Streams				Product Streams		
	MEOH-IN	WVO-IN		D2	B2	GLYCEROL
Temperature (°C)	25.0	25.0	Temperature (°C)	217.2	544	25
Pressure (kPa)	101.3	101.3	Pressure (kPa)	101.325	108.8	101.325
Molar flow (kmol/h)	3.24	1.31	Molar flow (kmol/h)	3.26	0.111	1.19
Mass flow (kg/h)	103.9	1050.00	Mass flow (kg/h)	960.4	96.7	96.7
Component mass fraction			Component mass fraction			
Methanol	1.000	0.000	Methanol	0.0000	0.0000	0.0003
Triolein	0.000	0.9500	Glycerol	0.0001	0.0000	0.9679
Oleic Acid	0.000	0.0500	Triolein	0.0000	0.9901	0.0316
			M-oleate	0.9995	0.0099	0.0000
			Oleic Acid	0.0000	0.0000	0.0000
			Water	0.0003	0.0000	0.0000

Figure B.2 Heterogeneous acid-catalyzed process flowsheet
(Source: West *et al.*, 2007)

APPENDIX C
Environmental Analysis
(WAR Algorithm)



Impact factors (Process)

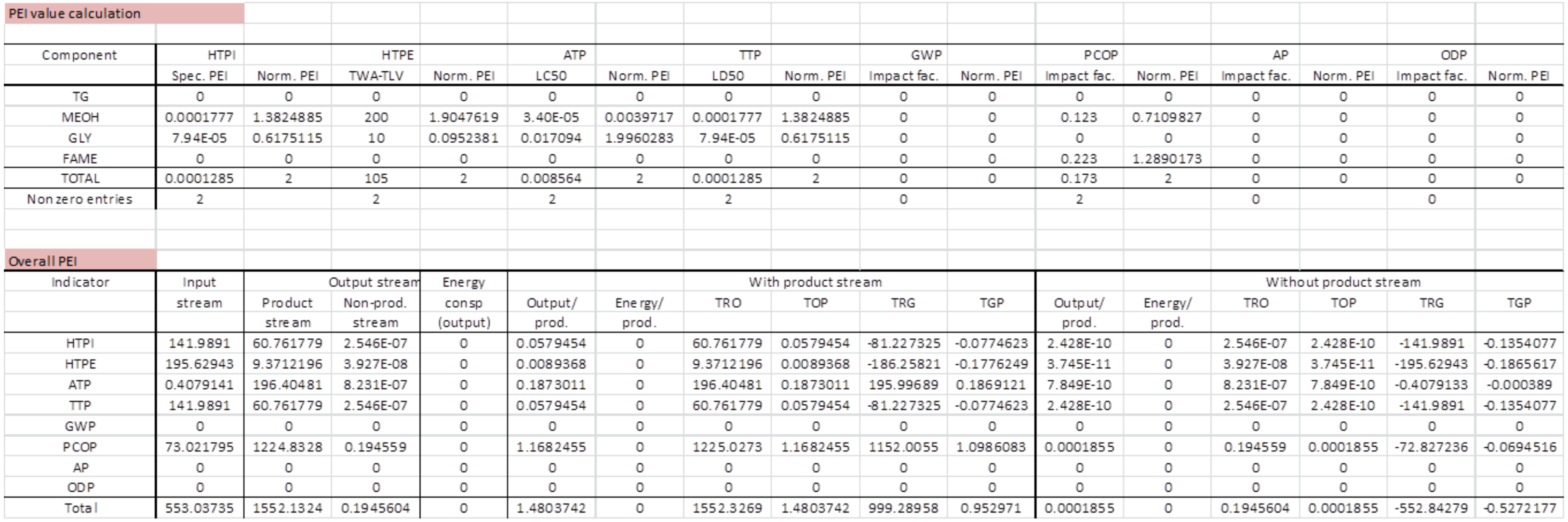
No.	Comp.	HTPI LD50	HTPE TWA-TLV	ATP LC50	TTP LD50	GWP	PCOP	AP	ODP
1	TG	0	0	0	0	0	0	0	0
2	MEOH	5628	200	29400	5628	0	0.123	0	0
4	GLY	12600	10	58.5	12600	0	0	0	0
5	FAME	0	0	0	0	0	0.223	0	0
6	WATER	0	0	0	0	0	0	0	0

No. of input streams :	2
No of product streams :	2
No. of non-products stream	1

Inventory Analysis Data Acquisition Form

Input Stream	Input 1	Input 2	Product Stream	Product 1	Product 2	Non-Product or Waste Streams	Non-Prod 1
Temp, C	25	25	Temp, C	344.2	50	Temp, C	791.8
Press, bar	1.013	1.013	Press, bar	1.013	1.013	Press, bar	1.088
Vapor frac	0	0	Vapor frac	0	0	Vapor frac	0
Mole flow, kmol/hr	3.205	1.186	Mole flow, kmol/hr	3.206	1.067	Mole flow, kmol/hr	0.118
Mass flow, kg/hr	102.70545	1050	Mass flow, kg/hr	950.35599	98.248415	Mass flow, kg/hr	104.10092
Vol flow, l/min	2.159	19.28	Vol flow, l/min	25.845	1.307	Vol flow, l/min	2.746
Enthalpy, MMkcal/hr	-0.183	-0.53	Enthalpy, MMkcal/hr	-0.378	-0.169	Enthalpy, MMkcal/hr	-0.053
TG	0	1	TG	1.94E-27	4.55E-14	TG	0.9985501
MEOH	1	0	MEOH	2.21E-13	4.33E-12	MEOH	3.20E-25
GLY	0	0	GLY	0.0001588	0.9999843	GLY	3.96E-09
FAME	0	0	FAME	0.9998412	1.57E-05	FAME	0.0014499
Component Mass Flowrate			Component Mass Flowrate			Component Mass Flowrate	
TG	0	1050	TG	1.84E-24	4.47E-12	TG	103.94998
MEOH	102.70545	0	MEOH	2.10E-10	4.25E-10	MEOH	3.33E-23
GLY	0	0	GLY	0.1509355	98.24687	GLY	4.12E-07
FAME	0	0	FAME	950.20505	0.0015442	FAME	0.1509359

Figure C.1 Data acquisition for heterogeneous process



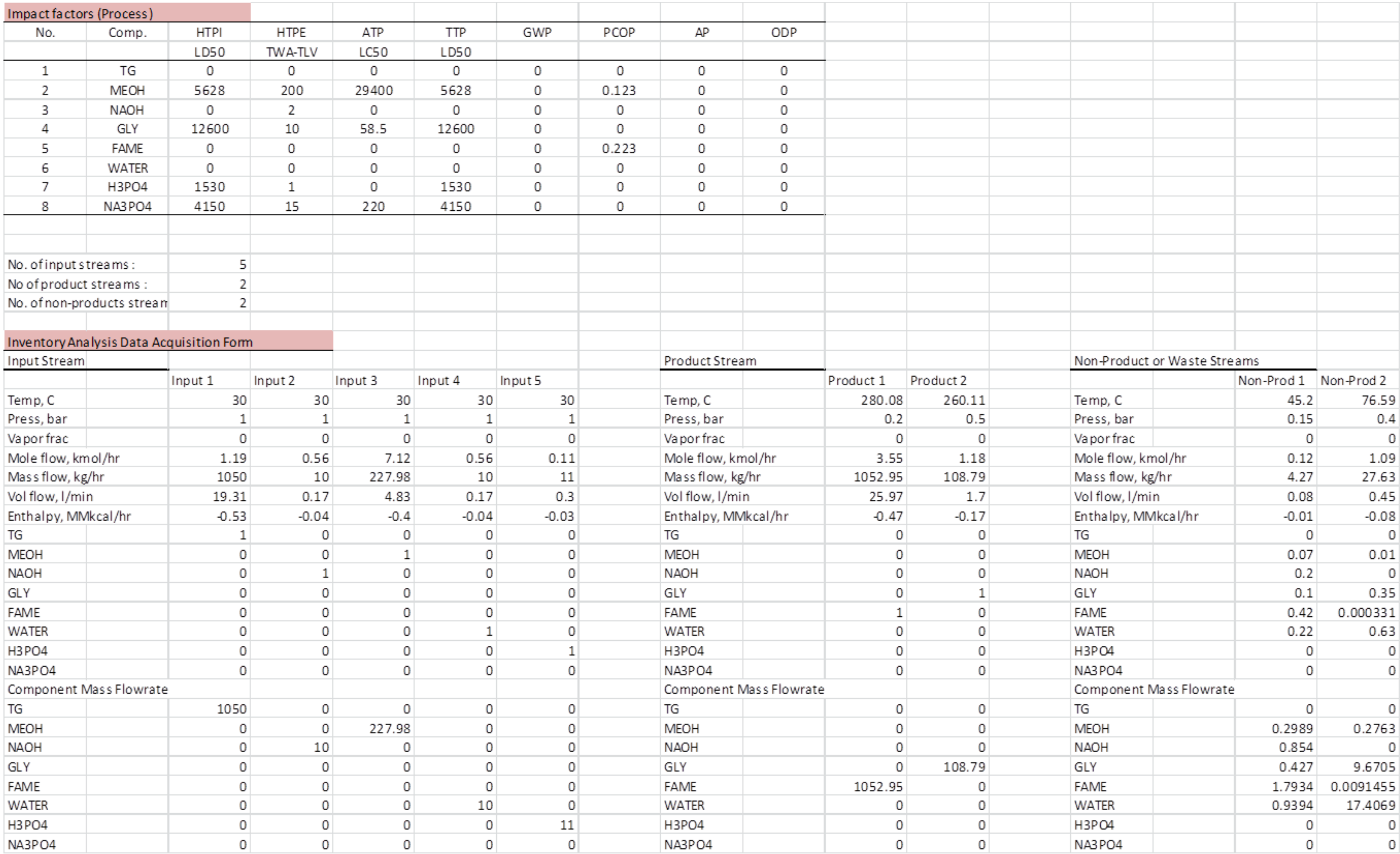
PEI value calculation

Component	HTPI		HTPE		ATP		TTP		GWP		PCOP		AP		ODP	
	Spec. PEI	Norm. PEI	TWA-TLV	Norm. PEI	LC50	Norm. PEI	LD50	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI
TG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MEOH	0.0001777	1.3824885	200	1.9047619	3.40E-05	0.0039717	0.0001777	1.3824885	0	0	0.123	0.7109827	0	0	0	0
GLY	7.94E-05	0.6175115	10	0.0952381	0.017094	1.9960283	7.94E-05	0.6175115	0	0	0	0	0	0	0	0
FAME	0	0	0	0	0	0	0	0	0	0	0.223	1.2890173	0	0	0	0
TOTAL	0.0001285	2	105	2	0.008564	2	0.0001285	2	0	0	0.173	2	0	0	0	0
Non zero entries	2		2		2		2		0		2		0		0	

Overall PEI

Indicator	Input stream	Output stream		Energy consp (output)	With product stream						Without product stream					
		Product stream	Non-prod. stream		Output/ prod.	Energy/ prod.	TRO	TOP	TRG	TGP	Output/ prod.	Energy/ prod.	TRO	TOP	TRG	TGP
HTPI	141.9891	60.761779	2.546E-07	0	0.0579454	0	60.761779	0.0579454	-81.227325	-0.0774623	2.428E-10	0	2.546E-07	2.428E-10	-141.9891	-0.1354077
HTPE	195.62943	9.3712196	3.927E-08	0	0.0089368	0	9.3712196	0.0089368	-186.25821	-0.1776249	3.745E-11	0	3.927E-08	3.745E-11	-195.62943	-0.1865617
ATP	0.4079141	196.40481	8.231E-07	0	0.1873011	0	196.40481	0.1873011	195.99689	0.1869121	7.849E-10	0	8.231E-07	7.849E-10	-0.4079133	-0.000389
TTP	141.9891	60.761779	2.546E-07	0	0.0579454	0	60.761779	0.0579454	-81.227325	-0.0774623	2.428E-10	0	2.546E-07	2.428E-10	-141.9891	-0.1354077
GWP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCOP	73.021795	1224.8328	0.194559	0	1.1682455	0	1225.0273	1.1682455	1152.0055	1.0986083	0.0001855	0	0.194559	0.0001855	-72.827236	-0.0694516
AP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ODP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	553.03735	1552.1324	0.1945604	0	1.4803742	0	1552.3269	1.4803742	999.28958	0.952971	0.0001855	0	0.1945604	0.0001855	-552.84279	-0.5272177

Figure C.2 PEI overall results for heterogeneous process



Impact factors (Process)

No.	Comp.	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

No. of input streams :	5
No of product streams :	2
No. of non-products stream	2

Inventory Analysis Data Acquisition Form

Input Stream

	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	1.19	0.56	7.12	0.56	0.11
Mass flow, kg/hr	1050	10	227.98	10	11
Vol flow, l/min	19.31	0.17	4.83	0.17	0.3
Enthalpy, MMkcal/hr	-0.53	-0.04	-0.4	-0.04	-0.03
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	227.98	0	0
NAOH	0	10	0	0	0
GLY	0	0	0	0	0
FAME	0	0	0	0	0
WATER	0	0	0	10	0
H3PO4	0	0	0	0	11
NA3PO4	0	0	0	0	0

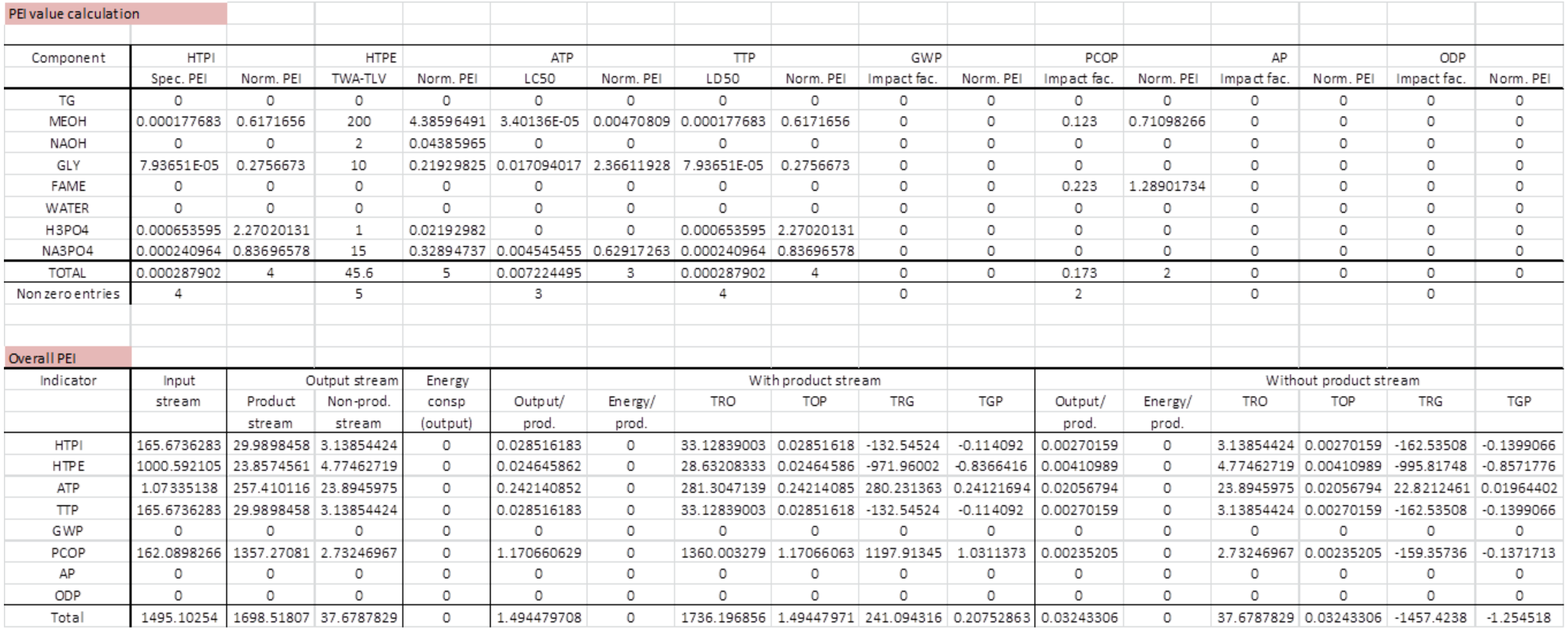
Product Stream

	Product 1	Product 2
Temp, C	280.08	260.11
Press, bar	0.2	0.5
Vapor frac	0	0
Mole flow, kmol/hr	3.55	1.18
Mass flow, kg/hr	1052.95	108.79
Vol flow, l/min	25.97	1.7
Enthalpy, MMkcal/hr	-0.47	-0.17
TG	0	0
MEOH	0	0
NAOH	0	0
GLY	0	1
FAME	1	0
WATER	0	0
H3PO4	0	0
NA3PO4	0	0
Component Mass Flowrate		
TG	0	0
MEOH	0	0
NAOH	0	0
GLY	0	108.79
FAME	1052.95	0
WATER	0	0
H3PO4	0	0
NA3PO4	0	0

Non-Product or Waste Streams

	Non-Prod 1	Non-Prod 2
Temp, C	45.2	76.59
Press, bar	0.15	0.4
Vapor frac	0	0
Mole flow, kmol/hr	0.12	1.09
Mass flow, kg/hr	4.27	27.63
Vol flow, l/min	0.08	0.45
Enthalpy, MMkcal/hr	-0.01	-0.08
TG	0	0
MEOH	0.07	0.01
NAOH	0.2	0
GLY	0.1	0.35
FAME	0.42	0.000331
WATER	0.22	0.63
H3PO4	0	0
NA3PO4	0	0
Component Mass Flowrate		
TG	0	0
MEOH	0.2989	0.2763
NAOH	0.854	0
GLY	0.427	9.6705
FAME	1.7934	0.0091455
WATER	0.9394	17.4069
H3PO4	0	0
NA3PO4	0	0

Figure C.3 Data acquisition for homogeneous process



PEI value calculation

Component	HTPI		HTPE		ATP		TTP		GWP		PCOP		AP		ODP	
	Spec. PEI	Norm. PEI	TWA-TLV	Norm. PEI	LC50	Norm. PEI	LD50	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI	Impact fac.	Norm. PEI
TG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MEOH	0.000177683	0.6171656	200	4.38596491	3.40136E-05	0.00470809	0.000177683	0.6171656	0	0	0.123	0.71098266	0	0	0	0
NAOH	0	0	2	0.04385965	0	0	0	0	0	0	0	0	0	0	0	0
GLY	7.93651E-05	0.2756673	10	0.21929825	0.017094017	2.36611928	7.93651E-05	0.2756673	0	0	0	0	0	0	0	0
FAME	0	0	0	0	0	0	0	0	0	0	0.223	1.28901734	0	0	0	0
WATER	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3PO4	0.000653595	2.27020131	1	0.02192982	0	0	0.000653595	2.27020131	0	0	0	0	0	0	0	0
NA3PO4	0.000240964	0.83696578	15	0.32894737	0.004545455	0.62917263	0.000240964	0.83696578	0	0	0	0	0	0	0	0
TOTAL	0.000287902	4	45.6	5	0.007224495	3	0.000287902	4	0	0	0.173	2	0	0	0	0
Non zero entries	4		5		3		4		0		2		0		0	

Overall PEI

Indicator	Input		Output stream	Energy	With product stream						Without product stream					
	stream	Product stream	Non-prod. stream	consp (output)	Output/ prod.	Energy/ prod.	TRO	TOP	TRG	TGP	Output/ prod.	Energy/ prod.	TRO	TOP	TRG	TGP
HTPI	165.6736283	29.9898458	3.13854424	0	0.028516183	0	33.12839003	0.02851618	-132.54524	-0.114092	0.00270159	0	3.13854424	0.00270159	-162.53508	-0.1399066
HTPE	1000.592105	23.8574561	4.77462719	0	0.024645862	0	28.63208333	0.02464586	-971.96002	-0.8366416	0.00410989	0	4.77462719	0.00410989	-995.81748	-0.8571776
ATP	1.07335138	257.410116	23.8945975	0	0.242140852	0	281.3047139	0.24214085	280.231363	0.24121694	0.02056794	0	23.8945975	0.02056794	22.8212461	0.01964402
TTP	165.6736283	29.9898458	3.13854424	0	0.028516183	0	33.12839003	0.02851618	-132.54524	-0.114092	0.00270159	0	3.13854424	0.00270159	-162.53508	-0.1399066
GWP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCOP	162.0898266	1357.27081	2.73246967	0	1.170660629	0	1360.003279	1.17066063	1197.91345	1.0311373	0.00235205	0	2.73246967	0.00235205	-159.35736	-0.1371713
AP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ODP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	1495.10254	1698.51807	37.6787829	0	1.494479708	0	1736.196856	1.49447971	241.094316	0.20752863	0.03243306	0	37.6787829	0.03243306	-1457.4238	-1.254518

Figure C.4 PEI overall results for homogeneous process